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SUBSTITUTION REACTIONS OF PLATINUM METAL COMPLEXES; A KINETIC AND MECHANISTIC STUDY

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Abstract

The rate of reaction of trans-$[Rhen_2I_2]^+$ with Y^{n-} ($Y^{n-} = Cl^-$, Br^-) and of hydrolysis of trans-$[Rhen_2X_2]^+$ in the presence of Y^{n-} (X = Cl, I, $Y^{n-} = F^-$, SO_4^{2-}, PO_4^{3-}; X = Cl, $Y^{n-} = Br^-$) is shown to depend on the concentration of Y^{n-}. This is ascribed to the dissociative reaction of an $\{Rhen_2X_2, Y\}^{(1-n)+}$ ion-pair. The ion-association constants are shown to be small.

The rates of base hydrolysis of trans-$[Rhen_2X_2]^+$ and trans-$[Rhen_2XOH]^+$ (X = Cl, Br, I) depend on the concentration of hydroxide. The hydroxide-dependent pathways are energetically similar to the other anion-dependent pathways of trans-diacidobisethylenediaminerhodium(III) complexes. The base hydrolyses of trans-$[Rhen_2XOH]^+$ (X = Cl, Br, I) are stereoretentive, but the dihalo-complexes give some cis-products. This is explained by the S_N1CB mechanism if it is assumed that the sigma-trans-effect of the amido-group is large and transmitted by rhodium p-orbitals. The possibility that the hydroxide-dependent reactions occur via a species intermediate between the conjugate base and a hydroxide ion-pair is discussed.

The kinetic trans-effect of hydroxide has been measured by the enthalpies of activation for the aquation of trans-$[Rhen_2OHX]^+$ and for anation of trans-$[Rhen_2OHOH_2]^{2+}$ by X^- (X = Cl, Br, I), but its value varies with the reaction. The intrinsic kinetic trans-effect (IKTE), however, is a constant. The IKTE series of ligands, L, is shown to correlate with the polarisability of L, although solvation effects are also important. The thermodynamic trans-effect (TTE) of hydroxide has also been measured. The TTE series of ligands, L, correlates with the covalency of the Rh-L bond as measured by the intensity of the first ligand field transition of trans-$[Rhen_2LCl]^{n+}$.

The rate of anation of trans-$[Pt(CN)_4BrOH_2]^-$ by bromide has been

studied as a function of the bromide concentration. The reaction is shown to occur by an intramolecular redox reaction within a $\{Br...BrPt(CN)_4OH_2\}^{2-}$ charge-transfer complex, and also by reductive attack of bromide on the charge-transfer complex.

To my parents and Dave

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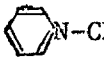
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Abbreviations

The following abbreviations are used in the text without further explanation.

Ligands

Me	methyl
Et	ethyl
n-Pr	n-propyl
t-Bu	t-butyl
Ph	phenyl
OAc^-	acetate ion
en	ethylenediamine
en-H	the mono-amido-derivative of ethylenediamine
pn	1,2-propanediamine
Et_4dien	1,1,7,7-tetraethyldiethylenetriamine
trien	triethylenetetramine
tet-b	D,L-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
trenen	4-aminoethyl-1,4,7,10-tetraazadecane
cyclam	1,4,8,11-tetraazacyclotetradecane
py	pyridine
β-pic	3-methylpyridine (β-picoline)
γ-pic	4-methylpyridine (γ-picoline)
pip	piperidine
bipy	2,2'-dipyridine
phen	1,10-phenanthroline
CHEtpy	pyridiniumpropyl 
ox^{2-}	oxalate ion

$EDTA^{4-}$	ethylenediaminetetraacetato-ion
$acac^{-}$	acetylacetonato-ion
DH^{-}	dimethylglyoximato-ion
diars	o-phenylene-bis(dimethylarsine)
DMSO	dimethylsulphoxide

Units

g	gram	hr	hour
mol	mole	deg	degree
mmol	millimole	cal	calorie
ml	millilitre	kcal	kilocalorie
cm	centimetre	e.u.	entropy unit (cal deg^{-1} mol^{-1})
nm	nanometre	a.u.	absorbance unit
s	second	M	molar
min	minute	N	normal

General

UV	ultra violet
i.r.	infra red
n.m.r.	nuclear magnetic resonance
k_{obsd}	a pseudo-first-order rate constant
λ	wavelength
λ_{max}	wavelength of an absorbance maximum
ϵ_{max}	extinction coefficient at an absorbance maximum
M.O.	molecular orbital
log, $\log_{10}$	logarithm to the base 10
ln	natural logarithm

B.D.H.	British Drug Houses, Limited
ca.	circa (about)
Fig.	figure
ed.	editor
edn.	edition
cmx	complex

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PART I

SUBSTITUTION REACTIONS OF *TRANS*-DIACIDOBISETHYLENEDIAMINERHODIUM(III) COMPLEXES

CHAPTER 1

Mechanisms of Substitution in Inert Metal Complexes; a Critical Review

Langford and Gray[1] have defined four modes of reaction available to an octahedral complex ML_5X undergoing the substitution reaction (1.1) in solution.

$$ML_5X + Y \longrightarrow ML_5Y + X \qquad (1.1)$$

These are a dissociative D mechanism characterised by production of a five co-ordinate intermediate ML_5; reaction by this mechanism can be considered to occur if competition ratios for the supposed intermediate can be shown to be independent of the means of generating it. Reaction via an associative A mechanism can be considered to occur if the presence during the reaction of a seven-co-ordinate intermediate ML_5XY is detected. The other two mechanisms envisage reaction occurring without the formation of an intermediate via an interchange, I, mechanism which can either involve slight bond-making to the incoming group and extensive breakage of the bond to the leaving group (Id mechanism), or the reverse situation which is designated an Ia reaction.

There have been several attempts to predict theoretically the mechanism of the reaction and the precise geometry of the transition state or intermediate for complexes of a particular metal. These have concentrated on the loss of crystal field stabilization energy (C.F.S.E.) on going from an octahedral ground state to a five (Id or D) or seven (Ia or A) co-ordinate transition state. Although loss of C.F.S.E., which is called the crystal field activation energy, C.F.A.E., is only one of several contributions to the overall activation energy,[2] predictions using this simple approach

have often been fruitful. Thus Swaddle et al.[3] have observed that the position of the ligand field band of $[Co(NH_3)_5OH_2]^{3+}$ changes with pressure and the ligand field volume of activation for H_2O loss from this ion is calculated to be +1.6 cm^3 mol^{-1}, in excellent agreement with the experimental value of +1.2 cm^3 mol^{-1}. C.F.A.E. calculated using one-electron parameters indicate that for d^0 to d^{10} ions the C.F.A.E. is lower for an associative, a, reaction via an octahedral wedge transition state [4] than for an a reaction via a pentagonal bipyramidal[5] transition state or a d mechanism via a square pyramidal transition state.[4] Companion[6] has emphasized the advantages of using many-electron formulae in these calculations, but it is unlikely that qualitative conclusions for a particular metal ion are affected by this complication. It is reassuring that C.F.A.E. calculated using an M.O. approach[7] are identical with Basolo and Pearson's.[5]

More specific calculations by Adamson et al.[8] have predicted that the lowest energy mode of reaction for Co(III) substitutions will be dissociative in nature and will involve a square pyramidal transition state, whereas Cr(III) has its lowest C.F.A.E. for reaction via an associative reaction and an octahedral wedge transition state. In general it can be predicted that the C.F.A.E. will become increasingly important in determining the mode of reaction as one descends a given group of the Periodic Table; this is a consequence of the larger ligand field splittings for second and third row transition metals.[9]

In addition to Crystal Field considerations, steric factors predict that an associative mechanism would be unfavourable for an octahedral complex. Thus although Pd(II) complexes generally react via an associative mechanism,[10] the sterically hindered complexes $[PdEt_4dienX]^+$ (X = Cl ,

Br , I) undergo reaction via a dissociative mechanism in dipolar aprotic solvents and an associative mechanism, for which only the solvent can act as an effective nucleophile, in protic solvents.[11] Steric factors are likely to be less restrictive for the larger second and third row transition metal ions than for the first row transition metals. Thus both steric and electronic factors suggest that increased associative character might be expected in reactions of second and third row transition metals compared with the first transition series.

So far as experimental results are concerned, Co(III) complexes have been extensively studied and their mechanisms used as models for comparison with complexes of other metals. Their mechanisms will be considered first, therefore, before discussing mechanisms available to Rh(III) complexes.

For reaction by a dissociative mechanism, the rate of loss of X from CoL_5X should be dependent on the strength of the Co-X bond. The $Co(NH_3)_5^{3+}$ moiety is a hard acid[12] and Co-X bond strengths decrease in the order X = F > Cl > Br > I , and rates of aquation increase in the order X = F < Cl < Br < I ,[13] correlating with the strength of the Co-X bond and not free energy of solvation of the leaving group.[14] There is a reasonably good correlation between the logarithm of the rate constant, k_{aq}, for the reaction

$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5OH_2]^{3+} + X^- \qquad (1.2)$$

and the basicity of the leaving group X (X = F, Cl, Br, SCN) as measured by the pK_a of HX.[15] A similar correlation exists when X is a series of carboxylate ligands;[16] aquation for the latter complexes occurs by Co-O

and not C-O bond breaking.[17] Where data are available, and when X is not a carboxylate ligand, logarithms of the rate constant for reaction (1.2) also correlate well with the logarithms of the rate constants for solvolysis of the corresponding alkyl halide.[15] All these facts point to a dissociative mode of activation.

Langford[18] showed that a plot of the logarithm of the rate constant for reaction (1.2) against the logarithm of the equilibrium constant, K, for the same reaction is a straight line of unit gradient. This implies that the transition state is very like the products in that the Co-X bond is almost completely broken to give a fully solvated anion, X^-. Haim[19] has pointed out that if the reverse of reaction (1.2) is assumed to occur by the Id mechanism

$$[Co(NH_3)_5OH_2]^{3+} + X^- \overset{K_{IP}}{\rightleftharpoons} \{[Co(NH_3)_5OH_2],X\}^{2+} \qquad (1.3)$$

$$\{[Co(NH_3)_5OH_2],X\}^{2+} \underset{k_{aq}}{\overset{k_{IP}}{\rightleftharpoons}} [Co(NH_3)_5X]^{2+} + OH_2 \qquad (1.4)$$

then a linear free energy relationship between k_{aq} and K with a gradient of unity implies that the product $k_{IP}K_{IP}$ is independent of X^-. This will obviously be true if K_{IP} and k_{IP} are separately independent of X^-. Neglecting specific interactions and assuming the distance between the ions in the ion pair is not greatly dependent on X^-, K_{IP} will be approximately constant for all anions of the same charge, so the linear free energy relationship implies that k_{IP} is independent of the nature of X^-. This is the criterion for a dissociative mechanism. Langford and Muir[20] have studied the reaction

$$[Co(NH_3)_5OH_2]^{3+} + X^- \longrightarrow [Co(NH_3)_5X]^{2+} + H_2O \qquad (1.5)$$

and shown that the rate law is

$$k_{obsd} = \frac{k_{IP}K_{IP}[X]}{1 + K_{IP}[X]} \qquad (1.6)$$

in accordance with the interchange mechanism. Values of K_{IP} agree with those determined spectrophotometrically which argues against the alternative interpretation of K_{IP} as a constant measuring the competition of X^- and H_2O for a five-co-ordinate intermediate. Values of k_{IP} varied by only a factor of two for $X^- = HPO_2^-$, Cl^-, SCN^-, SO_4^{2-}, and in all cases k_{IP} was about one fifth of the rate constant k_{ex} for H_2O exchange of $[Co(NH_3)_5OH_2]^{3+}$. This implies that the incipient $Co(NH_3)_5^{3+}$ moiety reacts unselectively with whichever nucleophile, H_2O or X^-, is suitably orientated in the outer sphere. The Bockris model[21] of ion-solvation considers a cation to be surrounded by a monolayer of H_2O molecules, some of which are orientated and bonded to the cation, and the rest of which are non-orientated and are bonded to solvent molecules in a solvent-structure-broken region lying between the monolayer and the bulk solvent. Since presumably only orientated H_2O molecules can react with the $Co(NH_3)_5^{3+}$ species, a ratio of 0.2 for k_x/k_{ex} means that on this model the second co-ordination sphere of the encounter complex contains five orientated H_2O molecules. Results similar to these were found[22] for anation of <u>cis</u>-$[Coen_2NO_2(DMSO)]^{2+}$ by Cl^-, NO_2^-, SCN^- in DMSO. For anation of $[Co(NH_3)_5OH_2]^{3+}$ by N_3^- in water, however, k_{N_3}/k_{ex} is about equal to unity; this has been explained[23] as being due to a specific orientation of N_3^- adjacent to the departing H_2O molecule, with possible proton transfer from the H_2O to the N_3^- to give HN_3 as the incoming nucleophile.

Powell[24] has considered the transition enthalpy ΔH_T for reaction (1.2); ΔH_T measures the enthalpy of the transition state relative to that

of the products

$$\Delta H_T = \Delta H^{\ddagger}_{aq} - \Delta H^0 \qquad (1.7)$$

where $\Delta H^{\ddagger}_{aq}$ is the enthalpy of activation for reaction (1.2) and ΔH^0 is the standard enthalpy change for reaction (1.2). Values of ΔH_T were approximately constant for X = Cl , Br , NO_3 ; this means that the nature of X affects the enthalpy of the transition state and the product in an identical way, and a linear relationship of unit gradient exists between $\Delta H^{\ddagger}_{aq}$ and ΔH^0.

The volumes of activation $\Delta V^{\ddagger}$ for reaction (1.2) reinforce the large body of evidence which suggests a dissociative mechanism. For the H_2O exchange of $[Co(NH_3)_5\ OH_2]^{3+}$ where electrostriction is minimal, $\Delta V^{\ddagger}$ is $+1.2\ cm^3\ mol^{-1}$; the positive value implies a dissociative mechanism,[25] especially when compared with the value of $-27\ cm^3\ mol^{-1}$ found for the associative reaction of Br^- with trans-$[Pt(PEt_3)_2Cl_2]$.[26] When values of $\Delta V^{\ddagger}$ for reaction (1.2) are plotted against ΔV^0, the molal volume change for the reaction, a straight line of unit gradient is found, indicating again that substantial Co-X bond breaking occurs in the transition state.[3] An earlier claim[27] that $\Delta V^{\ddagger}$ was equal to ΔV^0 has since been withdrawn.[3]

One final experiment which has indicated that reaction (1.2) occurs by an Id and not a D mechanism is the fact that loss of NO_3^- from $[Co(NH_3)_5NO_3]^{2+}$ in the presence of 0.5 M SCN^- leads to rapid formation of the aquo-complex followed by slow anation by SCN^-.[28] Data for the reaction of the five-co-ordinate species $[Co(NH_3)_5]^{3+}$, generated by action of HNO_2 on $[Co(NH_3)_5N_3]^{2+}$, with SCN^- in aqueous solution show that SCN^- competes very effectively with water in scavenging this species;[29] clearly $[Co(NH_3)_5]^{3+}$ is not generated during the spontaneous aquation of

$[Co(NH_3)_5NO_3]^{2+}$, even though NO_3^- is a very good leaving group.

Apart from anation reactions where formation of the encounter complex (ion-pair) leads to "accidental bimolecularity"[20] the concentration of the entering group does not generally enter into the rate law for substitution in Co(III) complexes. There are a few small [anion]-dependences found for reactions of cationic complexes; these have been ascribed to ion-pairing, and are discussed in Chapter 3. Apart from these, the only widespread exception to the above rule is found for OH^- in aqueous solution, or more generally, the lyate ion of the solvent. The general consensus of opinion is that this is due to reaction of the OH^- ion with the substrate to give a very reactive deprotonated species (S_N1CB mechanism), and this too is discussed in Chapter 3. The insensitivity of the rate of reaction to concentration of other entering nucleophiles again supports a dissociative mechanism.

The very extensive experiments used to elucidate the mechanism for Co(III) complexes, have not always been applied to other metal complexes, and investigators have sometimes assigned mechanisms to the latter on the basis of the effect of changing the charge of the substrate, the effect of non-labile ligands, solvent effects, and the stereochemistry of the reaction products. It is therefore necessary to consider the effect of these factors on Co(III) complexes.

For a dissociative reaction, increased positive charge on the substrate should lead to decreased reactivity; unfortunately, changing the electronic charge entails changing the non-labile ligands, and the two complexes may no longer be comparable. Chan and Chan[30] have found that the rate constants and activation parameters for loss of Cl^- from cis-

$[Coen_2LCl]^{n+}$ when L is the protonated diamine $[H_2N(CH_2)_3\text{-}NH_3]^+$ are very similar to those found when L is $CH_3\text{-}(CH_2)_3NH_2$. The insensitivity to charge is not, perhaps, surprising since the extra positive charge on the diamine is located not on the cobalt, but five atoms away from the departing Cl^-.

The effect of the non-labile ligands can be considered as due to a superposition of steric and electronic factors. Chan and co-workers have extensively studied the effect of steric strain in aquation of cis-$[Coen_2LCl]^{2+}$ where L is an amine; in all cases increased steric hindrance in the ground state leads to increased rates of aquation.[30-32] They have also shown[33] that the sterically hindered[34] complex $[Co(NH_2Me)_5Cl]^{2+}$ loses Cl^- very much more rapidly than $[Co(NH_3)_5Cl]^{2+}$. However, the importance of changing solvation of the substrate as the non-labile ligands are altered has been emphasised.[35] Chan and Poon[36] have elegantly demonstrated the effect of steric strain in trans-$[Co(tet\text{-}b)Cl_2]^+$. In this complex one Cl^- is in an "open" environment, and the other is compressed and shielded by the macrocyclic ligand. The shielded Cl^- aquates fourteen times faster than the non-sterically hindered Cl^-.

The electronic effects of non-labile ligands have been discussed for loss of CO_3^{2-} from cis-$[CoL_2CO_3]^+$,[37] loss of Cl^- from cis-$[CoL_2Cl_2]^+$[38] where L (in both complexes) is phen, bipy or en, and loss of Cl^- from cis-$[Coen_2ACl]^{2+}$[39] where A is a substituted pyridine. In all cases the order of increasing reactivity parallels the order of increasing basicity of the amine; this is in marked contrast with the associative replacement of Cl^- from $[Pt(phenX)Cl_2]$ (phenX is a substituted phenanthroline) by dithiooxamide where complexes of the least basic phenanthroline

react most rapidly.[40]

For loss of Cl^- from cis- and trans-$[Coen_2LCl]^{n+}$, the rate constants decrease in the orders[41]

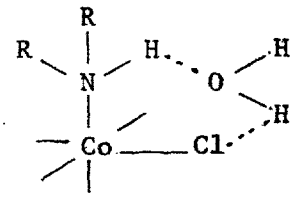
$$\underline{trans}\text{-}L = OH^- > NO_2^- > N_3^- > CN^- > Br^- > Cl^- > SO_4^{2-} > NCS^-,$$

$$\underline{cis}\text{-}L = OH^- > Cl^- > Br^- > NO_2^- > SO_4^{2-} > NCS^-.$$

Although very considerable enhancement of reactivity is achieved by changing L from NCS^- to OH^-, the above orders show that the effect of L does not depend greatly on its geometry in the complex relative to the leaving group. In order to explain the non-stereospecificity of electronic effects in Co(III) complexes, Pearson and Basolo[42] have suggested that the non-labile ligands affect the rates of reaction predominantly through π-interactions in the transition state and Langford[43] has argued that the lack of a specific trans-effect is due to Co(III) utilising 3d rather than 4p orbitals in its bonding.

Poon et al. have discussed[44-49] loss of Cl^- from trans-$[CoLACl]^{n+}$ where L is cyclam, 2en, 2pn, $4NH_3$ and A is SCN^-, CN^-, NO_2^-, Cl^-, NH_3 and have suggested that for a given trans-ligand, A, the relative reactivities of the complexes can be correlated with the position of L in the nephelauxetic series. Within the trans-$[CocyclamACl]^{n+}$ and trans-$[Coen_2ACl]^{n+}$ series the rate of loss of Cl^- has also been correlated with the position of A in the nephelauxetic series.[44]

One way that a cis-ligand can affect the reaction rate of a complex is by hydrogen-bonding interactions. Adamson and Basolo[50] postulated co-operative hydrogen-bonding between the leaving group, a water molecule in the second co-ordination sphere, and an acidic hydrogen atom on the cis-ligand:



Pearson et al.[51] have queried this interpretation for normal aquation of cis-amine complexes, but there is convincing evidence[3] that a basic leaving group, such as N_3^-, is so extensively hydrogen bonded in the transition state that aquation of $[Co(NH_3)_5N_3]^{2+}$ can be considered to involve loss of N_3H from a dipositive, deprotonated species. It is not clear whether proton loss has occurred from the co-ordinated NH_3 ligands, or from a water molecule in the solvation sheath; Swaddle[3] favours the latter interpretation.

The stereochemistry of spontaneous aquation of Co(III) complexes has been extensively discussed by Basolo and Pearson[52a] and reviewed by Archer.[52b] The general rule appears to be that stereochemical change occurs only for trans-isomers, and then only when the trans-ligand has π-donor properties. Under these circumstances, rearrangement to a trigonal bipyramidal transition state is energetically feasible, but for the cis-isomers the ligand is already in a position to give extensive π-bonding, and aquation via a square pyramidal transition state is indicated. Recently, however, there have been indications that stereochemical rearrangement does in fact occur with cis-complexes.[53,54] Tobe[55] correlated the occurence of stereochemical rearrangement with a large, positive entropy of activation, $\Delta S^{\ddagger}$, and pointed out that this assumes that "the grosser aspects of stereochemical change are determined in the transition state." However, trans-diacido-complexes of macrocyclic ligands aquate

with retention of configuration and still have positive values of $\Delta S^{\ddagger}$.[56,57] This behaviour is consistent with a general loosening of the macrocyclic ligands in the transition state,[56] which could well be trigonal bipyramidal,[57] but the large amount of steric strain in the cis-complexes makes their formation energetically unfavourable compared to formation of the trans-complexes.[57]

Solvation effects on reaction rates are difficult to predict from first principles; the general procedure has been to attempt to correlate trends in reaction rates with trends for a reaction of known mechanism. Thus Burgess et al.[58] have shown that for aquation of cis-$[Coen_2Cl_2]^+$ and $[Co(NH_3)_5Cl]^{2+}$ in aqueous organic solvents, a graph of the logarithm of the rate constant against the Grunwald-Winstein solvent parameter, Y, is linear with a slope of +0.30. This is taken to indicate a dissociative mechanism, but with rather different solvation requirements for the complex ion and its transition state compared with the alkyl halide and its transition state.[58,59] However, Burgess[60] also showed that the rate of aquation of cis-$[Coen_2Cl_2]^+$ in t-BuOH/H_2O mixtures decreases as the mole fraction of t-BuOH increases from 0 to 0.04, then increases as the mole fraction of t-BuOH is further increased. He has interpreted this behaviour as indicating that Co-OH_2 bond making has some importance in the transition state, since below 0.04 mole fraction t-BuOH the mixed solvent behaves as a "clathrate" water-structure-enhancing system, and above 0.04 mole fraction t-BuOH a "re-organised" water-structure-breaking model becomes appropriate.[61] However, this analysis has neglected the effect of solvation on the leaving Cl^- ion; it might reasonably be supposed that if a "free" water molecule would interact more readily with the Co(III) ion in an associative mechanism, it would also interact more readily with the

Cl^- ion in a dissociative mechanism.

Although the available evidence indicates that most Co(III) complexes react by an Id mechanism, there are several important exceptions. Co(III) haematoporphyrin is considered[62] to undergo anation by a D mechanism; the presence of a Co-imine linkage appears to enhance the lability of the complex and increase the tendency to react by a D pathway.[57] Anations of cis- and trans-$[Co(cyclam)ClOH_2]^{2+}$ are similarly considered to be D reactions; differing competition ratios for the intermediates derived from the two geometric isomers, and the complete retention of configuration observed in both cases, means that the reactions proceed through two different square pyramidal intermediates and not through a common trigonal bipyramidal species.[63] A D reaction pathway by a well-characterised intermediate has been found for Co(III) systems which contain the sulphite-ligand trans to the leaving group.[64-68] The strong trans-labilising effect of SO_3^{2-}, which apparently acts via stabilisation of the transition state (and also the intermediate) rather than bond-weakening in the ground-state,[68] is considered responsible for formation of the intermediate. In addition, penta-cyano-complexes of Co(III) show a D mechanism.[69] Presumably, here the high negative charge of the complex, as well as increased Co-CN bond strengths due to the π-acceptor properties of CN^- lead to reaction via a D pathway and stabilisation of the intermediate.[69]

Reaction by a five-co-ordinate intermediate also becomes more likely as the leaving group, X, becomes more weakly bound. Artificial weakening of the Co-X bond has been achieved by reacting Co complexes containing a halide or pseudo-halide leaving group, with Hg^{2+}. There is a large body of evidence which suggests that the reaction proceeds by pre-association

of the Hg^{2+} electrophile with the leaving group to give a binuclear complex;[70-72] this is followed by loss of HgX^{+} to give a five-co-ordinate intermediate.[70,29] The situation when other electrophiles are used to induce aquation is not so clear.[75,77,78]

Examples of Cobalt(III) complexes reacting by an associative mechanism are rare, and in every case the assignment is somewhat ambiguous. The rate law for reaction of $[Co(NH_3)_5S_2O_3]^{+}$ with Cl^{-}, OH^{-}, NH_3 contains a term which is first order in concentration of entering nucleophile.[79] The order of reactivity is $OH^{-} > Cl^{-} > NH_3 > H_2O$ which is similar, but not identical to the order of nucleophilic reactivity constants[80] $n^{\circ}_{CH_3I}$ for loss of I^{-} from CH_3I. The position of OH^{-} is ambiguous, since it can react via the S_NICB mechanism; similarly, it may be that the position of NH_3 is determined by its ability to provide OH^{-} ions in aqueous solution. Cl^{-} could be forming a reactive ion-pair with the substrate, although the very negative value of $\Delta S^{\neq}$ is hard to explain on this mechanism.

In order to explain the formation of cis-β-$[CotrienClOH_2]^{2+}$ as the sole product of the aquation of trans-$[CotrienCl_2]^{2+}$, Sargeson and Searle[81] have postulated an associative mechanism, with the incoming water molecule helping to evict the Cl^{-} ligand, and giving the observed product by Ingold's edge-displacement mechanism.[82] Niththyananthan and Tobe[83] have pointed out that the stereochemistry of the product is not inconsistent with a dissociative mechanism provided that account is taken of hydrogen-bonded and steric interactions in the transition state. An Ia mechanism has also been suggested for the aquation of $[Co(NH_3)_5PO_4H_3]^{3+}$ where the observed rate is a linear function of the activity of H_2O[84] and for the base hydrolysis of $[Co(NH_3)_5PO_4]$.[85] The mechanistic assignment

for the last complex is very ambiguous.

The only other inert octahedral complexes which have been studied in detail are those of Cr(III). Here there is no evidence for a D pathway in spontaneous aquation[86,87] but the Hg^{2+}-catalysed aquations are at least Id[88] in nature, and may well involve a D mechanism. An Id mechanism has been proposed[89] for aquation of $[Cr(NCS)_6]^{3-}$. The aquation of $[Cr(NH_3)_2(NCS)_4]^-$ also seems to be Id, but this complex requires the participation of two H_2O molecules in the transition state, one suitably orientated to form the product, and one to hydrogen-bond to the leaving NCS^- ion.[90,91] This model, which bears some resemblance to Adamson's original model for the reaction[92] might explain the slightly negative volume of activation for the reaction.[93]

Swaddle and his co-workers have accumulated convincing evidence that anation of $[Cr(H_2O)_6]^{3+}$ (and by microreversibility the aquation of $[Cr(H_2O)_5X]^{n+}$),[94-98] and also the corresponding reactions of the pentammine complexes[99] occur by an Ia mechanism. Powell[100] has also correlated transition enthalpies, ΔH_T (see equation 1.7) for the reaction

$$[Cr(H_2O)_5X]^{2+} + H_2O \longrightarrow [Cr(NH_3)_5OH_2]^{3+} + X^- \qquad (1.8)$$

with the enthalpies of solvation of X^-; for reactions of Cobalt(III) complexes ΔH_T is independent of the nature of X. An Ia mechanism is in agreement with Adamson's C.F.A.E. calculations[8] and with German and Dogonadze's quantum mechanical predictions.[101] Espenson,[102] however, prefers an Id mechanism for these reactions. The conflict between these two interpretations may be more apparent than real; whilst Espenson is emphasising that ligand-dissociation plays an important part in forming the transition state, Swaddle is indicating that reactions of cationic

Cr(III) complexes are nevertheless more associative than those of cationic Co(III) complexes. The term "ligand-assisted dissociative interchange"[102, 103] although cumbersome, at least indicates that both modes of activation are important.

Rhodium(III) is isoelectronic in its valence shell with Co(III) and its kinetics have generally been compared with those of its congener, but there are some similarities between reactions of Rh(III) and those of Cr(III).

The effect of the leaving group has been studied for halide loss from $[Rh(NH_3)_5X]^{2+}$,[104,105] <u>trans</u>-$[Rhen_2IX]^+$[106] and <u>trans</u>-$[Rhen_2BrX]^+$.[106] In each case the rate constants increase in the order X = I < Br < Cl . This trend is the reverse of that found for halide loss from $[Co(NH_3)_5X]^{2+}$, and Chan et al.[105] suggested that this indicated an I<u>a</u> mechanism for the Rh(III) complexes. However, Poë et al.[104] pointed out that the enthalpies of activation for $[M(NH_3)_5X]^{2+}$ follow the order I < Br < Cl , for both Co(III) and Rh(III) complexes, and using this criterion the relative reactivities of the complexes within the two series are similar, implying by Chan's reasoning that a common mechanism is operative. Thus mechanistic assignments on leaving group effects do not seem to be very reliable.

The entering groups in the substitution reaction

$$RhL_5X + Y^- \longrightarrow RhL_5Y + X^- \qquad (1.9)$$

appear to have little, if any, effect on the rate, provided that Y is not OH^- and X is not H_2O.[106-109] This has been interpreted to mean that, as for Co(III), the rate determining step is aquation of $[RhL_5X]$, followed by fast anation of $[RhL_5OH_2]$ by Y^-.

One of the most profound differences between Co(III) and Rh(III) chemistry is that stereochemical change in Rh(III) substitutions is extremely rare. Those examples which have been found have involved forcing conditions, and they are discussed in Chapter 3. This retention of topography may be one reason why Rh(III) exhibits a pronounced trans-effect; stereorigidity means the trans-ligand cannot become sterically and electronically equivalent to the cis-ligands by forming with them the axial plane of a trigonal bipyramidal transition state. The trans-effect in Rh(III) has been studied by Poë et al.[104,106,110,111] and by Klabunde[112] and will be discussed in detail in Chapter 4. The cis-ligands do exert a slight effect; the rate constant for Cl^- loss from trans-$[Rh(NH_3)_4Cl_2]^+$ is twice that of trans-$[Rhen_2Cl_2]^+$;[108] this is consistent with the ligand field strengths[108] and the nephelauxetic effects[49] of the amine ligands. However, Poë has pointed out[108] that the reverse order of reactivity occurs in anation of the corresponding chloroaquo-complexes, and that the effect of the cis-ligands is due to solvation rather than electronic effects.[107,113] It does seem to be generally agreed, however, that electronic effects in Rh(III) are governed by σ- and not π-bonding considerations.[106,107,114-116] Steric effects of the cis-ligands, although they follow the same trend as for Co(III), are not so important for the larger Rh(III) ion.[107]

The small effect of charge on rates of reaction of Rh(III) amine complexes was cited[107] as evidence that these complexes react by an associative mechanism. Poë[110] has noted that the effect of charge may be obscured by the trans-effect. However, for cis-$[Rhen_2Cl_2]^+$ and cis-$[Rhen_2NH_3Cl]^{2+}$ where the trans-ligand remains the same, the rates of Cl^- loss at 90.3°C differ by only one order of magnitude;[117] the corresponding

Co(III) complexes differ in rates by a factor of 480 at 25°C.[118] The rather small differences (ca. 2 kcal mol^{-1}) between activation energies for substitution in Rh(III) complexes and their Co(III) analogues, compared to the C.F.A.E. prediction of 5 kcal mol^{-1} has also been explained by assuming Rh(III) substitutions are more associative than Co(III) reactions.[107,119,120] In view of the rather tenuous nature of most of this evidence for an I<u>a</u> pathway in Rh(III) amine complexes, Poë has suggested that a precise assignment of mechanism for these complexes may not be possible.[110]

However, more definite evidence for an I<u>a</u> pathway in Rh(III) substitutions has been obtained from studies of anation reactions. Monacelli[121] and Poë[122,123] separately studied anation of $[Rh(NH_3)_5OH_2]^{3+}$ by Cl^-, Br^-, I^-, SCN^-, SO_4^{2-}. In some cases a rate law of the form

$$k_{obsd} = \frac{a[X]}{1 + b[X]} \qquad (1.10)$$

was found, where X^- is the incoming anion. Values of b agreed well with ion association constants K_{IP} determined spectrophotometrically for ion-pairing between the substrate and X. The rate law is consistent with the interchange mechanism shown for Co(III) anation in equations (1.3) and (1.4). From equation (1.6), a/b is equal to k_{IP} the rate constant for interchange of X from the second co-ordination sphere to the first. The value of k_{IP} seems to depend on the nature of X, its value being $X^- = Cl^- > Br^- > SO_4^{2-}$, and more importantly, it is up to 5 times greater than k_{ex}, the rate constant for H_2O exchange in $[Rh(NH_3)_5OH_2]^{3+}$. In 4.0 M Cl^- solution, the rate of H_2O exchange is only enhanced by a factor of 1.2,[124] so acceleration of H_2O loss from the $\{[Rh(NH_3)_5OH_2],X\}^{n+}$ ion pair

by electrostatic repulsion is not a valid explanation for the high values of k_{IP}/k_{ex}. The conclusion is that the rates of reaction are enhanced because there is a certain amount of bond formation to the entering anion in the transition state, i.e., that the mechanism is I<u>a</u>. The effects of changing the composition of the ionic atmosphere on the activity coefficients of the complex salt and the ion pair, and also of possible ion-pairing of the complex ion with ClO_4^- have been discussed by Poë et al.[123] They have concluded that although these effects will most probably increase the value of k_{IP}/k_{ex}, there is a remote possibility that they will actually decrease it; the decrease would not be sufficient, however, to invalidate the assignment of the mechanism as I<u>a</u>.

Swaddle and Stranks[97a] have determined the volume of activation $\Delta V^{\ddagger}$ for the H_2O exchange of $[Rh(NH_3)_5OH_2]^{3+}$ and found it to be -4.1 cm^3 mol^{-1}; the negative value indicates the reaction is much more associative than the corresponding Co(III) reaction ($\Delta V^{\ddagger}$ = +1.2 cm^3 mol^{-1}), but slightly less than the Cr(III) reaction ($\Delta V^{\ddagger}$ = -5.8 cm^3 mol^{-1}). It has been suggested, however, that curvature of the plot of log k_{ex} against pressure for the Rh(III) reaction indicates an I<u>a</u> mechanism at high pressures which changes to an I<u>d</u> mechanism at low pressures.[97a] Powell[125] has used transition enthalpies to show that $[Rh(NH_3)_5X]^{2+}$ aquations and $[Rh(NH_3)_5OH_2]^{3+}$ anations are more associative than the corresponding Co(III) reactions, but less associative than $[Cr(H_2O)_5X]^{2+}$ aquations and $[Cr(H_2O)_6]^{3+}$ anations. He feels, however, that the rhodium(III) pentammine reactions are dominated by their dissociative character.

Like Cr(III), Rh(III) can sometimes react by a dissociative mechanism; continuing the trend of more dissociative activation for Rh(III) than

Cr(III), the existence of a D pathway seems fairly certain for anionic Rh(III) complexes. The rate of approach to equilibrium in the system

$$[RhCl_6]^{3-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [RhCl_5OH_2]^{2-} + Cl^- \qquad (1.11)$$

obeys the rate law

$$k_{obsd} = k_1[RhCl_6^{3-}] + k_{-1}[RhCl_5OH_2^{2-}][Cl^-]. \qquad (1.12)$$

An Ia mechanism was originally[126] assigned, with $[RhCl_5OH_2]^{2-}$ undergoing direct nucleophilic attack by Cl^-. This contrasts with Cl^- exchange of $[RhCl_6]^{3-}$ which proceeds via aquochloro-intermediates, with no direct attack by Cl^-,[127] and is also inherently unlikely from electrostatic considerations. Further work on the reaction of the nucleophiles, X^-= Br^-, I^-, SCN^-, NO_2^-, N_3^- with $[RhCl_5OH_2]^{2-}$ showed that in some cases a rate law corresponding to equation (1.10) was obeyed.[128] With two anionic reactants, b is unlikely to be an ion-pairing constant, and the reaction was accordingly assigned a D mechanism.

$$[RhCl_5OH_2]^{2-} \rightleftharpoons [RhCl_5]^{2-} + H_2O \qquad (1.13)$$

$$[RhCl_5]^{2-} + X^- \longrightarrow [RhCl_5X]^{3-} \qquad (1.14)$$

Recently Pavelich and Harris have suggested[129] that $[Rh(H_2O)_5Cl]^{2+}$ undergoes Cl^- anation by a D mechanism. The rate law is that of equation (1.10), which can be explained by either a D mechanism or interchange within an ion-pair. The authors considered competitive ion-pairing by ClO_4^-, and also the formation of $[Rh(H_2O)_4OHCl]^+$ and have decided that an ion-pair interchange mechanism can be excluded because

assumption of this mechanism means that (a) the pH-dependence of the kinetic data is not consistent with the value of K_A, the acidity constant of $[Rh(H_2O)_5Cl]^{2+}$ obtained by potentiometric titration, (b) the pH-dependence of the reaction is not properly described at low pH, (c) a negative value is obtained for one of the ion-pairing constants. The sole product of the reaction is trans-$[Rh(H_2O)_4Cl_2]^+$, and Pavelich and Harris have argued that considering that only H_2O loss trans to the co-ordinated Cl^- ions leads to reaction, does not affect their conclusions. However, the possibility remains that the acidities of H_2O molecules cis and trans to the Cl^- ligand are not equal, and that a K_A value determined by titration may not refer to the stereospecific K_A appropriate to the anation. This casts some doubt on objections (a) and (b) to the ion-pairing mechanism, and also on (c), since the calculations on which this point was based assumed the potentiometric value for K_A. The authors have also re-interpreted earlier work[130] on the Cl^- anation of $[Rh(H_2O)_6]^{3+}$ in terms of a D mechanism. The H_2O exchange of $[Rh(H_2O)_6]^{3+}$ occurs with a much higher enthalpy of activation and a rather more positive entropy of activation than the corresponding values for H_2O exchange of $[Cr(H_2O)_6]^{3+}$. This was interpreted[131] as indicating a d mechanism for $[Rh(H_2O)_6]^{3+}$. Anation by Cl^- of $[Rh(H_2O)_6]^{3+}$ obeys the familiar rate law of equation (1.10).[130] The limiting rate, a/b is slightly larger than k_{ex}, the rate constant for H_2O exchange of $[Rh(H_2O)_6]^{3+}$, although the differences are within experimental error. This is consistent with a D formulation for the mechanism. If the reaction occurs by the alternative ion-pair interchange mechanism, a/b is equal to k_{IP}, the rate constant for interchange within the ion pair. A ratio of k_{IP}/k_{ex} of unity implies appreciable bonding to the incoming

nucleophile in the transition state.[20,121-123] Assignment of the mechanism for this reaction would be facilitated if a volume of activation were available for the water exchange of $[Rh(H_2O)_6]^{3+}$.

The only other simple reaction of Rh(III) which has been assigned a D mechanism is aquation of trans-$[Rh(DH)_2SO_3Cl]^{2-}$ which Syrtsova and Bolgar[132] have postulated follows a similar mechanism to that of its Co(III) analogue. A D mechanism has been postulated for anation of $[Co(DH)_2SO_3OH_2]^-$,[68] but an Id mechanism is not excluded.[66] A D mechanism has also been postulated for Hg^{2+}-induced aquation of $[Rh(NH_3)_5Cl]^{2+}$ and $[Rh(NH_3)_5Br]^{2+}$.[58a,76,133] Chan et al. have argued that the fact that the activation enthalpies $\Delta H^{\ddagger}_{Cl}$ and $\Delta H^{\ddagger}_{Br}$ for loss of Cl^- and Br^- respectively in induced aquations obey equation (1.15) and the corresponding parameters $\Delta H^{\ddagger}_{HgCl}$ and $\Delta H^{\ddagger}_{HgBr}$ for induced aquation obey equation (1.16) indicates that spontaneous aquation of these complexes proceeds by an associative mechanism.

$$\Delta H^{\ddagger}_{Cl} - \Delta H^{\ddagger}_{Br} = -1.9 \text{ kcal mol}^{-1} \qquad (1.15)$$

$$\Delta H^{\ddagger}_{HgCl} - \Delta H^{\ddagger}_{HgBr} = +2.0 \text{ kcal mol}^{-1} \qquad (1.16)$$

However, if the induced aquation proceeds by a pre-equilibrium formation of a binuclear complex, as in the Ag^+-catalysed aquation of $[Rh(NH_3)_5Br]^{2+}$,[135] $\Delta H^{\ddagger}_{HgCl}$ and $\Delta H^{\ddagger}_{HgBr}$ will include the heats of formation of this complex. If it is assumed that the relative affinity of Hg^{2+} for Cl^- and Br^- is unaffected by their complexation to Rh(III), equation (1.16) becomes

$$\Delta H^{\ddagger}_{HgCl} - \Delta H^{\ddagger}_{HgBr} - (\Delta H^{0}_{HgCl} - \Delta H^{0}_{HgBr}) = Y \qquad (1.17)$$

where ΔH^{0}_{HgX} is the heat of complexation of Hg^{2+} with X^- and Y measures

the relative activation parameters for loss of $HgCl^+$ and $HgBr^+$ from the corresponding binuclear complexes. Use of Christensen's values[135] for ΔH^0_{HgX} gives Y = -2.4 kcal mol^{-1} and of Arnek's[136] values gives Y = -2.0 kcal mol^{-1}. Both these values, and particularly the latter, are in good agreement with that for spontaneous aquation (equation (1.15)) which indicates that the mechanisms for spontaneous and induced aquation need not be completely dissimilar.

It might be expected that the pattern established for Co(III) and Rh(III) might be continued for Ir(III) complexes, with increased associative character in the reactions of cationic complexes, and probably D pathways for substitutions involving anionic complexes. This prediction appears to be true in practice. Bauer and Basolo[137] found that substitutions of trans-diacidobisethylenediamineiridium(III) show the familiar insensitivity to the nature of the entering group, indicating that reaction occurred by rate-determining aquation of the substrate followed by fast anation of the aquo-complex. Evidence very similar to that presented for $[Rh(NH_3)_5OH_2]^{3+}$ suggests that $[Ir(NH_3)_5OH_2]^{3+}$ undergoes H_2O exchange[138] and anation[139] by an I*a* process, and the order of increasing associative character in anations of $[M(NH_3)_5OH_2]^{3+}$ appears to be M = Co < Rh < Ir.[139]

Garner and co-workers have studied the anionic $[IrCl_n(H_2O)_{6-n}]^{(n-3)-}$ complexes. Although they have drawn no mechanistic conclusions from their results, they have shown that anation of $[IrCl_5OH_2]^{2-}$,[140], cis-$[IrCl_4(H_2O)_2]^-$,[141] 1,2,6-$[IrCl_3(H_2O)_3]$[142] and trans-$[Irpy_2Cl_3H_2O]$[143] by Cl^- all follow the rate law

$$k_{obsd} = k_2[Cl^-]. \qquad (1.18)$$

At very high $[Cl^-]$, the rate law for anation of $[IrCl_5OH_2]^{2-}$ becomes[144]

$$k_{obsd} = \frac{a[Cl^-]}{1 + b[Cl^-]} \qquad (1.19)$$

which indicates that for at least this reaction, the mechanism is D.

Rh(III) might also be expected to follow similar reaction mechanisms to the isoelectronic Ru(II) ion. However, the chemistry of Ru(II) seems dominated by its π-donor properties,[145-149] and from direct comparison of analogous complexes, it has been concluded that Ru(II) donates π-electron density much more readily that Rh(III).[114,115,148] Thus $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5py]^{2+}$ aquate by an acid-catalysed path which has been ascribed[146] to interaction of a proton with Ru^{2+} π-electron density to give an unstable seven-co-ordinate hydride of Ru(IV). Reactions of Ru(II) are stereoretentive,[150] implying either dissociative activation via a square pyramidal transition state or an associative reaction with cis-attack by the entering nucleophile. Reaction of $[Ru(NH_3)_5OH_2]^{2+}$ with substituted pyridines or organic nitriles,[151] N_2 or N_2O[152] are accurately first order in concentration of incoming nucleophile, and on the basis of the small variation of rates for the different nucleophiles have been assigned a D mechanism.[151] Since a limiting rate is not reached, Wilmarth's classification[68] would imply that the mechanism might be better formulated as Id. A dissociative mechanism has also been suggested for substitution reactions of cis-$[Ruphen_2py_2]^{2+}$.[150b]

Ru(III) lacks the π-donor ability of Ru(II)[147,148,153] and it might be predicted to show similarities of kinetic behaviour to Rh(III). Like Rh(III), Ru(III) amine complexes show retention of configuration; for Ru(III) this behaviour is found even in Hg^{2+}-induced aquation.[154] The effect of charge on the complex is parallel in the two systems, and for both the rate constants for halide loss from $[M(NH_3)_5X]^{2+}$ decrease in

the order X = Cl > Br > I .[155] From this evidence, the reaction mechanism for Ru(III) cationic complexes is considered to be Ia. However, the kinetics of reaction of the anionic complexes of Ru(III) do not seem to follow the trends established for Rh(III). Thus Cl^- exchange of $[RuCl_6]^{3-}$ is retarded, not accelerated, by Cl^-, which has been ascribed to a superposition of primary kinetic salt effects and decreased activity of H_2O in more concentrated HCl solutions, leading to lower rates of attack by H_2O in an Ia mechanism.[156] One rather surprising kinetic observation is that the $[Cl^-]$ has no effect on the rate of anation of cis- or trans-$[RuCl_3(H_2O)_3]$;[157] unless reaction occurs by a D mechanism where Cl^- competes very much more effectively than H_2O for the five-co-ordinate intermediate or by interchange within an ion-pair which is formed extremely readily, it is hard to explain this observation. Anation of $[RuCl_2(H_2O)_4]^+$ is, however, first order in $[Cl^-]$.[157]

In summary, anionic complexes of all the systems considered here, except those of Cr(III) and Ru(III), tend to undergo reaction by an extreme D mechanism. For the cationic complexes the order of increasing a activation, i.e., of increasing bond-formation to the entering nucleophile, appears to be Ru(II), Co(III) < Rh(III), Ir(III), Ru(III) < Cr(III). The position of Ru(III) will remain ambiguous until H_2O exchange studies on $[Ru(NH_3)_5OH_2]^{3+}$ are available, and the question of the $[Rh(H_2O)_6]^{3+}$ and $[RhCl_5(OH_2)_5]^{2+}$ anation data requires some further thought before it can be stated unambiguously that Rh(III) shows an associative mode of activation in its cationic aquo-complexes.

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CHAPTER 2

General Experimental

Preparation and characterisation of complexes *trans*-$[Rhen_2Cl_2]ClO_4$, *trans*-$[Rhen_2Br_2]ClO_4$, *trans*-$[Rhen_2I_2]ClO_4$, *trans*-$[Rhen_2ICl]ClO_4$

All these complexes were prepared by standard methods,[1][2] and were characterised by elemental analysis (performed by the Imperial College Microanalytical Department, London, England, and by the A. B. Gygli Microanalytical Laboratories, Toronto, Canada) and by UV-visible spectroscopy. For *trans*-$[Rhen_2IX]ClO_4$ (X = Cl , I), which undergoes partial aquation whilst being dissolved, the spectra were recorded using solutions that were at least 0.1M in NaX. The spectra of the less labile dichloro- and dibromo-complexes were recorded in water alone. Since all these complexes are slightly light-sensitive,[3][4] their solutions were generally handled in red light, and stored in the refrigerator in flasks wrapped in aluminium foil. Microanalyses of representative samples of the compounds are given in Table 2.1, and their spectra in Table 2.2.

trans-$[Rhen_2BrOH]ClO_4$

An attempt was made to prepare this complex as its aquobromo-derivative by refluxing *trans*-$[Rhen_2Br_2]ClO_4$ with one equivalent of silver perchlorate for 45 min. The silver bromide was filtered off and the UV spectrum of the filtrate (suitably diluted) was recorded. There was a shoulder at ca. 230 nm, which suggested the presence of residual *trans*-$[Rhen_2Br_2]^+$. Moreover, when an aliquot of the filtrate was heated with sodium hydroxide at 64.3°C, a fast reaction occurred, with pseudo-

first-order rate constant $k_f = 3.3 \times 10^{-4}\ s^{-1}$, followed by a slower reaction which had a pseudo-first-order rate constant k_s of $3.9 \times 10^{-5}\ s^{-1}$. The value of k_f agreed well with Shaw's preliminary data[5] for the base hydrolysis of trans-$[Rhen_2BrOH]^+$, and that of k_s with Bott's data[6] for the substitution reactions of trans-$[Rhen_2Br_2]^+$. A second attempt was made to prepare pure trans-$[Rhen_2BrOH_2]^{2+}$, this time by refluxing trans-$[Rhen_2Br_2]ClO_4$ with one equivalent of silver perchlorate, and sufficient perchloric acid that the pH of the final solution was less than 2. However, the product of this preparation was also contaminated with trans-$[Rhen_2Br_2]^+$.

A solution of pure trans-$[Rhen_2BrOH]^+$ was finally prepared by refluxing trans-$[Rhen_2Br_2]ClO_4$ (0.4457 g, 0.9243 mmol), dissolved in the minimum amount of hot water) with 1 ml of ca. 0.1M perchloric acid, and 10 ml 0.09245M silver perchlorate (one equivalent), in a foil-wrapped flask for 40 min. The solution was then placed on a 12 cm long column of Dowex 50 W (100-200 mesh) cation-exchange resin, using the vacuum ion-exchange apparatus shown in Fig. 2.1. The trans-$[Rhen_2Br_2]^+$ was eluted with 0.5M sodium perchlorate, the eluate being collected in 14 to 15 ml fractions. The UV-visible spectra of the fractions were monitored on a Perkin Elmer 402 spectrophotometer. When all the dibromo-complex had been eluted, the eluant was changed to 0.5M sodium perchlorate containing 0.1M sodium hydroxide, and the resulting trans-$[Rhen_2BrOH]^+$ eluted. From the known volumes and absorbances of the $[Rhen_2BrOH]^+$ and $[Rhen_2Br_2]^+$ fractions, and the extinction coefficients of these complexes (vide infra), it was calculated that the trans-$[Rhen_2BrOH]^+$/trans-$[Rhen_2Br_2]^+$ mixture before separation contained 14% trans-$[Rhen_2Br_2]^+$. The spectra of the bromohydroxy-fractions showed that the sodium hydroxide also eluted traces of an unidentified compound, which was probably an

impurity associated with the resin: the presence of this compound did not appear to affect the kinetics of any reaction of the trans-$[Rhen_2BrOH]^+$ complex. The solutions of trans-$[Rhen_2BrOH]^+$ were stored in the refrigerator in foil-wrapped flasks.

The UV-visible spectrum of a suitable trans-$[Rhen_2BrOH]^+$ fraction was recorded, and the fraction was then analysed by converting the trans-$[Rhen_2BrOH]^+$ to trans-$[Rhen_2Br_2]^+$. A suitably diluted aliquot of the bromohydroxy-fraction was heated with an acid bromide solution (final $[Br^-]$ = 0.2M, pH = 4 to 6) until there was no further change in the spectrum (1¼ hr). The absorbance of the product was measured at 278 nm, and the concentration of the original bromohydroxy-fraction calculated from the known extinction coefficient (3042 M^{-1} cm^{-1}) of trans-$[Rhen_2Br_2]^+$ at this wavelength. The spectroscopic parameters obtained for trans-$[Rhen_2BrOH]^+$ are given in Table 2.2.

trans-$[Rhen_2ClOH]^+$

This complex was initially prepared by refluxing trans-$[Rhen_2Cl_2]ClO_4$ with one equivalent of silver perchlorate. Spectroscopic determination of the purity of the product was more difficult than for the bromo-analogue, but curved rate plots were obtained for the base hydrolysis of the product, indicating that the solution was contaminated with residual trans-$[Rhen_2Cl_2]^+$.

A solution of pure trans-$[Rhen_2ClOH]^+$ was obtained by refluxing trans-$[Rhen_2Cl_2]ClO_4$ (0.5866 g, 1.49 mmol) dissolved in the minimum amount of hot water with one equivalent of silver perchlorate for ca. 3½ hr. The chlorohydroxy- and dichloro-complexes were then separated on a column of Dowex 50 W ion exchange resin, as outlined for their bromo-analogues.

The trans-$[Rhen_2ClOH]^+$ was eluted with 0.5M sodium perchlorate containing 0.1M sodium hydroxide. The chlorohydroxy-complex fractions were stored in the refrigerator in foil-wrapped vessels. Spectroscopic analysis of the chlorohydroxy- and dichloro-complex fractions showed that the original solution had contained 15% trans-$[Rhen_2Cl_2]^+$.

The spectroscopic parameters of trans-$[Rhen_2ClOH]^+$ were determined by recording the UV-visible spectrum of a suitable chlorohydroxy-fraction, which was then analysed by converting the trans-$[Rhen_2ClOH]^+$ to trans-$[Rhen_2Cl_2]^+$ as follows. An aliquot of the solution was heated with hydrochloric acid (final [HCl] = 0.6M) at 78.6°C until there was no further change in spectrum (ca. 1 hr). The absorbance of the resulting solution at 409 or 289 nm was measured, and its concentration calculated from the known extinction coefficients (82.2 and 124 M^{-1} cm^{-1} respectively) of trans-$[Rhen_2Cl_2]^+$ at these wavelengths. The spectroscopic parameters obtained for trans-$[Rhen_2ClOH]^+$ are given in Table 2.2.

trans-$[Rhen_2IOH]^+$

trans-$[Rhen_2IOH]^+$ was prepared *in situ* by heating an aliquot of standard trans-$[Rhen_2ICl]ClO_4$ with an aliquot of standard sodium hydroxide in a 1 cm quartz cell. There was an initial fast reaction,

$$\text{trans-}[Rhen_2ICl]^+ + OH^- \longrightarrow \text{Intermediate} \qquad (2.1)$$

which occurred with the spectroscopic changes shown in Fig. 2.2. The isosbestic points are diffuse because the rate of hydrolysis of the intermediate is not negligible compared to its rate of formation. By following the decrease in absorbance at 310 nm and the increase in absorbance at 277 nm, the rate constant, k_f, for reaction 2.1 was found to be 7.6×10^{-4} s^{-1}

and 9.9×10^{-4} s^{-1} respectively at 50.2°C. Because of the spectroscopic changes accompanying hydrolysis of the intermediate, these values represent upper and lower limits respectively for k_f. The average value of 8.8×10^{-4} s^{-1} agrees well with the data[6] for the reactions

$$\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{ICl}]^+ + \text{Br}^- \longrightarrow \underline{\text{trans}}\text{-}[\text{Rhen}_2\text{IBr}]^+ + \text{Cl}^- \qquad (2.2)$$

$$\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{ICl}]^+ + \text{I}^- \longrightarrow \underline{\text{trans}}\text{-}[\text{Rhen}_2\text{I}_2]^+ + \text{Cl}^- \qquad (2.3)$$

so the fast reaction is

$$\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{ICl}]^+ + \text{OH}^- \longrightarrow [\text{Rhen}_2\text{IOH}]^+ + \text{Cl}^- \qquad (2.4)$$

The spectra of the $[\text{Rhen}_2\text{IOH}]^+$ intermediate, and of the $[\text{Rhen}_2(\text{OH})_2]^+$ product of further hydrolysis

$$[\text{Rhen}_2\text{IOH}]^+ + \text{OH}^- \longrightarrow [\text{Rhen}_2(\text{OH})_2]^+ + \text{I}^- \qquad (2.5)$$

are both independent of the concentration of hydroxide used for reactions 2.4 and 2.5. As discussed in Chapter 3, this indicated that no stereochemical change occurred during either reaction 2.4 or reaction 2.5, and the $[\text{Rhen}_2\text{IOH}]^+$ product of reaction 2.4 was assigned the trans-geometry.

During reaction 2.4 the absorption maxima of $\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{ICl}]^+$ decreased in intensity, and new peaks grew at 274, 402 and 446 nm. The spectrum of $\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{IOH}]^+$ was obtained by assuming that when these peaks were at their maximum intensity the only complex present was $\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{IOH}]^+$. The extinction coefficients given for $\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{IOH}]^+$ in Table 2.2 are therefore lower limits for the values of ϵ_{max}

Chemicals

All chemicals were reagent grade and used as received unless otherwise stated. Sodium hydroxide for kinetic runs was obtained from Fisher Chemicals Ltd. as 2N certified reagent solutions which were diluted appropriately. Sodium perchlorate was obtained from B.D.H. Ltd. or Fisher Chemicals Ltd. as the hydrate, $NaClO_4.H_2O$. This was heated at 150°C for 24 hr, cooled and ground to a powder, then heated at 210°C for a further 12 hr to give anhydrous $NaClO_4$. Since commercial sodium perchlorate usually contains insoluble impurities, all sodium perchlorate solutions were filtered before use. Sodium chloride, bromide, iodide and fluoride were dried at 150 to 180°C for 12 hr prior to use. Sodium sulphate, Na_2SO_4, and sodium phosphate, $Na_3PO_4.12H_2O$, were used as received from B.D.H. Ltd. All solids which had been dried were stored in dessicators over silica gel.

Spectra

All UV-visible spectra were recorded on a Perkin Elmer 402 spectrophotometer. Spectra which were recorded during a kinetic run were recorded at the fast speed (full spectrum--190 to 850 nm--in 2 min); very precise measurements were recorded on the slow speed (full spectrum in 40 min). Routine spectra were recorded at the medium speed (full spectrum in 8 min). All spectra were calibrated with holmium glass.

Kinetics

All reactions were followed *in situ* in quartz 1 cm cells placed in the thermostatted cell compartments of either the Cary 16K or the Perkin Elmer 402 spectrophotometer. Temperatures in the 402 cell compartment were

measured with a precision thermometer, and emergent stem corrections were made. Temperatures in the Cary 16K were measured by a thermistor connected to a Wayne Kerr B221 conductivity bridge. The thermistor had previously been calibrated every 0.1 to 0.2°C from 6 to 85°C against a partial immersion thermometer. There were no discernible differences between the temperatures in the different cell holders of either the Perkin Elmer 402 or the Cary 16K. This was shown both by direct measurements with the thermistor, and by simultaneously measuring the rate constant for a standard reaction, under identical experimental conditions, in each holder of the cell compartment. The results are given in Table 2.3 and show that if there are temperature gradients within the cell compartments, or effects due to the amount of time a given cell spends in the light path, they are sufficiently small that they do not affect the kinetic data.

A given kinetic run was initiated by mixing aliquots of standard solutions of the reactants in the cell; this was then placed in the cell compartment of the spectrophotometer and allowed to come to thermal equilibrium for at least 10 min. The reaction was then followed by monitoring the change in absorbance at fixed wavelength, λ; all absorbances measured during kinetic runs were in the range 0 to 1.2 a.u. The pseudo-first-order rate constant k_{obsd} was obtained from the slope, s, of the graph of $\log_{10}(|D_t - D_\infty|)$ against time, where D_t, D_∞ are the absorbances at λ at time t, and after completion of the reaction, respectively. Thus

$$k_{obsd} = -2.3026(s) \qquad (2.6)$$

Fig. 2.3 shows a typical pseudo-first-order rate plot. When reactions were too slow to measure the value of D_∞ easily, this was obtained by

extrapolation of data for the first 3 to 5 half-lives, a second adjustment of D_∞ being performed if the initial extrapolation gave a curved rate plot. Alternatively, Guggenheim plots were used.

Ligand Dependences

In many of the reactions studied, the value of k_{obsd} depended on the concentration of added anion, Y^{n-}, at constant ionic strength, i.e. the rate law was

$$k_{obsd} = k_1 + k_2[Y] \qquad (2.7)$$

The values of k_1, k_2 were obtained from a weighted least squares programme which assumed a constant percentage error, P, in k_{obsd}. When a ligand dependence was performed at different temperatures to obtain activation parameters for k_1 and k_2, it was assumed that the percentage errors at each temperature belonged to a common population. The variances found for k_{obsd} at each temperature for a given system were therefore pooled to give a new percentage error, $\bar{P}$, which applied at all temperatures. $\bar{P}$ was then used to give the standard deviations in k_1 and k_2. All errors quoted in this thesis are standard deviations, unless otherwise stated, and are corrected for the number of degrees of freedom appropriate to the way they were determined.

Activation Parameters

Activation parameters were obtained under two sets of conditions:

(a) At low reactant concentrations, where the contribution of second-order terms to k_{obsd} was negligible.

In this case the enthalpy, $\Delta H^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$, of activation

were obtained from the slope and intercept of the straight line given by the unweighted least squares analysis of the temperature-dependence of the rate constant, k_r, according to the equation

$$\log_{10}(k_r/T) = \log_{10}(k/h) - \frac{\Delta H^{\ddagger}}{2.303RT} + \frac{\Delta S^{\ddagger}}{2.303R} \qquad (2.8)$$

where T is the absolute temperature, and k, h, R are Boltzmann's constant, Planck's constant, and the universal gas constant respectively.

(b) Using values of k_1 or k_2 which had been obtained from the ligand-dependence of k_{obsd}

In this case a weighted least squares analysis of the temperature-dependence of k_1 (or k_2) according to equation 2.8 was used to give the appropriate activation parameters. For any value, k_i, of the rate constant, the weighting factor, w_i, associated with the ordinate, $\log_{10}(k_i/T)$, is given by

$$w_i = 1/(\log_{10}(1 + \sigma i/ki))^2 \qquad (2.9)$$

where σ_i is the absolute value of the standard deviation of k_i.

Statistics

The statistical treatment used in determining both the ligand-dependences and the activation parameters is outlined in detail in appendix A. The computer programmes (written in the Watfiv high-speed modification of Fortran IV) which were used to perform the least squares calculations are given in appendix B.

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Table 2.1

Analyses of trans-diacidobisethylenediaminerhodium(III) complexes

Complex	Element	Found	Calculated
trans-$[Rhen_2Cl_2]ClO_4$	C	12.4%	12.2 %
	H	4.24%	4.06%
	N	14.3%	14.2 %
trans-$[Rhen_2Br_2]ClO_4$	C	10.1%	9.98%
	H	3.40%	3.33%
	N	11.8 %	11.6 %
trans-$[Rhen_2I_2]ClO_4$	C	8.58%	8.33%
	H	2.82%	2.78%
	N	9.58%	9.71%
trans-$[Rhen_2ICl]ClO_4$	C	9.73%	9.90%
	H	3.52%	3.30%
trans-$[Rhen_2(OH)OH_2](ClO_4)_2$	C	10.9 , 10.7%	10.5%
	H	4.21, 4.39	4.2%
	N	13.3, 13.5%	12.3%
	Cl	15.1	15.5%

Table 2.2

Visible and U V spectra of trans-diacidobisethylenediaminerhodium(III) complexes

Complex	This work		Published values		Ref.
	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	
trans-$[Rhen_2Cl_2]^+$	410	82	407	75	1
	289	121	286	125	
	∿241(sh)	1,690	-		
	207	39,600	-		
trans-$[Rhen_2Br_2]^+$	431	115	425	120	1
	277	2,930	276	3,000	
	234	37,800	231	31,000	
trans-$[Rhen_2I_2]^+$	467	271	462	260	2
	342	16,000	340	14,300	
	-	-	269	31,000	
	-	-	222	20,000	
trans-$[Rhen_2ICl]^+$	490	260	-	-	2
	∿440(sh)	∿160	440	154	
	301	4,300	300	4,350	
	241	38,000	242	38,500	
trans-$[Rhen_2IOH]^+$	446	150	400-450	71	7
	402	160			
	274	4,000	270	2,150	
trans-$[Rhen_2BrOH]^+$	376	105	370	103	7
	∿290(sh)	148	290(sh)	∿200	
trans-$[Rhen_2ClOH]^+$	370	93.5	∿360	52	7
	293	134	280	76	

Table 2.3

(a) Reproducibility of kinetic runs in the cell compartment of the Cary 16K

$$\underline{\text{trans}}\text{-}[Rhen_2I_2]^+ + Cl^- \longrightarrow \underline{\text{trans}}\text{-}[Rhen_2ICl]^+ + I^-$$

Temperature = 44.62°C $\quad [Cl^-] = 0.10M$

Cell number	$10^5 k_{obsd}$ (s^{-1})
1	6.466
2	6.501
3	6.492
4	6.492
5	6.430

(b) Reproducibility of kinetic runs in the cell compartment of the Perkin Elmer 402

$$\underline{\text{trans}}\text{-}[Rhen_2IOH]^+ + OH^- \longrightarrow \underline{\text{trans}}\text{-}[Rhen_2(OH)_2]^+ + I^-$$

Temperature = 55.4°C $\quad [OH^-] = 0.01M$

Cell number	$10^5 k_{obsd}$ (s^{-1})
1	2.642
3	2.625
4	2.617

Temperature = 81.0°C $\quad [OH^-] = 0.01M$

Cell number	$10^5 k_{obsd}$ (s^{-1})
1	62.04
2	61.70
3	61.34

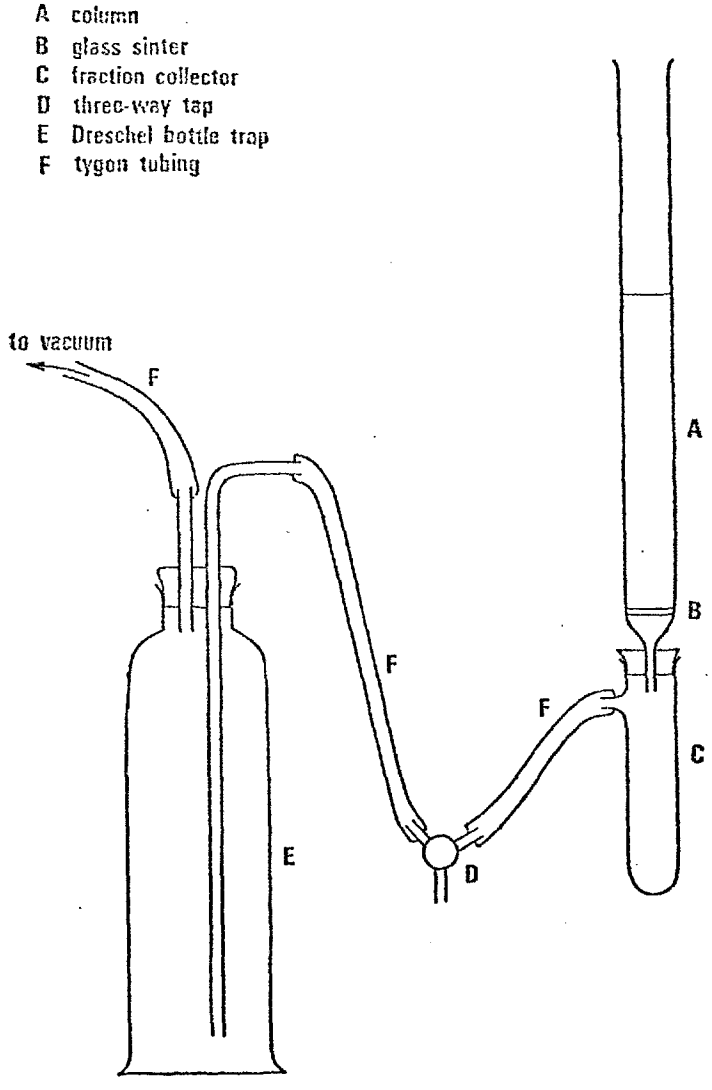


Fig. 2.1 Vacuum ion exchange apparatus

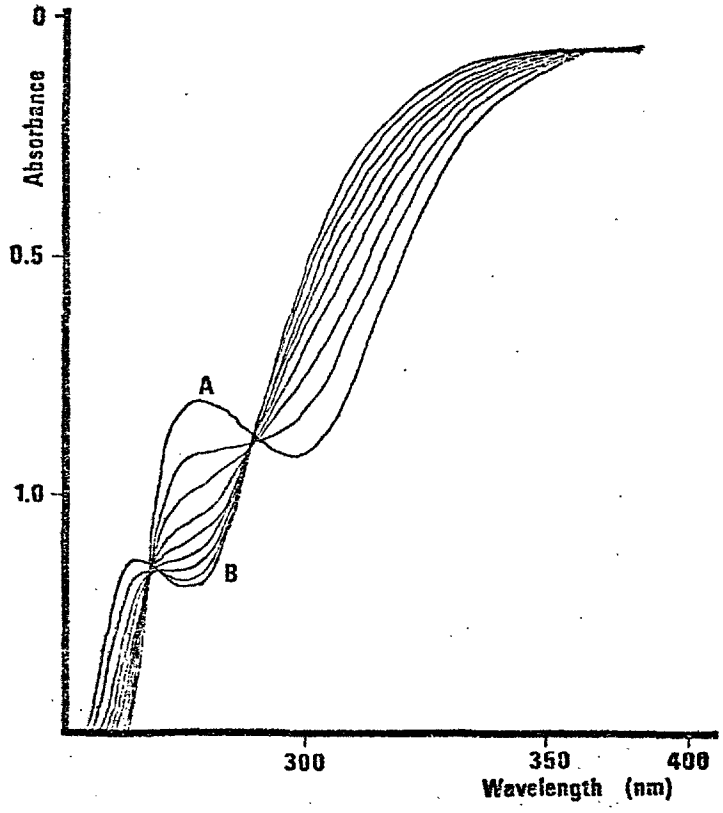


Fig. 2.2A Spectroscopic changes occurring during the first stage of the reaction of <u>trans</u>-$[Rhen_2ICl]^+$ with hydroxide

temperature = 49.16 °C
[complex] = 2.85×10^{-4} M
$[OH^-]$ = 0.100 M
A = substrate B = product

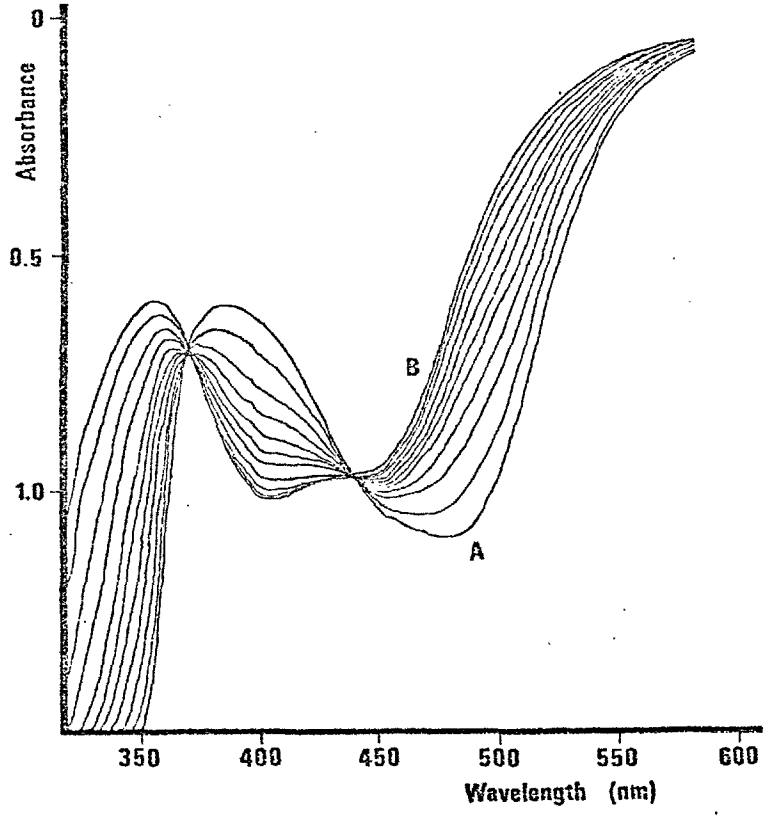


Fig. 2.2B Spectroscopic changes occurring during the first stage of the reaction of <u>trans</u>-$[Rhen_2ICl]^+$ with hydroxide

temperature = 49.16 ^{o}C
[complex] = 6.17×10^{-3} M
$[OH^-]$ = 0.030 M
A = substrate B = product

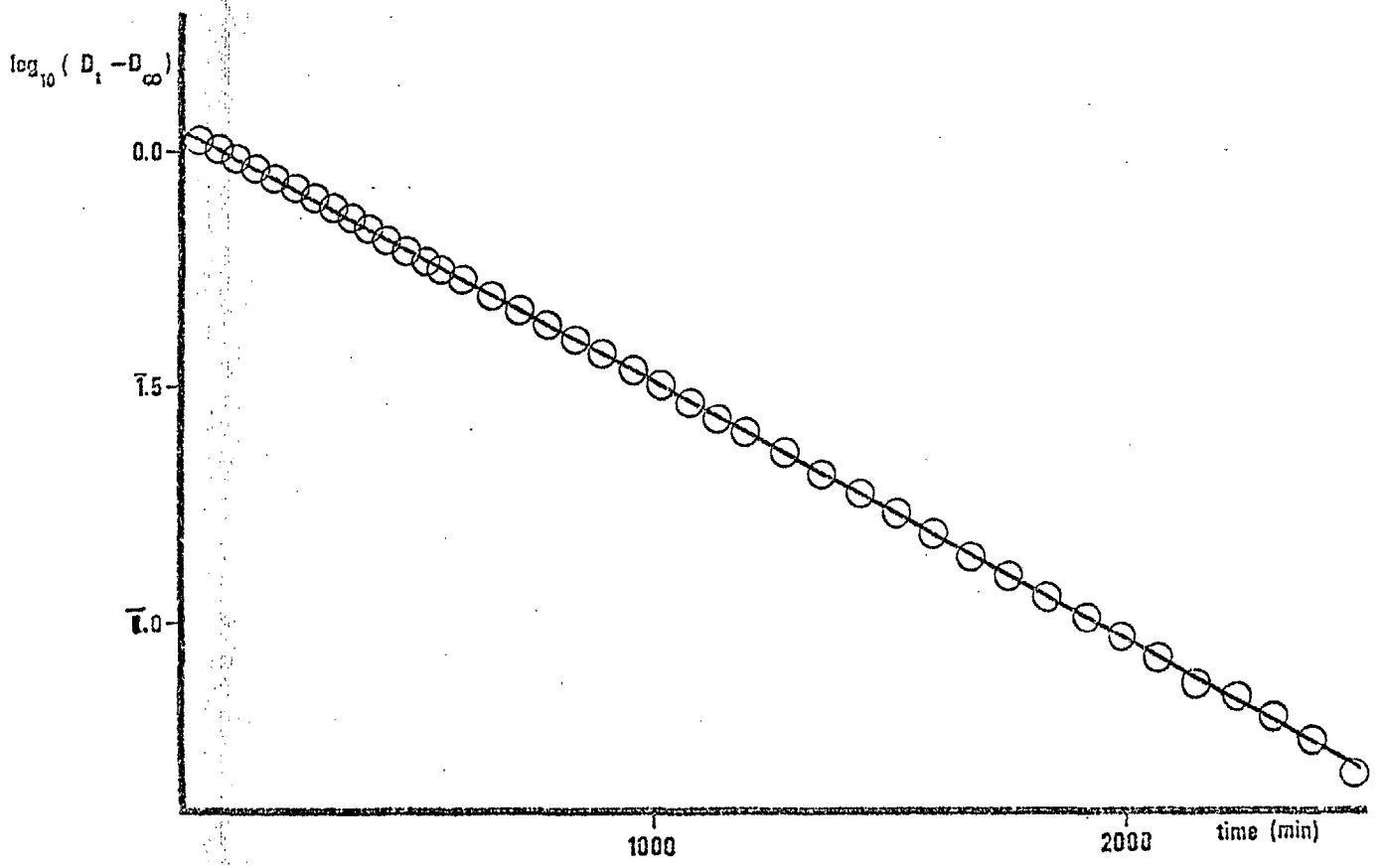


Fig. 2.3 Typical pseudo-first-order rate plot obtained for substitution reactions of trans-diacidobisethylenediaminerhodium(III) complexes

CHAPTER 3

Reactions for which the rate is dependent on the nature and concentration of added anions

Introduction

The S_N1IP mechanism

For several octahedral complexes the rates of substitution are dependent on the nature and concentration of the anions present in solution. Except when the anion is hydroxide, when the reaction appears to occur by the S_N1CB mechanism (vide infra), this dependence is small, and it has been ascribed to the S_N1IP mechanism of equations 3.1 to 3.3.

$$[ML_5X]^{m+} + H_2O \xrightarrow{k_o} [ML_5OH_2]^{(m+1)+} + X^- \qquad (3.1)$$

$$[ML_5X]^{m+} + Y^{n-} \rightleftharpoons \{ML_5X,Y\}^{(m-n)+} \qquad (3.2)$$

$$\{ML_5X,Y\}^{(m-n)+} + H_2O \xrightarrow{k_Y} [ML_5OH_2]^{(m+1)+} + X^- + Y^{n-} \qquad (3.3)$$

In cases where the final product is $[ML_5Y]^{(m+1-n)+}$ it is not possible to tell whether the formation of this product occurs by rapid anation of $[ML_5XOH_2]^{(m+1)+}$ or by a dissociative interchange within the $\{ML_5X,Y\}^{(m-n)+}$ ion-pair.

For association of sulphate with $[Coen_3]^{3+}$ or $[Co(NH_3)_6]^{3+}$, the rate of formation of the ion-pair is diffusion-controlled.[1] Assuming this is also true for ion-association reaction 3.2, the rate law for the S_N1IP mechanism is

$$k_{obsd} = \frac{k_o + K_Y k_Y [Y]}{1 + K_Y [Y]} \qquad (3.4)$$

If $K_Y[Y]$ is much less than unity, equation 3.4 becomes

$$k_{obsd} = k_o + K_Y k_Y [Y] \qquad (3.5)$$

Despite the belief[2] that reactions of chromium(III) complexes have some associative character, the reactions of ion-pairs of both chromium(III) and cobalt(III) complexes have been interpreted in terms of a dissociative mechanism. Jones et al.[3] and Walker and Monk[4] separately studied the reaction

$$[Cr(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Cr(NH_3)_5OH_2]^{3+} + Cl^- \qquad (3.6)$$

in the presence of divalent anions, and found the rate law of equation 3.4. When the added anion was citrate the product was exclusively the aquo-complex, even under conditions where the citrato-complex was stable;[3] it appears that in this case interchange within the ion-pair definitely does not occur. Furthermore, as can be seen in Table 3.1, ion-pairs are not generally much more reactive than the free complex, nor do the reactivities of the ion-pairs vary greatly with the nature of the anion. Both these observations agree with a dissociative mechanism, and the data in Table 3.1 show that this assignment is valid in non-aqueous solvents, as well as in water. Watts et al.[5]-[10] have extensively studied the substitution, isomerisation and solvolysis of chromium(III) and cobalt(III) complexes in non-aqueous solvents and suggested that, depending on the nature of the complex and the solvent, reaction 3.3 occurs by either an Id or a D mechanism.

The data in Table 3.1 show that ion-pairs are generally more reactive than the free complex; although Watts[6] has warned against over-simplifying the kinetic effects of ion-pairing, it is possible to explain the enhanced

reactivity of the ion-pair by invoking electrostatic repulsion between Y^{n-} and the leaving group X^-. In addition to the repulsion transmitted through space, electron density may be transmitted across the complex via hydrogen bonding between the anion and the protons of a co-ordinated amine. Circular dichroism,[11]-[17] n.m.r.[18] and x-ray crystallographic[17][19] studies show that such hydrogen-bonding is sufficiently extensive in the $\{Coen_3,PO_4\}^0$ ion-pair that it alters the conformations of the ethylenediamine rings. Direct charge-transfer from anion orbitals to the orbitals of the central atom of the cation can also occur: the n.m.r. spectrum of $\{Bu_4N^+,M(PPh_3)I_3^-\}^0$ (M = Co(II), Ni(II)) indicates transference of free spin density from the paramagnetic anion to the diamagnetic cation.[20] Formation of the ion-pair $\{ML_5X,Y\}^{(m-n)+}$ is often accompanied by the growth of charge-transfer bands in the spectrum of the cation, although it is not always clear whether these are due to direct Y to M charge-transfer[21] or interaction via the co-ordinated ligands.[22][23]

The S_N1IP mechanism seems to be fairly well-established for cobalt(III) and chromium(III) complexes, but only one study[25] of the kinetic effect of ion-pairing has appeared for rhodium(III) complexes, and only three[24]-[26] for iridium(III) complexes. Burgess et al.[25] studied the radiochloride exchange reactions of cis-$[RhtrienCl_2]^+$ and trans-$[Rhen_2Cl_2]^+$; in both cases the rate law was that of equation 3.4. The values of K_{Cl} found (25 M^{-1} for trans-$[Rhen_2Cl_2]^+$ at 80.6°C, and 60 M^{-1} for cis-$[RhtrienCl_2]^+$ at 60.2°C) are extremely high for association between two univalent electrolytes in water, particularly as no mention is made of correction to zero ionic strength and the chloride ion concentration ranged from 1×10^{-3} M to 1.00 M. However, for both

complexes the ion-pairs are approximately three times more reactive than the free ion, which fits the pattern established for cobalt(III) and chromium(III) complexes.

For the iridium(III) complexes not only were the ion-association constants found extremely high (K_{NO_2} for trans-$[Iren_2Cl_2]^+$ was said[26] to be 207 M^{-1} at 90°C), but the reactivity of the free complex was apparently negligible compared to that of the various ion-pairs. This was found for the reaction of trans-$[Iren_2Cl_2]^+$ with radiochloride,[24] bromide[26] and nitrite,[26] and the reaction of cis-$[Iren_2Cl_2]^+$ with radiochloride.[25] From these results, Burgess et al. claimed[26] that Basolo and Bauer's results[27] for the reaction of trans-$[Iren_2Cl_2]^+$ with 0.2 M iodide referred to the reaction of the $\{Iren_2Cl_2,I\}^0$ ion-pair. However, it is strange that the reactivity of this ion-pair should be the same[27] as the reactivity of whatever species are present in 3×10^{-3} M hydroxide solution.

The S_N1IP mechanism and reactions with hydroxide

Chan and his co-workers[28] consider the base hydrolysis of cobalt(III) complexes to occur by an S_N1IP mechanism, but they have given no explanation for the very high reactivity of the supposed hydroxide ion-pair. The major evidence for the operation of an S_N1IP mechanism in base hydrolysis was the claim[28] that the base hydrolyses of $[Co(NH_3)_5Cl]^{2+}$, $[Coen_2NH_3Cl]^{2+}$ and $[CotrienNH_3Cl]^{2+}$ all obeyed the rate law

$$k_{obsd} = \frac{kK[OH^-]}{1 + K[OH^-]} \qquad (3.4a)$$

instead of the usual second-order rate law

$$k_{obsd} = k_2[OH^-] \qquad (3.7)$$

The magnitude of K in equation 3.4a led to the conclusion that it was K_{OH}, the ion-pairing constant for association between the substrate and hydroxide. However, when Buckingham et al.[29] extended Chan's results[28] for $[Co(NH_3)_5Cl]^{2+}$ from $[OH^-]$ = 0.1 M to $[OH^-]$ = 1.0 M, they found that equation 3.7 was obeyed even up to 1.0 M hydroxide. Thus there appears to be no positive evidence that the base hydrolysis of cobalt(III) complexes occurs by the S_N1IP mechanism.

The S_N1CB mechanism for cobalt(III) complexes

The S_N1CB mechanism given in equations 3.8 and 3.9 has been found to be capable of rationalising all or almost all the data available for the base hydrolysis reactions of metal-amine-complexes.[30]

$$[ML_4(NR_2H)X]^{n+} + OH^- \overset{K_{CB}}{\rightleftharpoons} [ML_4(NR_2)X]^{(n-1)+} + H_2O \qquad (3.8)$$

$$[ML_4(NR_2)X]^{(n-1)+} + H_2O \xrightarrow{k_{CB}} [ML_4(NR_2H)OH]^{n+} + X^- \qquad (3.9)$$

Equation 3.8 is a fast pre-equilibrium, and equation 3.9 is the unimolecular reaction of the conjugate base.

Although the equilibrium concentration of the deprotonated species $[ML_4(NR_2)X]^{(n-1)+}$ is much less than that of the corresponding ion-pair,[31]-[33] such species have been detected by Navon et al.[33][34] in highly basic aqueous solutions, and have been formed in stoichiometric amounts using sodium in liquid ammonia.[35]-[39] Moreover, the complexes cis-$[CoL_4Cl_2]^+$ (L = py, β-pic, γ-pic) which have no acidic protons are not susceptible to base catalysis.[40] The most compelling evidence for the involvement of a deprotonated intermediate comes from Poon and Tobe's study[41] of

the base hydrolysis of trans-$[CoD_4\text{-cyclamCl}_2]^+$ (D_4-cyclam is the fully N-deuterated analogue of cyclam). This complex was allowed to undergo ca. 3% of total reaction with OH^- in H_2O, then the reaction was quenched with acid. The unreacted substrate had exchanged ca. 20% of its N-deuterons, but the trans-chlorohydroxy-product contained ca. 40% N-H bonds. The rate of deuterium exchange of the product was negligible compared to its rate of formation, so the extra exchange must have occurred during the base hydrolysis reaction, which implies a deprotonated intermediate.

There is much evidence for the dissociative nature of the conjugate base mechanism. Pearson and Edgington[42] showed that the second order rate constant k' for the reaction of $[Co(NH_3)_5Cl]^{2+}$ with the peroxide anion was smaller than the corresponding rate constant for reaction with hydroxide, and the diminution in reactivity was almost exactly what would be expected if the species catalysing the aquation of $[Co(NH_3)_5Cl]^{2+}$ were hydroxide ion produced by the equilibrium

$$HO_2^- + H_2O \rightleftharpoons H_2O_2 + OH^- \qquad (3.10)$$

Thus hydroxide was not acting as a nucleophile in an S_N2 reaction, because in this case the reaction with peroxide would have been faster than that with hydroxide, the alpha-effect of the extra oxygen atom in O_2H^- making peroxide a better nucleophile than hydroxide.

Green and Taube[43] also concluded that hydroxide was not acting as a nucleophile in the base hydrolysis of $[Co(NH_3)_5X]^{2+}$ ($X = Cl^-$, Br^-, I^-) when they showed the fractionation factor, F_1, for incorporation of $O^{16}H^-$ and $O^{18}H^-$ in the $[Co(NH_3)_5OH]^{2+}$ product was 1.004 in all cases. If hydroxide acted as a nucleophile, F_1 would have been 1.016, the value

given by considering the equilibrium constant for the reaction[44]

$$H_2O^{16} + O^{18}H^- \rightleftharpoons O^{16}H^- + H_2O^{18} \qquad (3.11)$$

Moreover, the lack of dependence of F_1 on the nature of the leaving group X suggested a dissociative mechanism with a common intermediate.

The values of F_1 in Green and Taube's experiment represent the competition of $O^{16}H_2$ and $O^{18}H_2$ for the intermediate $\{Co(NH_3)_4NH_2\}^{2+}$. The competition of anions, Y^{n-} ($Y = N_3^-$, SCN^-, NO_2^-, OAc^-, SO_4^{2-}, PO_4^{3-}) for this intermediate has also been investigated.[45] The competition ratio, f, defined as

$$f = \frac{\text{Percentage of } [Co(NH_3)_5Y] \text{ Product}}{\text{Percentage of } [Co(NH_3)_5OH] \text{ Product}} \qquad (3.12)$$

was independent of the nature of the leaving group X and of the concentration of hydroxide. It did depend on the concentration of Y^{n-}, and it varied from one anion to another. All these results are consistent with an S_N1CB mechanism where the intermediate $\{Co(NH_3)_4NH_2\}^{2+}$ is very reactive and does not distinguish greatly between different nucleophiles. Similar experiments[46] on the competition of azide and thiocyanate for the intermediate $\{Co(MeNH_2)_4MeNH\}^{2+}$ showed the same trends, but indicated that $\{Co(MeNH_2)_4MeNH\}^{2+}$ discriminated more between nucleophiles than $\{Co(NH_3)_4NH_2\}^{2+}$. The five co-ordinate intermediate derived from $[Co(MeNH_2)_5X]^{2+}$ is therefore more stable than that derived from $[Co(NH_3)_5X]^{2+}$; this is consistent with the large amount of steric strain imposed on $[Co(MeNH_2)_5Cl]^{2+}$ by the bulky methylamine ligands.[47]

The stereochemical consequences of the base hydrolysis of cobalt(III) complexes have been extensively studied. Buckingham et al.[48][49] determined the stereochemistry of the reaction

$$[Coen_2LX]^{n+} + OH^- \longrightarrow [Coen_2LOH]^{n+} + X^- \qquad (3.14)$$

and Tobe's earlier results have been summarised by Basolo and Pearson.[51][52] For trans-$[Coen_2LX]^+$ (L = Cl^-, NCS^-, N_3^-, OH^-, NO_2^-; X = Cl^-, Br^-, N_3^-, NCS^-) and for cis-$[Coen_2LX]^{n+}$ (L = Cl^-, NH_3, NCS^-, N_3^-, OH^-, NO_2^-; X = Cl^-, Br^-, NO_3^-, N_3^-, NCS^-) the stereochemistry of the product is independent of the leaving group, X. However, the stereochemistries of the products from the cis- and trans-isomers of the same complex are not identical; this has been rationalised[51][52] in terms of the two trigonal bipyramidal intermediates derivable from $[Coen_2LX]^{n+}$.

Detailed interpretation of the stereochemical changes accompanying base hydrolysis has relied on the assumption that there is extensive π-donation from the amido-group to the metal atom in the deprotonated intermediate. However, Buckingham et al.[53] showed that such π-bonding did not occur in the conjugate base derived from $[CotrenenCl]^{2+}$. This complex contains an asymmetric secondary nitrogen centre trans to the leaving group; the optical activity due to this asymmetric centre was not lost during base hydrolysis, implying that the tetrahedral nitrogen atom never achieved sp^2 hydridisation, and hence did not participate in π-donation to cobalt(III). However, this conclusion may only apply to the special case of $[CotrenenCl]^{2+}$, because in this complex π-donation by the amido-group trans to the leaving group would lead to considerable conformational strain because of the steric requirements of the macrocyclic ligand.[54] Thus in spite of Buckingham's experiment, interest still centres on the importance of π-bonding in the transition state. For a complex which contains amine-groups both cis and trans to the leaving group, Nordmeyer has suggested[55] that productive deprotonation occurs in the cis-position, because π-donation from the amido-group can then aid the formation of the

five co-ordinate intermediate. Moreover Green[56] has rationalised the stereochemistry of $[Coen_2LOH]^{n+}$ formed by the base hydrolysis of $[Coen_2LX]^{n+}$ ($L = NO_2^-$, OH^-, N_3^-, Br^-, NH_3, Cl^-, NCS^-) in terms of the π-donor properties of L.

Base hydrolysis of rhodium(III) complexes

Relatively few studies of the base hydrolysis of rhodium(III) complexes have been made. Johnson et al.[57] found that rhodium(III) complexes were less susceptible than cobalt(III) complexes to base hydrolysis, when measured by the ratio k_2/k_0. k_2 is the second order rate constant for base hydrolysis, and k_0 the first order rate constant for aquation, of the complex in question. Thus k_2/k_0 was ca. 2×10^3 M^{-1} for cis-$[Rhen_2Cl_2]^+$ and 4×10^2 M^{-1} for cis-$[RhtrienCl_2]^+$; the corresponding ratios for cis-$[Coen_2Cl_2]^+$ and cis-$[CotrienCl_2]^+$ were 4×10^6 and 1.3×10^9 M^{-1} respectively.[57] This difference may be partly due to a lower acidity of the amine protons of the rhodium(III) complex; the rate of exchange of these protons is certainly lower for rhodium(III) complexes than for their cobalt(III) analogues.[57][58]

Another difference between the two metals was that only those rhodium(III) complexes for which there was a primary or secondary amine trans to the leaving group showed an increased rate of substitution in basic solution. Thus the rate of aquation of trans-$[Rhen_2Cl_2]^+$ was the same at pH = 1.0 as in 0.1 M sodium hydroxide.[57] This was explained by assuming the cis-diacidobisethylenediamine-complexes and the trans-amine-complexes were more acidic than the trans-diacidobisethylenediamine-complexes, even though the rates of deuterium exchange of cis- and trans-$[Rhen_2Cl_2]^+$ differ by less than a factor of two at 58.6°C. The importance of acidity of the co-ordinated amine has been discussed by Klabunde,[59]

who showed that for trans-$[Rhen_2pyCl]^{2+}$ base hydrolysis was relatively important, even though the trans-ligand was not a primary or secondary amine. By considering the acidities of the co-ordinated water molecules in trans-$[Rhen_2pyOH_2]^{3+}$ and trans-$[Rhen_2ClOH_2]^{2+}$, Klabunde concluded that the acidity of the ethylenediamine ligand in trans-$[Rhen_2pyCl]^{2+}$ was greater than that in trans-$[Rhen_2Cl_2]^{+}$.

The base hydrolysis of trans-$[Rhen_2pyCl]^{2+}$ gives rise to 64% cis-$[Rhen_2pyOH]^{2+}$ product;[59] all other base hydrolysis reactions of rhodium(III) complexes are stereoretentive.[57][59] Stereochemical change occurring during rhodium(III) substitution reactions is very rare; the only other trans to cis transformations known are the reports that on heating with sodium oxalate, trans-$[Rhen_2Cl_2]^{+}$ gives 6% cis-$[Rhen_2ox]^{+}$,[60] and that in aqueous solution trans-$[Rhen_2NH_3H]^{2+}$ is in reversible equilibrium with its cis-isomer.[61] Similarly the only cis to trans reactions are direct isomerisations of complexes containing two cis-iodo-ligands,[62][63] where relief of steric strain provides the driving force for reaction.

Although there is some evidence that the aquation reactions of rhodium(III) complexes are Ia in nature, it appears that the base hydrolysis reactions, where they occur, are dissociative. Chan et al.[64] have claimed the base hydrolysis of $[Rh(NH_3)_5X]^{2+}$ ($X = Cl^-, Br^-, I^-$) is an A reaction because the group replacement factors parallel those for an S_N2Ar reaction, but assignment of mechanism on such a basis seems very dubious. Moreover Lalor et al.[65]-[67] have also studied the reaction

$$[Rh(NH_3)_5X]^{2+} + OH^- \longrightarrow [Rh(NH_3)_5OH]^{2+} + X^- \qquad (3.15)$$

and have shown[68] that a graph of $\Delta S_2^{\neq}$ against ΔS_X^0, the entropy of hydration of X, is a straight line of slope 0.8. The corresponding graph for the reaction

$$[Co(NH_3)_5X]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + X^- \qquad (3.16)$$

also has a slope of 0.8. From this fact, and from the general similarities[69] of the activation parameters from reactions 3.15 and 3.16 they concluded that reaction 3.15 occurs by an S_N1CB mechanism. This assignment agrees well with Panunzi and Basolo's study[70] of the competition of azide and nitrite ions for the intermediates formed during the base hydrolysis of <u>trans</u>-$[Rhen_2MeNH_2X]^{2+}$ (X = Cl^-, Br^-, I^-) and <u>cis</u>-$[Rhen_2NO_2X]^+$ (X = Cl^-, Br^-, I^-) in water and DMSO. The competition ratios, f, defined as

$$f = \frac{\text{Percentage } [Rhen_2LY] \text{ Product}}{\text{Percentage } [Rhen_2LOH] \text{ Product}} \qquad (3.17)$$

(L = <u>cis</u>-NO_2 or <u>trans</u>-$MeNH_2$; Y = N_3^-, NO_2^-) were independent of the nature of X and of the concentration of hydroxide, but were dependent on the concentration and nature of Y.

Finally, one reaction which follows a special mechanism is the base hydrolysis of $[Rh(NH_3)_5OCOCCl_3]^{2+}$ in methanol.[71] The rate law is

$$k_{obsd} = \frac{k_1 + k_2K[MeO^-]}{1 + K[MeO^-]} \qquad (3.18)$$

and the values (ca. 20 M^{-1}) of K are too large to refer to formation of the conjugate base. Monacelli[71] suggested that k_1 referred to aquation of the free complex and k_2 to aquation of a methoxide ion-pair. However, he could not exclude a mechanism where k_1 and k_2 referred to ~~aquation~~ methanolysis of a methoxide ion-pair and ion-triplet respectively. In water the base

hydrolysis of $[Rh(NH_3)_5OCOCCl_3]^{2+}$ occurs by a normal S_N1CB pathway, and by a pathway involving nucleophilic attack of hydroxide on the carbonyl atom of the co-ordinated trichloroacetate ligand.[72]

Results

(A) Kinetics of the Reactions of trans-diacidobisethylenediaminerhodium-(III) Complexes with Hydroxide

(1) The reaction of trans-$[Rhen_2IOH]^+$ with hydroxide

A solution of trans-$[Rhen_2IOH]^+$ was generated in situ by the base hydrolysis of trans-$[Rhen_2ICl]^+$ as outlined in chapter 2, and used to study the reaction

$$\text{trans-}[Rhen_2IOH]^+ + OH^- \longrightarrow [Rhen_2(OH)_2]^+ + I^- \qquad (3.19)$$

The spectroscopic changes occurring during the reaction are shown in Fig. 3.1; these changes were identical in 1.0 and 0.10 M sodium hydroxide, and there were sharp isosbestic points at 341 and 362 nm in both cases. The spectra of the dihydroxy-products are given in Table 3.8. Reaction 3.19 was studied by monitoring the decrease in absorbance at 272 nm, and absorbance changes of ca. 1.0 a.u. were obtained in 1 cm cells. The pseudo-first-order rate plots were straight for at least three half-lives. At a constant ionic strength of 1.0 M, maintained by sodium perchlorate, the rate law was

$$k_{obsd} = k_1 + k_2[OH^-] \qquad (3.20)$$

A typical graph of k_{obsd} against $[OH^-]$ is shown in Fig. 3.2. From the temperature dependence of k_1 and k_2, the associated activation parameters, $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$, $\Delta S_2^{\ddagger}$ were calculated. The values of k_{obsd}, k_1, k_2 and $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$, $\Delta H_2^{\ddagger}$, $\Delta S_2^{\ddagger}$ are given in Table 3.2.

(2) The reaction of trans-$[Rhen_2BrOH]^+$ with hydroxide

A solution of trans-$[Rhen_2BrOH]^+$ prepared as outlined in chapter 2 was used to study the reaction

$$\text{trans-}[Rhen_2BrOH]^+ + OH^- \longrightarrow [Rhen_2(OH)_2]^+ + Br^- \qquad (3.21)$$

The spectroscopic changes associated with reaction 3.21 are shown in Fig. 3.3; these changes were identical in 0.065 and 0.732 M sodium hydroxide. Good isosbestic points were maintained at 301 and 360 nm. The spectra of the dihydroxy-products are given in Table 3.8. Reaction 3.21 was studied by following the decrease in absorbance at either 250 or 255 nm; absorbance changes were at least 0.6 a.u. in 1 cm cells. The rate plots were straight for three half-lives. The dependence of k_{obsd} on the concentration of hydroxide at constant ionic strength of 1.0 M (maintained by sodium perchlorate) is described by the rate law

$$k_{obsd} = k_1 + k_2[OH^-] \qquad (3.20)$$

Values of k_{obsd}, k_1, k_2 and the corresponding activation parameters are given in Table 3.3.

(3) The reaction of trans-$[Rhen_2ClOH]^+$ with hydroxide

A solution of trans-$[Rhen_2ClOH]^+$, prepared as outlined in chapter 2, was used to study the reaction

$$\text{trans-}[Rhen_2ClOH]^+ + OH^- \longrightarrow [Rhen_2(OH)_2]^+ + Cl^- \qquad (3.22)$$

During the reaction, absorption maxima due to the chlorohydroxy-complex decreased in intensity, and new peaks which were ascribed to the dihydroxy-

product appeared at 298 and 347 nm. The spectroscopic changes depended slightly on the concentration of hydroxide used, there being isosbestic points at 253 and 266 nm in 0.067 M hydroxide that were lacking in 0.734 M hydroxide. Apart from this, as shown in Fig. 3.4A and Fig. 3.4B and in Table 3.8, the overall changes were very similar in 0.734 M and 0.067 M hydroxide.

The kinetics of reaction 3.22 were studied by following the decrease in absorbance at 240 nm where the absorbance changes were ca. 0.4 a.u. in 1 cm cells. The pseudo-first-order rate plots were straight for three half-lives. The dependence of k_{obsd} on the concentration of sodium hydroxide at a constant ionic strength of 1.0 M (maintained with sodium perchlorate) is shown in Fig. 3.5 and Table 3.4. At concentrations of hydroxide greater than 0.233 M the rate law

$$k_{obsd} = k_1 + k_2[OH^-] \qquad (3.20)$$

was obeyed, but at each of the seven temperatures studied, the point for $[OH^-]$ = 0.0335 M was much higher than the straight line predicted by the rate constants at the other hydroxide concentrations. This systematic deviation may be connected with the different spectroscopic changes observed at low concentrations of hydroxide. The values of k_1 were estimated (a) by assuming that at $[OH^-]$ = 0.0335 M k_{obsd} is approximately equal to k_1 and (b) by analysing the points for $[OH^-]$ > 0.233 M according to equation 3.20. The values of k_{obsd} and of k_1 and k_2 obtained by these methods are shown in Table 3.4. The activation parameters found from the temperature dependence of k_1 and k_2 are also given in Table 3.4. It can be seen that the values of $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ are very little affected by the method used to estimate k_1.

(4) The reaction of trans-$[Rhen_2Cl_2]^+$ and hydroxide

The reaction

$$\underline{trans}\text{-}[Rhen_2Cl_2]^+ + 2OH^- \longrightarrow [Rhen_2(OH)_2]^+ + 2Cl^- \qquad (3.23)$$

occurs with the spectroscopic changes shown in Fig. 3.6A and Fig. 3.6B. As shown in Table 3.8, the spectrum of the product depends on the concentration of hydroxide used, and this was ascribed to stereochemical rearrangement occurring during the reaction

$$\underline{trans}\text{-}[Rhen_2Cl_2]^+ + OH^- \longrightarrow [Rhen_2ClOH]^+ + OH^- \qquad (3.24)$$

This effect is discussed more fully in the next section. From the known rates of base hydrolysis of $\underline{trans}$-$[Rhen_2ClOH]^+$[78] and $\underline{cis}$-$[Rhen_2ClOH]^+$,[79] reactions 3.25 and 3.26

$$\underline{trans}\text{-}[Rhen_2ClOH]^+ + OH^- \longrightarrow [Rhen_2(OH)_2]^+ + Cl^- \qquad (3.25)$$

$$\underline{cis}\text{-}[Rhen_2ClOH]^+ + OH^- \longrightarrow [Rhen_2(OH)_2]^+ + Cl^- \qquad (3.26)$$

will be sufficiently fast compared to the rate of reaction 3.24 that reaction 3.24 will be rate-determining. Thus clean isosbestic points at 276 and 384 nm (1.0 M hydroxide) or 283 and 386 nm (0.1 M hydroxide) are observed during the reaction.

The rate of reaction 3.24 was determined by following the decrease in absorbance at 245 nm where absorbance changes of ca. 0.7 a.u. were obtained in 1 cm cells. The rate plots were straight for three half-lives and the values of k_{obsd} obtained are shown in Table 3.5. At constant ionic strength, the rate law

$$k_{obsd} = k_1 + k_2[OH^-] \qquad (3.20)$$

is obeyed; values of k_1, k_2 and the activation parameters associated with these rate constants are given in Table 3.5. Four kinetic runs were performed at a constant, low concentration of hydroxide and varying concentrations of sodium perchlorate; the values of k_{obsd} obtained are also given in Table 3.5.

(5) The reaction of trans-$[Rhen_2Br_2]^+$ with hydroxide

The spectroscopic changes occurring during the reaction

$$\underline{trans}\text{-}[Rhen_2Br_2]^+ + 2OH^- \longrightarrow [Rhen_2(OH)_2]^+ + 2Br^- \qquad (3.27)$$

are shown in Fig. 3.7A and 3.7B. These changes obviously depend on the concentration of hydroxide, as does the spectrum of the product (see Table 3.8). This was ascribed to formation of $\underline{cis}$-$[Rhen_2BrOH]^+$ during the reaction

$$\underline{trans}\text{-}[Rhen_2Br_2]^+ + OH^- \longrightarrow [Rhen_2BrOH]^+ + Br^- \qquad (3.28)$$

The occurrence of stereochemical rearrangement is discussed more fully in the next section. Sharp isosbestic points at 325 and 392 nm (1.0 M hydroxide) and 328 and 394 nm (0.1 M hydroxide) are found experimentally, so the rates of reactions 3.29 and 3.30

$$\underline{trans}\text{-}[Rhen_2BrOH]^+ + OH^- \longrightarrow [Rhen_2(OH)_2]^+ + Br^- \qquad (3.29)$$

$$\underline{cis}\text{-}[Rhen_2BrOH]^+ + OH^- \longrightarrow [Rhen_2(OH)_2]^+ + Br^- \qquad (3.30)$$

must be much faster than the rate of reaction 3.28; reaction 3.28 is therefore rate-determining.

Reaction 3.28 was studied by following the decrease in absorbance

at 250 nm, where absorbance changes of ca. 1.0 a.u. were obtained in 1 cm cells. The rate plots were straight for three half-lives, and the values of k_{obsd} obtained are shown in Table 3.6. At constant ionic strength the rate law

$$k_{obsd} = k_1 + k_2[OH^-] \qquad (3.20)$$

was obeyed. The values of k_1, k_2 and the corresponding activation parameters are given in Table 3.6.

(6) The reaction of trans-$[Rhen_2I_2]^+$ with hydroxide

The reaction

$$\underline{trans}\text{-}[Rhen_2I_2]^+ + 2OH^- \longrightarrow [Rhen_2(OH)_2]^+ + 2I^- \qquad (3.31)$$

takes place in two stages:

$$\underline{trans}\text{-}[Rhen_2I_2]^+ + OH^- \longrightarrow [Rhen_2IOH]^+ + I^- \qquad (3.32)$$

$$[Rhen_2IOH]^+ + OH^- \longrightarrow [Rhen_2(OH)_2]^+ + I^- \qquad (3.19)$$

The rate of reaction 3.19 is slower than that of reaction 3.32. Fig. 3.8 shows the spectroscopic changes associated with the overall reaction 3.31. During the later stages of this reaction, isosbestic points ascribable to reaction 3.19 clearly emerge at 346 and 362 nm. Fig. 3.9 refers to more dilute solutions and shows the spectroscopic changes associated with reaction 3.32 alone. The spectrum of the final $[Rhen_2(OH)_2]^+$ product depends slightly on the hydroxide concentration (see Table 3.8). This was ascribed to the formation of a small amount of cis-$[Rhen_2(OH)_2]^+$ in concentrated hydroxide solutions, and is dis-

cussed more fully in the next section.

The rate of reaction 3.32 was studied by following the decrease in absorbance at 341 nm, an isosbestic point for reaction 3.19, and absorbance changes of ca. 0.7 a.u. were obtained in 1 cm cells. The rate plots were straight for three half-lives, and the values of k_{obsd} found are given in Table 3.7. At constant ionic strength, the rate law

$$k_{obsd} = k_1 + k_2[OH^-] \qquad (3.20)$$

is obeyed, and values of k_1, k_2 and their associated activation parameters are given in Table 3.7.

(B) Stereochemical Rearrangement Occurring during Reactions with Hydroxide

(1) Reactions of trans-halohydroxy-complexes

As shown in Table 3.8, the spectra of the dihydroxy-products of base hydrolysis of trans-$[Rhen_2OHX]^+$ (X = Cl, Br, I) are independent of the nature of X, and of the concentration of hydroxide. Moreover, the full spectra, between 275 and 360 nm agree qualitatively with the spectrum of a sample of trans-$[Rhen_2(OH)_2]^+$ made by dissolving trans-$[Rhen_2OH(OH_2)](ClO_4)_2$ (prepared as in reference 75) in 0.1 M sodium hydroxide. However, the extinction coefficients of the dihydroxy reaction products were a constant factor of 1.12 ±0.02 times larger than those of the isolated sample. The difference could be due to co-precipitation of the diaquo-complex, or of hydrated species during the isolation of trans-$[Rhen_2OH(OH_2)](ClO_4)_2$. The spectrum of the product of hydrolysis of trans-$[Rhen_2I_2]^+$ in 0.100 M hydroxide also agrees with the spectra of the hydroxy-products of hydrolysis of trans-$[Rhen_2OHX]^+$ (X = Cl, Br, I),

and in each case the product was assumed to be pure trans-$[Rhen_2(OH)_2]^+$.

When, in later experiments, the spectrum of trans-$[Rhen_2(OH)_2]^+$ was required, the extinction coefficient of this complex at a given wavelength was taken as the unweighted mean of the extinction coefficients of the dihydroxy-products of hydrolysis of trans-$[Rhen_2OHCl]^+$ in 0.067 M hydroxide at 80.16°C, trans-$[Rhen_2OHBr]^+$ in 0.065 M hydroxide at 80.13°C, trans-$[Rhen_2OHI]^+$ in 0.100 M hydroxide at 80.0°C, and trans-$[Rhen_2I_2]^+$ in 0.100 M hydroxide at 80.27°C. The spectrum obtained in this way is shown as curve A in Fig. 3.10.

(2) Reactions of trans-dihalo-complexes

The dependence of the spectroscopic changes accompanying the base hydrolysis of trans-$[Rhen_2X_2]^+$ (X = Cl, Br, I) on the concentration of hydroxide present was ascribed to the formation of cis-hydroxy-products. Since the acid hydrolysis reactions of these complexes give only trans-products,[73] and since the product spectra differed most from the spectrum of trans-$[Rhen_2(OH)_2]^+$ when the reaction was carried out at high hydroxide concentrations, all stereochemical rearrangement was assumed to occur during the second-order pathway for hydrolysis. Moreover, since no rearrangement occurs during the base hydrolysis of trans-$[Rhen_2OHX]^+$ (X = Cl, Br, I), any cis-dihydroxy-complexes formed during the base hydrolysis of trans-$[Rhen_2X_2]^+$ must have been formed from cis-$[Rhen_2XOH]^+$ produced in the reaction

$$\text{trans-}[Rhen_2X_2]^+ + OH^- \longrightarrow [Rhen_2XOH]^+ + X^- \qquad (3.33)$$

Finally, it was shown that the spectrum of trans-$[Rhen_2(OH)_2]^+$ (prepared from an isolated sample of trans-$[Rhen_2OH(OH_2)](ClO_4)_2$) was

unaffected by heating in 1.00 M sodium hydroxide at 80.9°C for 7½ hr. Thus no direct trans to cis isomerisation of $[Rhen_2(OH)_2]^+$ occurs during the base hydrolysis reactions.

Determination of the mole fraction of cis-product

(a) For the reactions of trans-$[Rhen_2Cl_2]^+$ and trans-$[Rhen_2Br_2]^+$ with 1.0 M hydroxide

The mole fraction, X_c of cis-$[Rhen_2OHX]^+$ formed during the reaction of trans-$[Rhen_2X_2]^+$ (X = Cl, Br) with 1.00 M hydroxide was calculated in three ways.

Method 1

A known weight of trans-$[Rhen_2X_2]ClO_4$ was refluxed with an aliquot of standard sodium hydroxide in a foil-wrapped flask for 30 half-lives of the reaction

$$\text{trans-}[Rhen_2X_2]^+ + 2OH^- \longrightarrow [Rhen_2(OH)_2]^+ + 2X^- \qquad (3.34)$$

The dihydroxy-product solution (A) was cooled, suitably diluted and its spectrum run. The solution was quantitatively transferred to another foil-wrapped flask, an aliquot of standard HX added, and the mixture refluxed till no further change in the spectrum occurred. (For the reaction with HBr of the $[Rhen_2(OH)_2]^+$ product of hydrolysis of trans-$[Rhen_2Br_2]^+$, nitrogen was bubbled through the solution to prevent oxidation of the HBr.) The dihalo-product solution (B) was cooled and its spectrum run. It was then placed on a column of Dowex 50 W cation exchange resin (100-200 mesh) and separated by the usual vacuum ion-exchange technique. 0.1 M sodium perchlorate was used to elute the trans-$[Rhen_2X_2]^+$, and 1.0 M sodium perchlorate to elute the cis-$[Rhen_2X_2]^+$.

The eluate was collected in 14 ml fractions, and the progress of the elution followed by running the visible and UV spectrum of the fractions in 1 cm cells. The absorbance of trans-$[Rhen_2Cl_2]^+$ was measured at 205, 241, 250 or 290 nm, and that of cis-$[Rhen_2Cl_2]^+$ at 230, 240, 296 or 356 nm. The absorbance of trans-$[Rhen_2Br_2]^+$ was measured at 234, 250 or 279 nm and that of cis-$[Rhen_2Br_2]^+$ at 240, 276 or 372 nm.

From the known extinction coefficients of trans-$[Rhen_2X_2]^+$ (X = Cl, Br), the number of moles N_t of trans-$[Rhen_2X_2]^+$ can be calculated from the equation

$$N_t = \sum_{i=1}^{n} \frac{V_i(A_i-B_i)}{\epsilon_i} \qquad (3.35)$$

where V_i, A_i, B_i, ϵ_i are the volume, absorbance, base line and appropriate extinction coefficient of the "i"th fraction, and n is the total number of trans-fractions. The mole fraction X_c of cis-$[Rhen_2X_2]^+$ is then given by the equation

$$X_c = \frac{N_o-N_t}{N_o} \qquad (3.36)$$

where N_o is the total number of moles of $[Rhen_2X_2]^+$ present. For the reaction of trans-$[Rhen_2Cl_2]^+$ X_c was 0.17, and for the reaction of trans-$[Rhen_2Br_2]^+$ X_c was 0.41.

The cis-$[Rhen_2Cl_2]^+$ fractions had absorbance maxima at 356 and 296 nm, and the cis-$[Rhen_2Br_2]^+$ fractions had maxima at 372 and 276 nm. The extinction coefficients of these peaks can be found in the following way. By choice of suitable fractions, the ratio, f_λ, of the extinction coefficient at a reference wavelength (356 nm for cis-$[Rhen_2Cl_2]^+$ and 372 nm for cis-$[Rhen_2Br_2]^+$) to the extinction coefficient at any other wavelength λ could be determined. Hence the equivalent absorbance A_j°

of a given fraction at the reference wavelength is given by

$$A_j^\circ = (A_j - B_j) f_\lambda \qquad (3.37)$$

where A_j, B_j are the absorbances of the solution and the base line at λ nm. Since

$$N_j = A_j^\circ \epsilon^\circ V_j \qquad (3.38)$$

where N_j, V_j are the number of moles and volume of the "j"th fraction and ϵ° is the extinction coefficient of cis-$[Rhen_2X_2]^+$ at the reference wavelength, and since

$$X_c = \frac{\sum N_j}{N_o} \qquad (3.39)$$

it follows that

$$\epsilon^\circ = \frac{\sum_{j=1}^{m} (A_j - B_j) f_\lambda V_j}{X_c N_o} \qquad (3.40)$$

where m is the number of cis-fractions. Using equation 3.40 the absorption spectrum of cis-$[Rhen_2Cl_2]^+$ was calculated to be λ_{max} = 356, 296 nm; ϵ_{max} = 192, 188 M^{-1} cm^{-1}. This is in excellent agreement with Klabunde's results[80] of λ_{max} = 352, 294 nm; ϵ_{max} = 190, 190 M^{-1} cm^{-1}. Similarly the spectrum of cis-$[Rhen_2Br_2]^+$ was found to be λ_{max} = 372, 276 nm; ϵ_{max} = 220, 943 M^{-1} cm^{-1}. This is in reasonable agreement with the results of Johnson et al.[62] (λ_{max} = 362, 276 nm; ϵ_{max} = 210, 900 M^{-1} cm^{-1}).

The full spectrum of cis-$[Rhen_2X_2]^+$ was calculated in two ways. In the first (method A), the concentration, c_j, of a suitable cis-fraction was calculated by the equation

$$c_j = \frac{A_j^\circ}{\epsilon^\circ} \qquad (3.41)$$

The extinction coefficient of cis-$[Rhen_2X_2]^+$ at any wavelength was then calculated from the known concentration and absorbance of the fraction at the given wavelength. The second method (B) used the unseparated mixture of dihalo-products (solution B). In this solution the extinction coefficient, ϵ_{app} at any wavelength is given by

$$\epsilon_{app} = \epsilon_t(1-X_c) + \epsilon_c X_c \qquad (3.42)$$

where ϵ_t is the extinction coefficient of trans-$[Rhen_2X_2]^+$ at that wavelength. All the quantities in equation 3.42 are known except ϵ_c, which can thus be calculated. The spectra calculated by the two methods are given in Table 3.9A (X = Cl) and 3.9B (X = Br). In both cases, the spectra from the two methods agree qualitatively, but the extinction coefficients calculated by method B are always considerably higher than those found by method A. The reason for this difference will be discussed later, but as the extinction coefficients calculated by method A agree with those of previous workers, these were the values used in all subsequent calculations. The spectra of cis- and trans-$[Rhen_2Cl_2]^+$ are shown in Fig. 3.11, and the spectra of cis- and trans-$[Rhen_2Br_2]^+$ in Fig. 3.12.

The spectrum of cis-$[Rhen_2(OH)_2]^+$ can also be calculated from these experiments, since equation 3.42 applies to the mixture (solution A) of dihydroxy-products. At all wavelengths, the extinction coefficients ϵ_c calculated for cis-$[Rhen_2(OH)_2]^+$ using the dihydroxy-products of hydrolysis of trans-$[Rhen_2Cl_2]^+$ and trans-$[Rhen_2Br_2]^+$ differed by less than 17%. The "best" extinction coefficient for cis-$[Rhen_2(OH)_2]^+$ at a given wavelength was taken to be a weighted average of the two values of ϵ_c at that wavelength. The weighting factor was X_c^2 where X_c is the mole fraction of cis-products found in the experiment.

Methods 2 and 3

These methods were used to calculate X_c from other experiments than those used in method 1. In method 2 a 1 cm quartz cell containing a solution of known trans-$[Rhen_2X_2]^+$ and hydroxide concentrations was heated in the thermostatted cell compartment of the Perkin Elmer 402 spectrophotometer until no further spectroscopic change occurred. The solution was cooled, shaken, and its spectrum run. From this spectrum, the known spectrum of trans-$[Rhen_2(OH)_2]^+$ and the spectrum of cis-$[Rhen_2(OH)_2]^+$ given by the analysis of method 1, the value of X_c was calculated every 5 nm from 275 to 350 nm and at 360 nm. The "best" value of X_c was taken as the weighted mean of all these values, using a weighting factor of $(\epsilon_c-\epsilon_t)^2$. ($\epsilon_c$ and ϵ_t are the extinction coefficients of cis- and trans-$[Rhen_2X_2]^+$ respectively.)

In method 3 an aliquot of the dihydroxy-product was heated with an aliquot of standard HX until no further spectroscopic change occurred; the product was assumed to be a mixture of cis- and trans-$[Rhen_2X_2]^+$. From the spectrum of this mixture and the spectra of cis- and trans-$[Rhen_2X_2]^+$ given in Fig. 3.11 (X = Cl) and Fig. 3.12 (X = Br) the mole fraction, X_c, of cis-product was calculated every 5 nm from 285 to 350 nm, then every 10 nm from 350 to 390 nm (X = Cl) and every 5 nm from 330 to 350 nm, then every 10 nm from 350 to 410 nm (X = Br). The calculations are outlined in Table 3.10. In each of the two cases, the "best" value of X_c was taken as the weighted mean of all the values of X_c calculated in the experiment, the weighting factor being $(\epsilon_c-\epsilon_t)^2$ (ϵ_c and ϵ_t are now the extinction coefficients of cis- and trans-$[Rhen_2X_2]^+$).

For the reaction of trans-$[Rhen_2Cl_2]^+$ with 1.00 M hydroxide at 80.58°C method 2 gave X_c as 0.31 and method 3 gave X_c as 0.61. For the

reaction of trans-$[Rhen_2Br_2]^+$ with 1.00 M hydroxide at 80.09°C, X_c was calculated to be 0.28 by method 2 and 0.68 by method 3. These values can be compared with those found in the ion-exchange experiments (method 1) if the percentage rearrangement, P.R., occurring during the hydroxide-dependent pathway is calculated. P.R. is given by

$$P.R. = 100\left(\frac{X_c}{F}\right) \qquad (3.43)$$

where F, the fraction of the reaction proceeding via the hydroxide-dependent pathway can be calculated from the known kinetics of the reaction. For trans-$[Rhen_2Cl_2]^+$, P.R. is 23% by method 1, 53% by method 2 and 100% by method 3; for trans-$[Rhen_2Br_2]^+$, P.R. is 51% by method 1, 43% by method 2 and 100% by method 3. This could be explained if there was some isomerisation of cis- to trans-$[Rhen_2X_2]^+$ during the ion-exchange separation of the two isomers. This isomerisation could be photochemical in nature since the separation procedure took several hours and no attempt was made to shield the column from the fluorescent laboratory lights; the photoisomerisation of cis-$[Rhen_2Cl_2]^+$ has recently been reported by Muir and Huang.[135] Alternatively, the reaction could be a thermal aquation which is catalysed by the resin.

Regardless of the exact mechanism, isomerisation during separation of cis- and trans-$[Rhen_2X_2]^+$ (X = Cl, Br) would explain the difference between the extinction coefficients found for cis-$[Rhen_2X_2]^+$ using separated and unseparated solutions (methods 1A and 1B). If the value of X_c found by the ion-exchange separation is less than the mole-fraction of cis-products formed during the hydrolysis of trans-$[Rhen_2X_2]^+$, then the extinction coefficients of cis-$[Rhen_2X_2]^+$ calculated from the unseparated mixture will be too large. This is what is found in practice. Furthermore,

the extinction coefficients calculated for cis-$[Rhen_2(OH)_2]^+$ using the unseparated dihydroxy-products will also be too high. When these values of the extinction coefficients are applied to the analysis of other mixtures of cis- and trans-$[Rhen_2(OH)_2]^+$ they will give values of X_c which are too low. Again, this is exactly the behaviour that is observed.

It thus appears that the most reliable value of X_c for hydrolysis of trans-$[Rhen_2X_2]^+$ (X = Cl, Br) is that given by method 3. Assuming this value of X_c and the spectrum of trans-$[Rhen_2(OH)_2]^+$ given in Fig. 3.10 curve A, the spectrum of cis-$[Rhen_2(OH)_2]^+$ was recalculated from the mixtures of dihydroxy-products formed in method 2. At all wavelengths, the extinction coefficients of cis-$[Rhen_2(OH)_2]^+$ calculated from the $[Rhen_2(OH)_2]^+$ products of hydrolysis of trans-$[Rhen_2Cl_2]^+$ and trans-$[Rhen_2Br_2]^+$ in 1.0 M hydroxide differed by less than 8%. At each wavelength the weighted mean of the two values for the extinction coefficient was calculated, using X_c^2 as the weighting factor, where X_c is the mole fraction of cis-product. The spectrum of cis-$[Rhen_2(OH)_2]^+$ so obtained is shown as curve B in Fig. 3.10.

(b) Determination of the mole fractions for the cis-products of the reactions of trans-$[Rhen_2Cl_2]^+$ and trans-$[Rhen_2Br_2]^+$ with 0.1 M hydroxide and of trans-$[Rhen_2I_2]^+$ with 1.0 M hydroxide

An aliquot of a solution of known trans-$[Rhen_2X_2]^+$ (X = Cl, Br, I) concentration, and of the required sodium hydroxide concentration, was heated in the Perkin Elmer 402 spectrophotometer until no further spectroscopic change occurred. From the spectrum of the dihydroxy-product, and the spectra of cis- and trans-$[Rhen_2(OH)_2]^+$ given in Fig. 3.10, the mole fraction, X_c, of cis-product was calculated at 360 nm and every 5 nm from

275 to 350 nm. This calculation is outlined in Table 3.10 for the reaction of trans-$[Rhen_2I_2]^+$ with 1.00 M hydroxide. The "best" value of X_c was taken as the weighted mean of all these values, the weighting factor being $(\epsilon_c-\epsilon_t)^2$. ($\{\epsilon_c-\epsilon_t\}$ is the difference in extinction coefficients at the given wavelength of cis- and trans-$[Rhen_2(OH)_2]^+$.)

For the reactions of trans-$[Rhen_2Cl_2]^+$ and trans-$[Rhen_2Br_2]^+$ an aliquot of the dihydroxy-complex solution was heated with standard HCl or HBr until no further spectroscopic change occurred. From the spectrum of the dihalo-products, and the spectra of cis- and trans-$[Rhen_2X_2]^+$ given in Fig. 3.11 (X = Cl) and Fig. 3.12 (X = Br), the mole fraction, X_c, of cis-products was estimated. For the dichloro-product, X_c was calculated every 5 nm from 285 to 350 nm and every 10 nm from 350 to 390 nm; for the dibromo-product X_c was calculated every 5 nm from 330 to 350 nm, then every 10 nm from 350 to 410 nm. In each case, the "best" value of X_c was taken as the weighted mean of the values determined at each of the above wavelengths, the weighting factor being $(\epsilon_c-\epsilon_t)^2$. ($\epsilon_c$ and ϵ_t are now the extinction coefficients at the given wavelength of cis- and trans-$[Rhen_2X_2]^+$.)

For the reaction of trans-$[Rhen_2Cl_2]^+$ with 0.100 M hydroxide at 80.58°C, X_c was 0.22 by analysis of the dihydroxy-product and 0.17 by analysis of the dichloro-product. For the reaction of trans-$[Rhen_2Br_2]^+$ with 0.100 M hydroxide at 80.09°C, X_c was 0.20 by analysis of the dihydroxy-products and 0.20 by analysis of the dibromo products. As expected, there is good agreement between values of X_c calculated from dihydroxy- and dihalo-products, although the estimated uncertainty in X_c of ±0.1 makes discussion of the precise values of X_c meaningless.

For the reaction of trans-$[Rhen_2I_2]^+$ with 1.00 M hydroxide at 80.27°C,

the value of X_c was found (from the dihydroxy-product) to be 0.21. From equation 3.43 and the known kinetics of base hydrolysis of trans-$[Rhen_2I_2]^+$, the percentage rearrangement, P.R., occurring in the hydroxide-dependent pathway is 46%.

The values of X_c and P.R. obtained from all the stereochemical rearrangement experiments are summarised in Table 3.11.

(C) Kinetics of the Reactions of trans-diacidobisethylenediamine-rhodium(III) Complexes with Anions other than Hydroxide

(1) The reaction of trans-$[Rhen_2I_2]^+$ with chloride

The reaction

$$\text{trans-}[Rhen_2I_2]^+ + Cl^- \longrightarrow \text{trans-}[Rhen_2ICl]^+ + I^- \qquad (3.44)$$

has been studied previously[73] and the spectroscopic changes which occur have been well documented.[74] Replacement of the second iodide in trans-$[Rhen_2ICl]^+$ is auto-catalytic, but below 55°C the rate of this reaction is negligible compared to that of reaction 3.44.[73] In this work the extinction coefficient, ϵ_{300}, at 300 nm of the iodochloro-products of all kinetic runs was 3800 ±110 M^{-1} cm^{-1}. The value of ϵ_{300} for an isolated sample of trans-$[Rhen_2ICl]^+$ dissolved in 0.1 M sodium chloride is 4350 M^{-1} cm^{-1}; the difference between these values was caused by a slight alkalinity of the sodium chloride solutions used in the kinetic runs. However, the concentration of hydroxide was too low to affect the rate of reaction 3.44.

The rate of reaction 3.44 was determined by following the decrease in absorbance at 342 nm. Absorbance changes of ca. 0.8 a.u. were obtained in 1 cm cells and the pseudo-first-order rate plots were straight for

four half-lives. The dependence of k_{obsd} on the concentration of chloride at a constant ionic strength of 1.0 M (maintained with sodium perchlorate) was investigated at a variety of temperatures. The rate law found was

$$k_{obsd} = k_1 + k_2[Cl^-] \qquad (3.45)$$

and a typical graph of k_{obsd} against $[Cl^-]$ is shown in Fig. 3.13. The activation parameters $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$, $\Delta S_2^{\ddagger}$ associated with the first- and second-order pathways respectively were obtained from the temperature dependence of k_1 and k_2. The values of k_{obsd} and all parameters derived from them are given in Table 3.12. Some kinetic runs were performed at constant temperature and various ionic strengths, I, such that $I = [Cl^-]$. The values of k_{obsd} obtained under these conditions are shown in Table 3.13. Table 3.13 also gives the values of k_{obsd} obtained in a series of runs carried out at constant temperature and varying concentrations of sodium perchlorate so that $I = [ClO_4^-]$. The concentration of sodium chloride was low enough that the contribution to k_{obsd} from the second order pathway was negligible, but sufficiently high that reaction 3.44 went to completion.

(2) The reaction of trans-$[Rhen_2I_2]^+$ with bromide

The reaction

$$\underline{trans}\text{-}[Rhen_2I_2]^+ + Br^- \longrightarrow \underline{trans}\text{-}[Rhen_2IBr]^+ + I^- \qquad (3.46)$$

has also been studied by Bounsall et al.[73] Replacement of the second iodide in $\underline{trans}$-$[Rhen_2IBr]^+$ is autocatalytic, but below 55°C the rate of this reaction is negligible compared to that of reaction 3.46. In this work, the extinction coefficient ϵ_{311} at 311 nm of the iodobromo-products

of all kinetic runs was 6060 ±370 M^{-1} cm^{-1}, considerably lower than the value of 7500 M^{-1} cm^{-1} reported by Bounsall[74] for an isolated sample of trans-$[Rhen_2IBr]ClO_4$. Again, this difference was caused by a slight alkalinity of the sodium bromide solutions, but the concentration of hydroxide was insufficient to affect the rate of reaction 3.46. Reaction 3.46 was studied by following the decrease in absorbance at 342 nm. Absorbance changes of ca. 0.7 a.u. were obtained in 1 cm cells and the pseudo-first-order rate plots were straight for at least four half-lives. At a constant ionic strength of 1.0 M, maintained with sodium perchlorate, the rate law

$$k_{obsd} = k_1 + k_2[Br^-] \qquad (3.47)$$

was found. A typical ligand-dependence plot of k_{obsd} against $[Br^-]$ is shown in Fig. 3.14. Values of k_{obsd}, k_1, k_2 and the associated activation parameters are given in Table 3.14.

(3) The reaction of trans-$[Rhen_2I_2]^+$ with hydroxide in the presence of fluoride, phosphate or sulphate

In order to investigate the effect of other anions on the rate of the reaction

$$\text{trans-}[Rhen_2I_2]^+ + H_2O \longrightarrow [Rhen_2IOH_2]^{2+} + I^- \qquad (3.48)$$

four kinetic runs were simultaneously performed in the thermostatted cell compartment of the Cary 16K. The four cells contained

(A) trans-$[Rhen_2I_2]^+$ + 0.200 M sodium fluoride + 0.80 M sodium perchlorate + 0.01 M sodium hydroxide

(B) trans-$[Rhen_2I_2]^+$ + 0.334 M sodium sulphate + 0.01 M sodium hydroxide

(C) trans-$[Rhen_2I_2]^+$ + 0.167 M sodium phosphate + 0.01 M sodium hydroxide

(D) trans-$[Rhen_2I_2]^+$ + 1.00 M sodium perchlorate + 0.01 M sodium hydroxide The hydroxide was present to prevent hydrolysis of the anions, and to provide a well-characterised product (trans-$[Rhen_2IOH]^+$). The effect of this low a concentration of hydroxide ion on the rate of reaction 3.48 was negligible. The reactions were followed by observing the decrease in absorbance at 341 nm, an isosbestic point for the reaction

$$\text{trans-}[Rhen_2IOH]^+ + OH^- \longrightarrow [Rhen_2(OH)_2]^+ + I^- \qquad (3.19)$$

Absorbance changes in 1 cm cells were ca. 0.9 a.u. in all cases, and the pseudo-first-order rate plots were straight for at least four half-lives. The rate constants, k_{obsd}, found are given in Table 3.15.

It was assumed that the rate law for these reactions was

$$k_{obsd} = k_1 + k_2[Y] \qquad (3.49)$$

where $Y = F^-$, SO_4^{2-} or PO_4^{3-}, and where k_1 is the rate constant found in cell D. The values of k_2 found for the various anions, using equation 3.49, are also given in Table 3.15.

(4) The reaction of trans-$[Rhen_2Cl_2]^+$ with hydroxide in the presence of bromide

An initial kinetic run for the reaction of 6.5×10^{-3} M trans-$[Rhen_2Cl_2]^+$ with 0.025 M sodium hydroxide and 1.01 M sodium bromide showed that under these conditions the product of the reaction was predominantly $[Rhen_2(OH)_2]^+$ formed by the reaction

$$\text{trans-}[Rhen_2Cl_2]^+ + 2OH^- \longrightarrow [Rhen_2(OH)_2]^+ + 2Cl^- \qquad (3.23)$$

Further kinetic runs on the base hydrolysis of trans-$[Rhen_2Cl_2]^+$ in the

presence of bromide were performed using a lower concentration of substrate, 0.100 M sodium hydroxide, varying concentrations of sodium bromide, and sufficient sodium perchlorate to keep the ionic strength constant at 1.0 M. The reaction was followed by measuring the decrease in absorbance at 241 nm, and the rate plots were straight for three half-lives. The rate law was

$$k_{obsd} = k_1' + k_2[Br^-] \qquad (3.50)$$

and the values of k_{obsd}, k_1' and k_2 found are given in Table 3.16. Since the rate of hydrolysis of trans-$[Rhen_2Cl_2]^+$ is dependent on the concentration of hydroxide, k_1' is not a true unimolecular rate constant, but is given by

$$k_1' = k_1 + k_2'[OH^-] \qquad (3.51)$$

where k_1 is the rate constant for unimolecular aquation of trans-$[Rhen_2Cl_2]^+$ and k_2' is the second order rate constant for the reaction of this complex with hydroxide. At 77.87°C, k_2' is 4.00×10^{-5} M^{-1} s^{-1}, so k_1 can be calculated from equation 3.51 to be 3.143×10^{-5} s^{-1} at this temperature.

(5) The reaction of trans-$[Rhen_2Cl_2]^+$ with hydroxide in the presence of sulphate

An initial kinetic run on the reaction of 6.30×10^{-3} M trans-$[Rhen_2Cl_2]^+$ with 0.025 M sodium hydroxide and 0.35 M sodium sulphate showed that the product of the reaction was predominantly $[Rhen_2(OH)_2]^+$ produced by reaction 3.23. Further kinetic runs were performed using a lower concentration of substrate, 0.010 M sodium hydroxide, varying concentrations

of sodium sulphate, and sufficient sodium perchlorate to keep the ionic strength constant at 1.0 M. The reaction was followed by measuring the decrease in absorbance at 242 nm. The rate law was

$$k_{obsd} = k_1' + k_2[SO_4^{2-}] \qquad (3.52)$$

where k_1' is given by equation 3.51. Values of k_{obsd}, k_1', k_1 and k_2 are given in Table 3.17.

(6) The reaction of trans-$[Rhen_2Cl_2]^+$ with hydroxide in the presence of phosphate

A preliminary kinetic run on the reaction of 6.42×10^{-3} M trans-$[Rhen_2Cl_2]^+$ with 0.025 M sodium hydroxide and 0.167 M sodium phosphate showed that the product of the reaction was $[Rhen_2(OH)_2]^+$ with possibly some phosphato-complexes or ion-pairs. Further kinetic runs using a lower concentration of substrate, 0.010 M sodium hydroxide, varying concentrations of sodium phosphate and sufficient sodium perchlorate to keep the ionic strength constant at 1.0 M were performed. The reaction was studied by following the decrease in absorbance at 242 nm and the rate plots obtained were straight for three half-lives. The pseudo-first-order rate constants found are given in Table 3.18; they obey a rate law

$$k_{obsd} = k_1' + k_2[PO_4^{3-}] \qquad (3.53)$$

where k_1' is defined by equation 3.51. The values of k_1', k_2 and k_1 calculated are given in Table 3.18.

(7) The reaction of trans-$[Rhen_2Cl_2]^+$ with hydroxide in the presence of fluoride

The reaction of trans-$[Rhen_2Cl_2]^+$ with 0.01 M sodium hydroxide, varying concentrations of sodium fluoride, and sufficient sodium perchlorate to keep the ionic strength constant at 1.0 M was investigated by following the decrease in absorbance at 242 nm. The pseudo-first-order rate plots were straight for three half-lives. The rate law obeyed was

$$k_{obsd} = k_1' + k_2[F^-] \qquad (3.54)$$

and values of k_{obsd}, k_1', k_1 and k_2 are given in Table 3.19.

(8) The reaction of trans-$[Rhen_2Br_2]^+$ with fluoride

The reaction of trans-$[Rhen_2Br_2]^+$ with fluoride in neutral solutions has been investigated by Bott et al.,[73] but these authors give no information about the spectroscopic changes occurring during the reaction. A solution of trans-$[Rhen_2Br_2]^+$ was heated with 0.20 M sodium fluoride; although the solution was too dilute to characterise the products, the final spectrum showed almost complete loss of substrate.

Three further kinetic runs were performed using solutions containing varying concentrations of potassium fluoride and sufficient potassium nitrate to keep the ionic strength constant at 1.0 M. The reaction was followed by measuring the decrease in absorbance at 270 nm, and the rate plots were straight for two half-lives. The large background absorbance of the nitrate ion made the overall absorbance of the solutions very high; for the solution of highest nitrate concentration, only the last part of the reaction could be followed. The values of k_{obsd} found are given in Table 3.20; because of the experimental difficulties, the precision of

these values is low so that although the aquation of trans-$[Rhen_2Br_2]^+$ seems to be slightly dependent on the concentration of fluoride present, it is not possible to assign a value to the second-order rate constant for the reaction with fluoride.

(D) Spectroscopic Interactions between trans-diacidobisethylenediamine-rhodium(III) Complexes and Added Anions

(1) Trans-$[Rhen_2Cl_2]^+$ and iodide

A solution of trans-$[Rhen_2Cl_2]ClO_4$ in water was prepared with the minimum amount of heating. A 1 ml aliquot of this solution was mixed with a 2 ml aliquot of a standard sodium iodide solution. The spectrum of the mixture was recorded on the Perkin Elmer 402 spectrophotometer using a "blank" composed of 1 ml of water and 2 ml of the sodium iodide solution. The absorbance at 285 nm of the complex/iodide solution was also measured against that of the blank on the Cary 16K spectrophotometer; the measurements were made at least three times with the same solutions, then averaged. The experiment was repeated using the same concentration of trans-$[Rhen_2Cl_2]^+$ and several different concentrations of sodium iodide. All handling of the solutions was performed in red light. The dependence of the spectrum of trans-$[Rhen_2Cl_2]^+$ on the iodide concentration of the final solution is shown in Fig. 3.15. The values of the absorbance at 285 nm recorded on the Cary 16K are shown in Table 3.21 and are plotted against the concentration of iodide in Fig. 3.16.

(2) Trans-$[Rhen_2Cl_2]^+$ and bromide

A 1 ml aliquot of a standard trans-$[Rhen_2Cl_2]^+$ solution was mixed

with a 2 ml aliquot of a standard sodium bromide solution. The spectrum of the mixture was recorded on the Perkin Elmer 402, against a "blank" solution composed of 1 ml of water mixed with 2 ml of the sodium bromide solution. The experiment was repeated using several different concentrations of bromide. All the solutions were handled in red light. The dependence of the spectrum of trans-$[Rhen_2Cl_2]^+$ on the concentration of bromide is shown in Table 3.22 and Fig. 3.17.

(3) Trans-$[Rhen_2Cl_2]^+$ and iodide in the presence of other anions

A 1 ml aliquot of a standard trans-$[Rhen_2Cl_2]^+$ solution was mixed with a 2 ml aliquot of a solution containing 0.75 M sodium iodide and a known concentration of the sodium salt of the anion under investigation. The spectrum of the resultant solution was recorded on the Perkin Elmer 402 spectrophotometer, the "blank" being a mixture of 1 ml of water and 2 ml of the appropriate sodium iodide/anion solution. The experiment was performed using chloride, bromide, fluoride, hydroxide, sulphate and phosphate as the added anion. The concentrations of these anions in the final solution and the extinction coefficients of this solution at 285 and 290 nm are given in Table 3.23.

(4) Trans-$[Rhen_2I_2]^+$ and iodide in the presence of other anions

The spectroscopic interaction between trans-$[Rhen_2I_2]^+$ and iodide has been studied by Bott;[81] at ca. 300 nm there is a very marked intensification of the absorbance of the complex. In the present experiments a standard solution of trans-$[Rhen_2I_2]^+$ was prepared with the minimum amount of heating in red light. A 1 ml aliquot of this solution was mixed with a 2 ml aliquot of a solution containing 0.75 M sodium iodide, a known

concentration of the sodium salt of the anion (Y^{n-}) under investigation, and sufficient sodium perchlorate to maintain the ionic strength of the final mixture at 1.5 M. The spectrum of the mixture was recorded on the Perkin Elmer 402 spectrophotometer, using a solution composed of 1 ml of water mixed with 2 ml of the iodide/anion/perchlorate solution as the "blank". The concentrations of the anions in the final solution, and the extinction coefficients of these solutions at 300 nm are given in Table 3.24.

Discussion

The most important question raised by all these results is the exact nature of the mechanism producing the second order term in the rate law. In addition to the classical S_N1IP and S_N2IP reactions, there is also the possibility of redox-catalysed pathways similar to those found for platinum(IV) complexes.

Redox Mechanisms

In addition to the normal interchange mechanism for aquation of rhodium(III) complexes (equations 3.62 and 3.63), it is possible to consider a redox mechanism (equations 3.64 and 3.65) similar to that proposed by Poë et al.[82] for platinum(IV) complexes.

$$[Rhen_2LX]^+ + H_2O \xrightarrow{k_0} [Rhen_2LOH_2]^{2+} + X^- \qquad (3.62)$$

$$[Rhen_2LOH_2]^{2+} + Y^{n-} \xrightarrow{fast} [Rhen_2LY]^{(2-n)+} + H_2O \qquad (3.63)$$

$$Y^{n-} + [LRhen_2X]^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} YL^{(n-1)-} + [Rhen_2]^+ + X^- \qquad (3.64)$$

$$YL^{(n-1)-} + [Rhen_2]^+ + Y^{n-} \xrightarrow{k_s} Y^{n-} + [LRhen_2Y]^{(2-n)+} \qquad (3.65)$$

Applying the steady state assumption to the concentration of $[Rhen_2]^+$, the mechanism of equations 3.62 to 3.65 predicts the rate law

$$k_{obsd} = k_0 + \frac{k_f k_s [Y]^2}{k_r(1 + (k_s/k_r)[Y])} \qquad (3.66)$$

which reduces to

$$k_{obsd} = k_0 + k_f[Y] \qquad (3.67)$$

if under all conditions studied

$$k_s[Y]/k_r \gg 1 \qquad (3.68)$$

It is also possible to consider a rhodium(I) catalysed pathway; such a reaction pathway is found for the reactions of trans-$[Rhpy_4Cl_2]^+$ and its analogues.[83)-(90)] trans-$[Rh(DH)_2Cl_2]^+$[91)] and cis-$[Rhbipy_2Cl_2]^+$.[92)] The rhodium(I)-catalysed mechanism is given by equations 3.62, 3.63, 3.69 and 3.70.

$$Y^{n-} + [Rhen_2]^+ \overset{K}{\rightleftharpoons} \{Rhen_2Y\}^{(1-n)+} \qquad (3.69)$$

$$\{YRhen_2\}^{(1-n)+} + [LRhen_2X]^+ \xrightarrow{fast} [YRhen_2L]^{(2-n)+} + [Rhen_2]^+ + X^- \qquad (3.70)$$

The $[Rhen_2]^+$ must be present in low, steady-state concentrations or autocatalysis and sigmoid rate plots would be obtained. Applying the steady state assumption to $[Rhen_2]^+$, the mechanism of equations 3.62 to 3.64 and 3.69 to 3.70 gives

$$k_{obsd} = k_0 + k_f[Y] \qquad (3.67)$$

It thus appears that whatever the details of the redox mechanism, the rate-determining step is reduction of the substrate by Y^{n-}. The most important evidence against the redox mechanism is that phosphate and sulphate catalyse the hydrolysis of trans-$[Rhen_2Cl_2]^+$ and trans-$[Rhen_2I_2]^+$ more effectively than chloride and bromide. This is incompatible with the rate-determining step being reduction of the rhodium(III) species, since the reducing power of phosphate and sulphate is much less than that of chloride or bromide.

The Ion-Pairing Mechanism

The ion-pairing mechanism is outlined in equations 3.62, 3.63, 3.71 and 3.72.

$$[Rhen_2LX]^+ + H_2O \xrightarrow{k_0} [Rhen_2LOH_2]^{2+} + X^- \quad (3.62)$$

$$[Rhen_2LOH_2]^{2+} + Y^{n-} \xrightarrow{fast} [Rhen_2LY]^{(2-n)+} + H_2O \quad (3.63)$$

$$[Rhen_2LX]^+ + Y^{n-} \rightleftharpoons^{K_Y} \{Rhen_2LX,Y\}^{(1-n)+} \quad (3.71)$$

$$\{Rhen_2LX,Y\}^{(1-n)+} \xrightarrow{k_Y} [Rhen_2LY]^{(2-n)+} + X^- \quad (3.72)$$

If the interchange reaction 3.72 is I<u>a</u> in nature the reaction has an S_N2IP mechanism; if reaction 3.72 is I<u>d</u> in nature, the mechanism is designated S_N1IP. The rate law predicted by either mechanism is

$$k_{obsd} = \frac{k_0 + k_Y K_Y [Y]}{1 + K_Y [Y]} \quad (3.73)$$

When Y^{n-} is OH^-, the "ion-pair" $\{Rhen_2LX,OH\}^0$ may in fact be the deprotonated intermediate $\{Rhen(en-H)LX\}^0$. Because of this ambiguity, the remarks made below are not considered to apply to hydroxide. Once a pattern has been established for the reactions with other anions, the reactions with hydroxide will be discussed in terms of their agreement with, or departure from, this pattern.

I. Reactions with anions other than hydroxide

Under the experimental conditions of these experiments, equation 3.73 is an over-simplified form of the rate law. Two sets of conditions can be considered, depending on whether or not the ionic strength is controlled by addition of $NaClO_4$. If $NaClO_4$ is added, the reactions

$$ClO_4^- + [Rhen_2LX]^+ \rightleftharpoons^{K_{ClO_4}} \{Rhen_2LX,ClO_4\} \quad (3.74)$$

$$\{Rhen_2LX,ClO_4\} \xrightarrow{k_{ClO_4}} [Rhen_2LOH_2]^{2+} + X^- + ClO_4^- \quad (3.75)$$

$$[Rhen_2LOH_2]^{2+} + Y^{n-} \xrightarrow{fast} [Rhen_2LY]^{(2-n)+} + H_2O \quad (3.76)$$

must be considered, and equation 3.73 becomes

$$k_{obsd} = \frac{k_0 + k_Y K_Y [Y] + k_{ClO_4} K_{ClO_4} [ClO_4]}{1 + K_{ClO_4} [ClO_4] + K_Y [Y]} \qquad (3.77)$$

At a constant ionic strength of 1.0M, equation 3.77 becomes 3.78, 3.79 and 3.80 for a uni-, di- and tri-valent anion respectively.

$$k_{obsd} = \frac{k_0 + k_{ClO_4} K_{ClO_4} + (K_Y k_Y - K_{ClO_4} k_{ClO_4})[Y]}{1 + K_{ClO_4} + (K_Y - K_{ClO_4})[Y]} \qquad (3.78)$$

$$k_{obsd} = \frac{k_0 + k_{ClO_4} K_{ClO_4} + (K_Y k_Y - 3K_{ClO_4} k_{ClO_4})[Y]}{1 + K_{ClO_4} + (K_Y - 3K_{ClO_4})[Y]} \qquad (3.79)$$

$$k_{obsd} = \frac{k_0 + k_{ClO_4} K_{ClO_4} + (K_Y k_Y - 6K_{ClO_4} k_{ClO_4})[Y]}{1 + K_{ClO_4} + (K_Y - 6K_{ClO_4})[Y]} \qquad (3.80)$$

The term $(K_Y - mK_{ClO_4})$, where m = 1, 3, 6, in the denominator of equations 3.78, 3.79, 3.80 means that even if substantial amounts of ion-association occur, this might not be detected by curvature of the graph of k_{obsd} against [Y].

If sodium perchlorate is not added to maintain the ionic strength, I, constant, K_Y in equation 3.73 varies with the ionic strength, and is given[93] by the equation

$$K_Y = K_Y^0 \gamma^2 \qquad (3.81)$$

where K_Y^0 is the ion-association constant at I = 0.0 M and γ is the mean activity coefficient of the unassociated salt $[Rhen_2LX]_nY$. Substitution of equation 3.81 in equation 3.73 gives

$$k_{obsd} = \frac{k_0 + k_Y K_Y^0 \gamma^2 [Y]}{1 + K_Y^0 \gamma^2 [Y]} \qquad (3.82)$$

Interpretation of the results in this chapter requires a knowledge of (a) the magnitude of K_Y, and especially, of K_{ClO_4}, and (b) the relative magnitudes of k_Y, or the relative reactivities of the ion-pairs. The latter should enable a distinction to be made between the S_N1IP and S_N2IP mechanisms. Because K_{ClO_4} is not known for these complexes, initial estimates of K_Y must be made using the data obtained in the absence of perchlorate.

(A) Calculation of Ion-Association Constants using Experiments Performed in the Absence of Perchlorate

(1) Association between trans-$[Rhen_2I_2]^+$ and chloride (from kinetic data)

The value of K_{Cl}^0 for the association

$$\underline{trans}\text{-}[Rhen_2I_2]^+ + Cl^- \rightleftharpoons \{Rhen_2I_2,Cl\}^0 \qquad (3.83)$$

was estimated using equation 3.82 and the results given in Table 3.13 for the dependence of k_{obsd} on the $[Cl^-]$ at $I = [Cl^-]$. By extrapolation of the graph of k_{obsd} against $[Cl^-]$ to $[Cl^-] = 0.0$ M, k_0 was found to be 2.310×10^{-4} s^{-1}. Values of γ were calculated using the Davies equation[94]

$$\log\gamma = -0.5(\sqrt{I}/(1+\sqrt{I}) - 0.3I) \qquad (3.84)$$

Although equation 3.84 is not strictly valid above $I = 0.3$, it was used up to 1.0 M because there is no other equation available for calculation of activity coefficients at high ionic strengths. Rearrangement of equation 3.82 gives

$$\frac{k_{obsd} - k_0}{\gamma^2[Y]} = y = -K_Y k_{obsd} + k_Y K_Y \qquad (3.85)$$

The standard deviation, σ_y, of any value of y was calculated assuming that the standard deviation in k_0 and in each value of k_{obsd} was 7×10^{-5} s^{-1} (i.e. ca. 3%). The values of y and σ_y obtained are shown in Table 3.25; a weighted least squares analysis of these data according to equation 3.85, and assuming the error in k_{obsd} was negligible compared to that in y gave $K^0_{Cl} = 1.2 \pm 1.4\ M^{-1}$.

(2) Association between trans-$[Rhen_2Cl_2]^+$ and bromide (from spectroscopic data)

The equilibrium constant K^0_{Br} for the association

$$\underline{trans}\text{-}[Rhen_2Cl_2]^+ + Br^- \rightleftharpoons \{Rhen_2Cl_2,Br\}^0 \qquad (3.86)$$

was calculated from the spectroscopic interaction between trans-$[Rhen_2Cl_2]^+$ and bromide. If this interaction is assumed to be due to ion-pair formation, equation 3.87 applies.

$$\frac{\epsilon_{app} - \epsilon_0}{[Br^-]\gamma^2} = z = -\epsilon_{app}K^0_{Br} + K^0_{Br}\epsilon_{Br} \qquad (3.87)$$

(ϵ_{app} is the observed extinction coefficient of the rhodium(III) species and ϵ_0, ϵ_{Br} are the extinction coefficients of the free $[Rhen_2Cl_2]^+$ ion and the $\{Rhen_2Cl_2,Br\}^0$ ion-pair respectively.) The activity coefficient, γ, was calculated from equation 3.84 and the values of z calculated from the results at 260 nm as listed in Table 3.26. An unweighted least squares

treatment of these data according to equation 3.87 gave $K^0_{Br} = 0.7 \pm 0.5$ M^{-1} and $\epsilon_{Br} = 700 \pm 600\ M^{-1}\ cm^{-1}$. In view of the systematic errors associated with extension of the Davies equation to such high ionic strengths, the standard deviation of K^0_{Br} is probably an underestimate of the actual error.

(3) Association of trans-$[Rhen_2Cl_2]^+$ and iodide (from spectroscopic data)

The equilibrium constant, K^0_I, for the association

$$\text{trans-}[Rhen_2Cl_2]^+ + I^- \rightleftharpoons \{Rhen_2Cl_2,I\}^0 \qquad (3.88)$$

was calculated using the equation

$$\frac{\epsilon_{app} - \epsilon_0}{[I^-]\gamma^2} = w = -\epsilon_{app}K^0_I + K^0_I\epsilon_I \qquad (3.89)$$

where ϵ_I is the extinction coefficient of the ion-pair $\{Rhen_2Cl_2,I\}$ and ϵ_{app}, ϵ_0 have their previous meanings. Calculation of the activity coefficient, γ, is more difficult in this set of experiments, because the Davies equation[94] is inappropriate at the highest ionic strengths used. Using Burnett's[93] adaptation of the Scatchard equation it can be shown that at a given ionic strength, I,

$$\log\gamma = \tfrac{1}{2}(\log\gamma_{SI} + \log\gamma_{NaI}) \qquad (3.90)$$

where γ_{SI} and γ_{NaI} are the mean activity coefficients in pure solutions of ionic strength I of $[Rhen_2Cl_2]I$ and NaI respectively. A graph of γ_{NaI} against I was drawn using published[95] values of γ_{NaI}, and γ_{NaI} was read off at any desired ionic strength (see Fig. 3.18). Values of γ_{SI} were calculated by assuming that the mean activity coefficients of unassociated $[Rhen_2Cl_2]I$ were equal to those of the hypothetical

unassociated salt trans-$[Coen_2NO_2X]Cl$ (X is a univalent anion). Values of γ_{SI} for $[Coen_2NO_2X]Cl$ were calculated from Burnett's[93] tabulation of the corresponding activity coefficients, γ_{ref}, of trans-$[Coen_2NO_2NH_3]Cl_2$ using the equation[93]

$$\log \gamma_{SI} = \frac{Z_1}{Z_2} \log \gamma_{ref} \qquad (3.91)$$

($Z_1 = 1$ = the valency of the $[Coen_2NO_2X]^+$ ion and $Z_2 = 2$ = the valency of the $[Coen_2NH_3NO_2]^{2+}$ ion). Values of γ_{ref} were interpolated from the graph of γ_{ref} against I given in Fig. 3.19. Since Burnett's data[93] for trans-$[Coen_2NH_3NO_2]Cl_2$ do not extend below I = 0.5M, it was not possible to calculate γ for points below this ionic strength, and they were accordingly omitted in the subsequent calculations. Values of ϵ_{app} at 285 nm, γ, and the function w are listed in Table 3.27. An unweighted least squares analysis of the results of Table 3.27 according to equation 3.89 gives $K_I^0 = 0.38 \pm 0.02\ M^{-1}$ and $\epsilon_I = 1440 \pm 80\ M^{-1}\ cm^{-1}$. In view of the systematic errors associated with the method of calculating γ, the standard deviations associated with K_I^0 and ϵ_I are probably much larger than the values quoted above.

(B) Calculation of Theoretical Ion-Association Constants using the Fuoss Equation

The values of K_γ^0 for these three ion-pairs can be compared with the values predicted by the Fuoss[96] equation.

$$K_\gamma^0 = \frac{4\pi N}{3000} a^3 \exp(|Z_1 Z_2| e^2/\epsilon akT) \qquad (3.92)$$

where N is Avogardro's number, Z_1, Z_2 are the valencies of the anion and cation respectively, e is the electronic charge, ϵ the dielectric constant of the medium, k is Boltzman's constant, T the absolute

temperature, and a is the distance between the centres of the two ions when they are in contact. In the calculation of K_Y^0 from equation 3.92 the only parameter which was not known with certainty was a. No data seem to be available on the x-ray structures of ethylenediamine complexes of Rh(III), but a study of $[Coen_3]_2(HPO_4)_3$ has been carried out.[19] Fig. 3.20 shows the molecular dimensions of the $[Coen_3]^{3+}$ ion and lists the equations used to calculate r_+, the radius of this cation. (It was assumed, as an aid to calculation, that the ethylenediamine ring was planar.) Since the Rh-N bond distance cis to the hydride ligand in trans-$[Rh(NH_3)_5H]^{2+}$ is 2.07 Å,[97] which is close to the Co-N distance of 1.96 Å in $[Coen_3]^{3+}$,[19] it was felt that the value of r_+ calculated for $[Coen_3]^{3+}$ was a reasonable estimate of the value of r_+ for $[Rhen_3]^{3+}$ or trans-$[Rhen_2LX]^+$. The last assumption was justified by the fact that the plane of the ethylenediamine rings presents the largest radius in the non-spherical trans-$[Rhen_2LX]^+$ cations. The radius, r_-, of the anion, Y^{n-} (Y^{n-} = Cl^-, Br^-, F^-, OH^-, SO_4^{2-}, PO_4^{3-}, ClO_4^-), was taken as the crystallographic radius of the ion (Cl^-,[98] I^-,[98] Br^-,[98] F^-,[98] OH^-,[99]) or was estimated from known covalent radii (SO_4^{2-}, ClO_4^-, PO_4^{3-}). The SO_4^{2-} ionic radius was estimated as the average of the S=O and S-OH bonds in H_2SO_4[100] plus the van der Waals[101] radius, V_O of oxygen. The PO_4^{3-} ionic radius was similarly estimated as the average of the three P-O bond lengths in HPO_4^{2-}[19] plus V_O and the ClO_4^- radius as the average of the Cl-O bond lengths in ClO_4^-[102] plus V_O. The distance of closest approach, a in equation 3.92, is then given by

$$a = r_+ + r_- \qquad (3.93)$$

Values of r_+ and r_- are listed in Table 3.28. Table 3.28 also gives the

corresponding values of K_Y^0 calculated by equation 3.92 for association of Y with trans-$[Rhen_2LX]^+$ and also for association of Y with di- and trivalent cations of the same radius as trans-$[Rhen_2LX]^+$.

From Table 3.28 it can be seen that the values of K_Y^0 found here for the ion-pairs $\{Rhen_2I_2,Cl\}$, $\{Rhen_2Cl_2,Br\}$ and $\{Rhen_2Cl_2,I\}$ are of the same order of magnitude as those predicted by the Fuoss equation. This contrasts sharply with the work of Burgess et al.[25] who claimed that the ion-association constant K_{Cl}^0 for the equilibrium

$$\text{trans-}[Rhen_2Cl_2]^+ + Cl^- \rightleftharpoons \{Rhen_2Cl_2,Cl\} \qquad (3.94)$$

was 25 ± 5 M^{-1} in water at 80.7°C. Moreover, the results of this work are in reasonable agreement with Palmer and Watts' value[10] of 9 ± 6 M^{-1} for the ion-association constant of equation 3.94 measured in DMSO at 25°C. (In DMSO under these conditions the Fuoss equation predicts K_{Cl}^0 will be 3.9 M^{-1}.) From these results it appears that association constants of trans-$[Rhen_2LX]^+$ with univalent anions are rather small in water.

(C) Ion-Association Constants from Competitive Association Experiments

(1) Association with trans-$[Rhen_2Cl_2]^+$

The conclusion that the association constants for the ion pairs $\{Rhen_2LX,Y\}^0$ (L, X, Y = Cl^-, Br^-, I^-) are rather small is reinforced by the results given in Table 3.23 for the effect of an added anion, Y^{n-}, on the spectroscopic interaction between trans-$[Rhen_2Cl_2]^+$ and I^-. In the presence of Y^{n-}, the equilibrium

$$[Rhen_2Cl_2]^+ + Y^{n-} \overset{K_Y}{\rightleftharpoons} \{Rhen_2Cl_2,Y\}^{(1-n)+} \qquad (3.95)$$

obtains as well as equation 3.88, and equation 3.96 is replaced by equation 3.97.

$$\epsilon_{app} = \frac{\epsilon_0 + \epsilon_I K_I[I^-]}{1 + K_I[I^-]} \qquad (3.96)$$

$$\epsilon_{app} = \frac{\epsilon_0(1 + K_Y[Y]) + \epsilon_I K_I[I^-]}{1 + K_Y[Y] + K_I[I^-]} \qquad (3.97)$$

(It is assumed in equation 3.97 that the extinction coefficient of the $\{Rhen_2Cl_2,Y\}^{(1-n)+}$ ion-pair is the same as that of free $[Rhen_2Cl_2]^+$; even for the bromide ion-pair, where a slight spectroscopic interaction occurs (Table 3.22), this seems to be true to a first approximation.) Adding Y^{n-} affects ϵ_{app} in two ways; it changes K_{Cl} because it increases the ionic strength and thereby alters γ, and it decreases ϵ_{app} because of the term $K_Y[Y]$ in the denominator of equation 3.97. Table 3.23 shows that ϵ_{app} is in fact little affected by the addition of even relatively large amounts of Y. This indicates that γ is little changed by the increasing ionic strength, probably because the activity coefficient of pure unassociated $[Rhen_2Cl_2]I$ decreases with increasing ionic strength, I (Fig. 3.19), whereas that of pure unassociated NaI increases with increasing I (Fig. 3.18). The fact that ϵ_{app} is essentially unaffected by the presence of Y^{n-} also means that at the ionic strength of the experiment

$$K_Y[Y] \ll 1 + K_I[I] \qquad (3.98)$$

Since K_I apparently has the same value in the solution of sodium iodide plus Na_nY as in sodium iodide alone, and the value of K_I in 0.5M sodium iodide is 0.19 M^{-1} from equation 3.81 (assuming $K_I^0 = 0.38$ ~~1.2~~ M^{-1}) it follows that

$$K_Y[Y] \ll 1.19 \qquad (3.99)$$

It is possible to assign more definite limits to the value of K_Y if it is further assumed that the minimum lowering of ϵ_{app} which can be detected and unambiguously assigned to ion-association by Y^{n-} is 10% of the original value of ϵ_{app}. This treatment gives the upper limits listed for K_Y in Table 3.29. Table 3.29 also gives upper limits for the values of K_Y^0, the ion-association constants at zero ionic strength: these were calculated from the limits found at the ionic strength of the competition experiments, using equations 3.81 and 3.84. Equations 3.81 and 3.84 were also used to calculate K_Y at I = 1.0M, the ionic strength used in most of the kinetic runs; these values are also given in Table 3.29. The results in Table 3.29 can be summarised by saying that the ion-association constants at zero ionic strength (K_Y^0) are quite consistent with the Fuoss equation, and that at the ionic strength of 1.0M used for most of the experiments reported here, K_Y for <u>trans</u>-$[Rhen_2Cl_2]^+$ is rather small.

(2) Association with <u>trans</u>-$[Rhen_2I_2]^+$

Because the ionic strength was kept constant with sodium perchlorate, the results for the spectroscopic interaction between <u>trans</u>-$[Rhen_2I_2]^+$ and iodide in the presence of other anions (Table 3.24) give no information about the absolute values of K_Y for this complex. Nevertheless, with the exception of hydroxide, the effect of the added anions is little different from that of perchlorate at the constant ionic strength of 1.5M. Thus at this ionic strength, the ion-association constants are all similar to that for perchlorate. The large effect of hydroxide may be connected with the ease of aquation of <u>trans</u>-$[Rhen_2I_2]^+$ and the presence of iodoaquo-

complexes in the solution: the effect of hydroxide is in no way unusual in the trans-$[Rhen_2Cl_2]^+/I^-$ interaction. Since the sizes and charge-distributions are probably similar in trans-$[Rhen_2Cl_2]^+$ and trans-$[Rhen_2I_2]^+$, the results found for the former complex can probably be extended to the latter, i.e., values of K_Y are small at 1.0M ionic strength.

(D) Ion-Association with Perchlorate

The question of ion-association involving perchlorate is controversial. Many authors have assumed that because perchlorate does not readily form inner-sphere complexes,[103] it is equally inert towards the formation of outer sphere complexes. To a certain extent there is a theoretical justification for this view. If as a first approximation the crystal field theory is assumed to obtain, the sole binding force in the inner sphere is electrostatic and the free energy ΔG^0_{is} for the process

$$[ML_5OH_2]^{m+} + Y^{n-} \longrightarrow [ML_5Y]^{(m-n)+} + H_2O \qquad (3.100)$$

is given by the equation

$$\Delta G^0_{is} = \Delta G^0_{es} + \Delta G^0_{solv} - G^0_{H_2O} \qquad (3.101)$$

where ΔG^0_{es} is the free energy due to the electrostatic attraction between ML_5 and Y^-, $G^0_{H_2O}$ is the free energy due to attraction between ML_5 and H_2O and ΔG^0_{solv} is the free energy change association with change in solvation of $[ML_5OH_2]^{m+}$ and Y^{n-}. In outer-sphere complexation an equation exactly corresponding to equation 3.101 can be written for ΔG^0_{os}, the free energy of formation of the outer sphere complex; although the absolute sizes of the terms in equation 3.101 will differ in the two cases (probably being smaller for outer sphere complexation), for a given pair of ions their

relative magnitudes may well remain the same. Thus if, as with perchlorate, G^0_{is} is large and positive, G^0_{os} may also be fairly large and positive. Recently, however, several authors[93][104][105] have queried this view.

The results given here do not shed much light on the value of K_{ClO_4}. It appears that the rates of substitution in trans-$[Rhen_2Cl_2]^+$, trans-$[Rhen_2I_2]^+$ and trans-$[Rhen_2IOH]^+$ are independent of the concentration of perchlorate, under conditions where second order reactions with other anions are not occurring (see Tables 3.5, 3.13 and 3.2). This suggests that for these complexes either K_{ClO_4} is zero, or the reactivity of the perchlorate ion-pair is identical with that of the free ion.

An attempt was made to calculate $K^0_{ClO_4}$ for trans-$[Rhen_2I_2]^+$ by using the data at I = 1.0M and 55.0°C for the reaction

$$\text{trans-}[Rhen_2I_2]^+ + Cl^- \longrightarrow \text{trans-}[Rhen_2ICl]^+ + I^- \qquad (3.19)$$

From equation 3.78 and knowing that

$$k_{ClO_4} = k_0 \qquad (3.102)$$

we obtain

$$K_{ClO_4} = \frac{1}{1 - [Cl^-]} \left\{ \frac{K_{Cl}[Cl^-](k_{Cl}-k_{obsd})}{(k_{obsd}-k_0)} - 1 \right\} \qquad (3.103)$$

The experiments at 55.0°C in the absence of perchlorate gave k_0 = 2.310×10^{-4} s^{-1}, $k_{Cl} = 3.313 \times 10^{-4}$ s^{-1} and $K^0_{Cl} = 1.2 \pm 1.2$ M^{-1}. Using equations 3.81 and 3.84, K_{Cl} at 1.0M ionic strength is 0.76 ± 0.89 M^{-1}. The values found for $K^0_{ClO_4}$ using equation 3.103 are given in Table 3.30: the points at 0.100 and 0.300M chloride were ignored since the values of k_{obsd} were very close to the value for k_0. Even at $[Cl^-]$ = 0.550 and

0.800M, the errors of the estimates of $K^0_{ClO_4}$ must be at least as large as the estimates themselves. However, the values obtained are not significantly different from those for other univalent anions, and if $K^0_{ClO_4}$ is not zero, it is at least not very large.

The uncertainty about the magnitude of association constants for perchlorate ion-pairs extends to work on similar systems. Nyman and Plane[106] studied the association

$$[Pten_3]^{4+} + Cl^- \rightleftharpoons \{Pten_3,Cl\}^{3+} \qquad (3.104)$$

spectrophotometrically, and showed that at a constant ionic strength of 0.5M, replacement of Cl^- by ClO_4^- increased, rather than decreased the apparent association constant. This suggests that variation of K_{Cl} for equilibrium 3.104 occurs due to changes in the activity coefficients of the participating species, and that at an ionic strength of 0.5M, K_{ClO_4} is very small. Mironov et al.[107] feel that perchlorate is only capable of forming solvent-separated ion-pairs with the corresponding complex $[Coen_3]^{3+}$, although no experimental evidence is advanced for this viewpoint. On the other hand, Johansson[108] has claimed that a weak complex between $[Coen_3]^{3+}$ and ClO_4^- does exist, and from conductance data Burnett[93] has calculated that the ion association constant at zero ionic strength is 28 M^{-1}. Conductivity studies have also indicated that $K^0_{ClO_4}$ for $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5Cl]^{2+}$ is 25 M^{-1}[109] and 14 M^{-1}[110] respectively. Although the controversy[111]-[113] about whether or not different methods of measuring association constants should give the same value for K_Y obscures the interpretation of this evidence, it appears that at the very least the ion-association constants involving perchlorate are not greater than those involving other univalent anions, and they may well be

much less.

(E) The Relative Reactivities of Ion-Pairs and Assignment of the Mechanism Using Kinetic Results at Constant Ionic Strength

For all the reactions studied the rate law at constant ionic strength was

$$k_{obsd} = k_1 + k_2[Y] \qquad (3.105)$$

This may be because at all concentrations of Y^{n-} studied the term $(K_{ClO_4}[ClO_4^-] + K_Y[Y])$ in the denominator of equation 3.77 was a constant. Alternatively, if, as found for the analogous cobalt(III) and chromium(III) complexes, the reactivities of the ion-pairs are not very different from the reactivity of the free complex, the curvature of the graph of k_{obsd} against [Y] might not be experimentally detectable.

However, a lower limit for k_Y can be calculated because k_Y can never be less than the highest value of k_{obsd} obtained, so

$$k_Y \geq k_1 + k_2[Y]_{max} \qquad (3.106)$$

where $[Y]_{max}$ is the highest concentration of Y^{n-} used. If the term $(K_Y - mK_{ClO_4})[Y]$ in the denominator of equations 3.78 (m = 1), 3.79 (m = 3) and 3.80 (m = 6) is not negligible compared to unity, the points of the graph of k_{obsd} against [Y] will define a curve which is slightly convex upwards, and a straight line drawn through these points will give an intercept, k_1, which is greater than k_0 and a slope, k_2, which is less than $k_Y K_Y$. From the inequalities 3.107

$$k_0 \leq k_1 \tag{3.107}$$

and 3.106 it follows that

$$\frac{k_Y}{k_0} \geq \frac{k_1 + k_2[Y]_{max}}{k_1} \tag{3.108}$$

The limits obtained for the relative reactivities of the ion-pairs and the free ions are given in Table 3.31 for all the reactions studied.

The limits of Table 3.31 give no information about the reactivity of the ion-pair of one anion, Y^{n-}, compared to that of another anion, Z^{P-}. However, it is possible to estimate such relative reactivities if it is assumed that at an ionic strength of 1.0M the association constants of the ion-pair $\{\underline{trans}\text{-}[Rhen_2LX],Y\}^{(1-n)+}$ are independent of the charge on the anion, Y^{n-}. (Calculations using the theoretical ion-association constants given by the Fuoss equation and the Davies equation to predict the variation of activity coefficients with ionic strength suggest that this is indeed true. Q.v. Table 3.32, column three.) In this case, the effect of the term $(K_{ClO_4}[ClO_4] + K_Y[Y])$ in the denominator of equation 3.77 in causing curvature of the graph of k_{obsd} against [Y] will be similar for all anions Y^{n-}, and the relative values of k_2/k_1 will reflect the relative values of $k_Y K_Y/k_0$. For a given cation, $\underline{trans}\text{-}[Rhen_2LX]^+$, both K_Y and k_0 are constant, so k_2/k_1 becomes a measure of k_Y, the relative nucleophilicity of the anion Y^{n-}. Values of k_2/k_1 are listed in Table 3.33.

From the results given in Tables 3.31 and 3.33 the intimate nature of the mechanism can be assigned. Poë et al.[114][115] and Monacelli and Viel[116][117] have tentatively suggested that the bromide anation of $[Rh(NH_3)_5OH_2]^{3+}$ is I$\underline{a}$, because the rate of interchange within the $\{Rh(NH_3)_5OH_2,Br\}^{2+}$ ion-pair is twice as fast as the rate of water exchange

in the free ion. They made the assumption that the location of the bromide ion in the second co-ordination sphere of $[Rh(NH_3)_5OH_2]^{2+}$ was completely random; in this case loss of water results in detectable reaction for only ca. 20% of the exchanges, and interchange within the ion-pair becomes effectively ten times faster than water exchange. Poë et al.[115] have admitted that if the bromide ion is specifically located adjacent to the leaving group, so that all exchanges were fruitful, the evidence for an Ia mechanism was less conclusive.

In the present work the lower limits found (Table 3.31) for k_Y/k_0 show that the ion-pair is not necessarily even twice as reactive as the free ion. Moreover, in order to demonstrate nucleophilic assistance by Y^{n-}, a higher value of k_Y/k_0 would be required for the reaction of trans-$[Rhen_2LX]^+$ than for the reaction of $[Rh(NH_3)_5OH_2]^{3+}$. This is because even with an Id mechanism, the rate enhancement due to electrostatic repulsion between Y^{n-} and the leaving group will be greater when the latter is an anionic ligand than when it is a neutral molecule. The results in Table 3.31 thus offer no positive support for an Ia mechanism for trans-$[Rhen_2LX]^+$.

The variation of reactivities amongst the ion-pairs (Table 3.33) also fails to support an associative mode of activation for the bis-ethylenediamine-complexes. For anions of the same charge (F^-, Cl^-, Br^-) there is little variation in reactivity, in spite of the fact that the nucleophilicities of these anions towards platinum(II) vary very greatly.[134] The reactivity of the ion-pair seems to correlate with the charge on the anion, but even for the ion-pairs $\{trans\text{-}[Rhen_2Cl_2],PO_4\}^{2-}$ and $\{trans\text{-}[Rhen_2I_2],PO_4\}^{2-}$, k_2/k_1 is only 19 and 5.4 times greater than k_2/k_1 for the corresponding bromide ion-pairs. These relative reactivities may

still include a contribution from the larger association constant for the trivalent ion, if K_{PO_4} is not as susceptible to the ionic strength as the data of Table 3.32 suggest. These relative reactivities are consistent with an I*d* mechanism where a greater negative charge on the anion, Y^{n-}, leads to increased repulsion between Y^{n-} and the leaving group, and hence a greater reactivity of the ion-pair. All the evidence thus supports the assignment of a dissociative mode of activation to the reactions of *trans*-diacidobisethylenediaminerhodium(III) complexes.

The observation of a possible I*a* mechanism for the anation of $[Rh(NH_3)_5OH_2]^{3+}$ and an I*d* mechanism for the aquation of *trans*-$[Rhen_2X_2]^+$ (X = Cl, I) is consistent with the different charges of the complexes. The lower the positive charge on the substrate, the easier it is for the leaving group to depart without the assistance of bonding to an incoming nucleophile. Rhodium(III) complexes appear to lie very much on the borderline between associative and dissociative activation, the charge on the complex determining the intimate nature of the reaction pathway.

(II) Second-Order Reactions with Hydroxide

The hydroxide-dependent reactions suffer from the same difficulties of interpretation due to possible association of the complex with perchlorate as do the other anion-dependent reactions. If the hydroxide-dependent reactions occur by the S_N1IP mechanism, these difficulties are caused by the fact that an unknown fraction of the substrate is present as perchlorate ion-pairs. If the reactions occur by the S_N1CB mechanism, on the other hand, the acidity of a perchlorate ion-pair is not likely to be the same as that of the free complex. Moreover, if association with perchlorate occurs, the first- and second-order rate constants, k_1 and k_2, for both

the hydroxide- and other anion-dependent reactions will be complex functions of rate constants. As well as making comparison of the rate constants themselves rather difficult, this complicates the interpretation of the activation parameters calculated from the rate constants.

However, for all the reactions studied, the Eyring plots for k_1 and for k_2 were linear within a reasonably small experimental error. It was therefore assumed that even if $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$, $\Delta S_2^{\ddagger}$ did not refer exactly to simple reactions of the free complex and its ion-pair (equations 3.1 to 3.3) or conjugate base (equations 3.1, 3.8 and 3.9), nevertheless the values of these activation parameters were a measure of the relative energetics of these reactions.

(A) The S_N1IP Mechanism

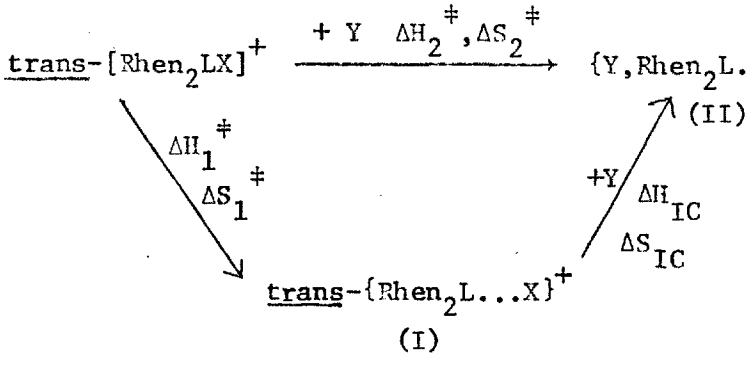
The S_N1IP mechanism assumes that hydroxide behaves simply as a centre of negative charge, and on this model its kinetic behaviour should not differ markedly from that of the other anions studied. In the present work, there were indeed similarities between the hydroxide-dependent reactions of trans-$[Rhen_2LX]^+$ and the reactions involving other anions. Thus Fig. 3.21 shows that the isokinetic plot of $\Delta H_2^{\ddagger}$ against $\Delta S_2^{\ddagger}$ for the reaction

$$\text{trans-}[Rhen_2I_2]^+ + Y^- \longrightarrow \text{trans-}[Rhen_2IY]^+ + I^- \qquad (3.109)$$

where Y = Cl, Br, OH, is linear. Leffler and Grunwald[118] have concluded that, for substituent effects on the rates of organic reactions, a linear plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ means the same mechanism is followed in all the reactions being compared. Apart from the complications introduced by possible ion-pairing with perchlorate, the extension of this conclusion

to reaction 3.109 is dubious, since changing one of the reactants is hardly equivalent to changing a substituent which is remote from the reaction site. Nevertheless, Fig. 3.21 suggests that the mechanism of the hydroxide-dependent reactions is energetically similar to the mechanism of the other anion-dependent reactions.

This point is demonstrated more dramatically in Fig. 3.22 where values of $\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ are plotted against $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ for all the anion-dependent reactions of trans-$[Rhen_2LX]^+$ studied. Within experimental error a straight line can be drawn through all the points, regardless of whether they represent the relative activation parameters for the reactions of a variety of different substrates with a common anion (hydroxide), or of a common substrate (trans-$[Rhen_2I_2]^+$) with several different anions. This pseudo-isokinetic plot can be explained qualitatively by neglecting perchlorate ion-pairing and considering the thermodynamic cycle



(3.110)

Here (I) is the transition state for the first-order (Id) reaction, and (II) is the transition state for the second-order reaction: H_{IC} and S_{IC} are the enthalpy and entropy for interconversion of the two transition states. By the laws of thermodynamics

$$\Delta H_2^{\ddagger} = \Delta H_1^{\ddagger} + \Delta H_{IC} \qquad (3.111)$$

$$\Delta S_2^{\ddagger} = \Delta S_1^{\ddagger} + \Delta S_{IC} \qquad (3.112)$$

ΔH_{IC} and ΔS_{IC} will be functions of the amount of stereochemical rearrangement occurring during the second-order reaction, and also of the desolvation of Y and transition state (I) which is necessary to form (II). If extensive stereochemical rearrangement occurs during the formation of (II), then ΔH_{IC} will become rather highly positive, because energy is required to overcome the crystal field stabilisation effects which oppose distortion of (I); however, because the ligands have greater freedom of movement in (II), ΔS_{IC} will concurrently become large and positive. There is a similar correlation between the effects on ΔH_{IC} and ΔS_{IC} caused by desolvation of Y^{n-}. The greater the desolvation of Y^{n-}, the larger ΔH_{IC} will be, because desolvation involves breaking $HOH...Y^{n-}$ hydrogen bonds; but ΔS_{IC} concurrently becomes more positive because of the increased freedom of the water molecules. The importance of desolvation of Y^{n-} is shown in Fig. 3.23 and Fig. 3.24 where $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ for reaction 3.109 are plotted against the enthalpy and entropy respectively of desolvation[119] of Y^-. The slopes of Fig. 3.23 and Fig. 3.24 are 0.10 ±0.03 and 2.6 ±0.7 respectively, so it appears that the effect of entropy is much more important than that of enthalpy. It is not clear why the slope of the entropy plot should be greater than unity, but this may simply show that other factors such as stereochemical rearrangement are important in determining the value of $\Delta S_2^{\ddagger}$. Indeed, the effects of stereochemical rearrangement and of desolvation of Y^{n-} are not entirely distinct, since ion-association constants are generally greater for cis-complexes than their trans-isomers. The greater the stereochemical rearrangement occurring in the formation of II, the larger will be the ion-pairing constant for association of Y^{n-} with II, and the more extensive will be the desolvation of Y^{n-}.

Although the energetics of the hydroxide-dependent reactions are similar to those of the other anion-dependent reactions of trans-$[Rhen_2LX]^+$, there are differences between the two types of reaction. In general, the hydroxide-dependent pathways are rather faster than those of the other anions. The most important difference, however, is that the hydroxide-dependent pathways sometimes give rise to extensive stereochemical change, whereas the other anion-dependent reactions do not. Although, as shown above, this effect can be included in the rationalisation of the energetics of the S_N1IP process, the S_N1IP mechanism offers no explanation as to why hydroxide should be unique in this respect.

(B) The S_N1CB Mechanism

The S_N1CB mechanism of equations 3.62, 3.63, 3.113 and 3.114 does explain both the relative reactivities of rhodium(III) complexes towards base hydrolysis, and the stereochemical rearrangement which occurs during this reaction.

$$[Rhen_2LX]^+ + OH^- \underset{}{\overset{K_{CB}}{\rightleftharpoons}} [Rhen(en\text{-}H)LX]^0 + H_2O \qquad (3.113)$$

$$[Rhen(en\text{-}H)LX]^0 + H_2O \xrightarrow{k_{CB}} [Rhen_2LOH]^+ + X^- \qquad (3.114)$$

The results obtained in this work for the base hydrolysis of trans-$[Rhen_2LX]^+$ are compared in Table 3.34 with the results for the base hydrolyses of other rhodium(III) complexes. In agreement with the observations of Johnson et al.[57] and of Klabunde,[59] the complexes studied here are much less susceptible to base-catalysis than those which have an amine ligand trans to the leaving group. This difference between the cis- and trans-isomers of trans-$[Rhen_2LX]^+$ has been ascribed to a higher acidity of the

cis-complexes, and also a higher reactivity of the deprotonated intermediate derived from cis-$[Rhen_2LX]^+$.[57][59]

Klabunde[59] has suggested that one reason why cis-$[Rhen_2LX]^+$ is so reactive towards base is that the amido-group can be generated trans to the leaving group, and that the trans-effect of the amido-group is high. This hypothesis can be expanded by considering the nature of the trans-effect in rhodium(III) complexes. Poë et al.[73][76] have shown that in rhodium(III) complexes the trans-effect is transmitted by σ-bonding interactions, so the high trans-effect of NR_2^- is probably a σ-effect, analogous to that of H^-[120] or $C_2H_5^-$.[120] Langford[121] has suggested that in rhodium(III) the σ-trans-effect is transmitted by p-orbitals, a common p-orbital being shared by the trans-ligand and the leaving group. As the leaving group, X, departs, it leaves an empty hybrid orbital on the rhodium(III) centre; a trans amido-group can stabilise the square pyramidal transition state by acquiring a larger share of the p-orbital common to the Rh-NHR and Rh-X bonds (see Fig. 3.25a). In a square pyramidal transition state this cannot happen if the amido-group is cis to X, because NHR^- and X no longer share a common p-orbital (Fig. 3.25b). However, if rearrangement to a trigonal bipyramidal transition state occurs, then the amido-group will obtain a share in the p-orbital originally shared by X and L, and will therefore be able to stabilise the transition state (Fig. 3.25c). Since statistical addition of water to a trigonal bipyramidal transition state gives two-thirds cis-$[Rhen_2LOH]^+$ as product, the hypothesis that the amido-group has a high sigma-trans-effect which is transmitted via the rhodium p-orbitals predicts that trans-$[Rhen_2LX]^+$ may rearrange during base hydrolysis, but cis-$[Rhen_2LX]^+$ will not. This is exactly the situation found in practice.

The production of a trigonal bipyramidal transition state from trans-$[Rhen_2LX]^+$ requires more energy than the formation of a square pyramidal transition state because the loss of crystal field stabilisation energy is greater for the first case.[122] Table 3.35 shows the relative activation parameters, $\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ and $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$, for the base hydrolyses of several rhodium(III) complexes. For the trans-diacido-complexes, reactions which occur with stereochemical change have $\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ = 8.10 ±1.1 kcal mol^{-1} and $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ = 23 ±4 eu; for reactions which are stereoretentive, $\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ = 0 ±1.5 kcal mol^{-1} and $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ = 1 ±4 eu. Thus rearrangement involves a sizeable increase in the relative enthalpy of activation, in agreement with the predictions of crystal field theory. The large, positive values of $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ found for the reactions which occur with stereochemical change agree with Tobe's correlation[133] of positive entropies of activation with stereomobility, and suggest that an appreciable amount of the molecular motion necessary for rearrangement has occurred by the time the transition state is formed. This correlation does not extend to the cis-diacido-complexes, where $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ = ca. 22 kcal mol^{-1}, and the reactions occur with retention of configuration. However, the relative enthalpies of activation are significantly lower (2.2 ±1.6 kcal mol^{-1}) than for the trans-complexes, indicating again the effect that stereochemical rearrangement has on the crystal field of activation. Finally, the data for the pentammine complexes cannot be compared directly with the results for the ethylenediamine complexes, because the charge on the complex, and hence the effect of solvation, is different in the two cases. The high values of $\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ and very positive values of $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ probably reflect the extensive desolvation which occurs on converting the transition state $\{Rh(NH_3)_5...X\}^{2+}$ to $\{Rh(NH_3)_4NH_2...X\}^{+}$.

(C) The S_N1CB/S_N1IP Spectrum

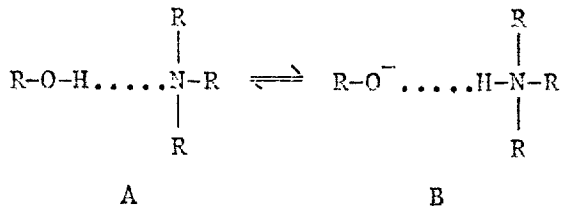
It appears from the above evidence that the details of the hydroxide-dependent reactions of trans-$[Rhen_2LX]^+$ are best explained by the S_N1CB mechanism, although the energetics of this reaction are very similar to those predicted by the S_N1IP mechanism. Chan and Lau[123] have suggested that there is a conjugate base/ion-pair spectrum for the interaction of metal amine complexes with hydroxide. The N...H...OH system is assumed to be linked by hydrogen bonds; if the proton is closer to the nitrogen atom, the species is an hydroxide ion-pair: if the proton is closer to the OH^- ion, the species is a conjugate base. Chan and Lau envisaged species intermediate between the ion-pair and the conjugate base where the proton was equidistant from the nitrogen atom and the hydroxide ion. It is possible that such a species is responsible for the hydroxide-dependent pathway for substitution of trans-$[Rhen_2LX]^+$. However, Navon et al.[33] detected both $\{Coen_3,OH\}^{2+}$ and $[Coen_2(en\text{-}H)]^{2+}$ in very basic solutions of $[Coen_3]^{3+}$; the equilibrium constants for reactions 3.115 and 3.116 are 29 M^{-1} and 0.7 M^{-1} respectively.

$$[Coen_3]^{3+} + OH^- \overset{K_{OH}}{\rightleftharpoons} \{Coen_3,OH\}^{2+} \qquad (3.115)$$

$$[Coen_3]^{3+} + OH^- \overset{K_{CB}}{\rightleftharpoons} [Coen_2(en\text{-}H)]^{2+} + H_2O \qquad (3.116)$$

This suggests that for the aggregate $\{L_5MNR_2H...OH\}^{n+}$ a single energy minimum at a unique N-H distance does not occur: instead there are two energy minima, corresponding to two distinct species, with a fairly large activation energy governing their interconversion. As the nitrogen atom of the co-ordinated amine becomes less basic, the proportion of the conjugate base increases because the potential well of this species deepens relative to that of the ion-pair, but the equilibrium N-H and O-H distances

of the ion-pair and conjugate base do not change. A similar situation has been found[124] for the equilibrium between the hydrogen-bonded (A) and proton-transfer (B) complexes of phenols and amines.



(3.117)

A B

However, single-minima complexes are sometimes formed for the adducts of substituted benzoic acids and substituted pyridines, when the difference between the pK_a values of the acid and the pyridine is close to the critical difference necessary for proton-transfer to occur.[125] It may be that the basicity of ethylenediamine in trans-$[Rhen_2LX]^+$ is sufficiently close to the critical value for the proton-transfer reaction

$$\{Rhen_2LX,OH\}^0 \rightleftharpoons \{Rhen(en\text{-}H)LX,H_2O\}^0 \qquad (3.118)$$

that a single complex, intermediate between the ion-pair and the conjugate base is produced.

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Table 3.1

Relative rates of substitution of ion-pairs $\{MA_4LX,Y\}^{(m-n)+}$ and free ions $[MA_4LX]^{m+}$ of cobalt(III) and chromium(III) complexes

complex	Y^{n-}	solvent	k_Y/k_0	reference
$[Co(NH_3)_5Cl]^{2+}$	SO_4^{2-}	H_2O	1.95	127
	malonate	H_2O	2.0	127
	tartarate	H_2O	2.25	127
	phthalate	H_2O	2.85	127
	maleate	H_2O	3.05	127
	NO_3^-	H_2O	1.1	128
	glycollate	H_2O	1.15	128
$[Co(NH_3)_5Br]^{2+}$	SO_4^{2-}	H_2O	2.25	127
	malonate	H_2O	2.0	127
	tartarate	H_2O	2.55	127
	phthalate	H_2O	2.8	127
	maleate	H_2O	2.75	127
$[Co(NH_3)_5I]^{2+}$	SO_4^{2-}	H_2O	2.1	127
	malonate	H_2O	2.1	127
	tartarate	H_2O	2.2	127
	phthalate	H_2O	3.0	127
	maleate	H_2O	3.1	127
$[Cr(NH_3)_5Cl]^{2+}$	SO_4^{2-}	H_2O	1.6	4
	malonate	H_2O	2.5	4
	tartarate	H_2O	2.3	4
	phthalate	H_2O	2.25	4
	NO_3^-	H_2O	1.1	4

(cont.)

Table 3.1 (cont.)

complex	Y^{n-}	solvent	k_Y/k_0	reference
cis-$[Coen_2Cl_2]^+$	SO_4^{2-}	H_2O	1.14	129
cis-$[Coen_2Cl_2]^+$	N_3^-	MeOH	5.0	130
	$CH_3CO_2^-$	MeOH	3.0	130
	Cl^-	MeOH	2.25	131
cis-$[Coen_2Br_2]^+$	Br^-	DMSO	0.7	132
trans-$[Coen_2Br_2]^+$	Br^-	DMSO	1.3	132
cis-$[Cren_2Br_2]^+$	Br^-	DMSO	0.8	9
cis-$[Cren_2BrDMSO]^{2+}$	Br^-	DMSO	0.67	9
trans-$[Cren_2Br_2]^+$	Br^-	DMSO	1.0	9
trans-$[Cren_2BrDMSO]^{2+}$	Br^-	DMSO	1.0	9

Table 3.2

Kinetic data for the reaction of trans-$[Rhen_2IOH]^+$ with OH^-

$[cmx] = 2.7 \times 10^{-4}$M I = 1.00M

Temperature (°C)	$[OH^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
81.0	1.00	95.4
	0.900	84.8
	0.800	84.2
	0.700	75.8
	0.600	78.5
	0.500	76.2
	0.400	77.7
	0.300	72.7
	0.200	69.8
	0.100	62.6
	0.0100	65.8, 62.0, 61.2, 61.7, 61.3
75.7	1.00	53.5, 53.8
	0.900	48.3
	0.800	46.2
	0.700	47.0
	0.600	44.4
	0.500	42.5
	0.400	42.9, 38.9
	0.300	39.5
	0.200	38.0
	0.100	36.2
	0.0100	34.1, 34.0, 34.1

(cont.)

Table 3.2 (cont.)

Temperature (°C)	$[OH^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
70.3	1.00	29.1
	0.900	27.1
	0.800	25.2
	0.700	23.3
	0.600	23.4
	0.500	22.2
	0.400	21.0
	0.300	20.6
	0.200	19.0
	0.100	18.9, 19.6
	0.0100	19.0
65.5	1.00	15.9
	0.900	13.0
	0.800	13.8
	0.700	13.2
	0.600	13.1
	0.500	12.9
	0.400	11.8
	0.300	11.7
	0.200	11.3
	0.100	10.0
	0.0100	10.5, 10.6

(cont.)

Table 3.2 (cont.)

Temperature (°C)	$[OH^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
60.9	1.00	8.32
	0.900	7.51
	0.800	7.67
	0.700	7.19
	0.600	7.04
	0.500	7.05
	0.400	6.56
	0.300	6.06
	0.200	6.23
	0.100	5.97
	0.0100	5.33, 5.80
55.4	1.00	3.82
	0.900	3.37
	0.800	3.52
	0.700	3.34
	0.600	3.31
	0.500	3.07
	0.400	3.07
	0.300	3.00
	0.200	2.80
	0.100	2.71
	0.0100	2.63, 2.62, 2.64

(cont.)

Table 3.2 (cont.)

Temperature (°C)	$10^5 k_1$ (s^{-1})	$10^5 k_2$ ($M^{-1} s^{-1}$)
81.0	62.18 ±0.89	27.76 ±2.08
75.7	33.95 ±0.57	17.77 ±1.17
70.3	17.99 ±0.37	9.224 ±0.762
65.6	10.26 ±0.20	4.359 ±0.397
60.9	5.573 ±0.108	2.484 ±0.216
55.4	2.619 ±0.045	1.051 ±0.094

Standard deviation of k_{obsd} = 3.7%

$\Delta H_1^{\ddagger}$ = 27.81 ±0.18 kcal mol^{-1}

$\Delta S_1^{\ddagger}$ = 5.01 ±0.52 e.u.

$\Delta H_2^{\ddagger}$ = 29.34 ±0.85 kcal mol^{-1}

$\Delta S_2^{\ddagger}$ = 7.93 ±2.48 e.u.

Experiments at varying concentrations of perchlorate

$[ClO_4^-]$ (M)	$[OH^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
0.200	0.02	16.4, 16.8
1.00	0.02	16.5, 16.6

Temperature = 69°C [cmx] = 2.8×10^{-4}M

Table 3.3

Kinetic data for the reaction of trans-$[Rhen_2BrOH]^+$ with OH^-

[cmx] = 1.3×10^{-3}M I = 1.00M

Temperature (°C)	$[OH^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
78.94	0.8301	171.4
	0.6301	164.7
	0.4301	160.0
	0.2301	149.1
	0.0301	142.9
69.72	0.8301	65.80
	0.6301	62.87
	0.4301	58.87
	0.2301	53.21
	0.0301	53.16
63.38	0.8301	31.97
	0.6301	28.84
	0.4301	27.70
	0.2301	26.14
	0.0301	25.35
56.51	0.8301	13.60
	0.6301	12.62
	0.4301	11.89
	0.2301	11.15
	0.0301	10.93

(cont.)

Table 3.3 (cont.)

Temperature (°C)	$[OH^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
50.06	0.8301	6.019
	0.6301	5.684
	0.4301	5.374
	0.2301	4.975
	0.0301	4.855

Temperature (°C)	$10^5 k_1$ (s^{-1})	$10^5 k_2$ ($M^{-1}\ s^{-1}$)
78.94	141.9 ±2.7	36.52 ±5.62
69.72	51.28 ±1.00	17.32 ±2.12
63.38	24.66 ±0.48	7.698 ±1.015
56.51	10.60 ±0.21	3.326 ±0.436
50.06	4.734 ±0.092	1.502 ±0.194

Standard deviation of k_{obsd} = 2.3%

$\Delta H_1^{\ddagger}$ = 25.99 ±0.19 kcal mol^{-1}

$\Delta S_1^{\ddagger}$ = 1.91 ±0.57 e.u.

$\Delta H_2^{\ddagger}$ = 25.08 ±1.30 kcal mol^{-1}

$\Delta S_2^{\ddagger}$ = -3.11 ±3.88 e.u.

Table 3.4

Kinetic data for the reaction of trans-$[Rhen_2ClOH]^+$ with OH^-

[cmx] = 3×10^{-3}M I = 1.00M

Temperature (°C)	$[OH^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
75.76	0.8332	118.8
	0.6332	113.2
	0.4332	106.8
	0.2332	98.68
	0.0332	107.9
71.80	0.8332	80.97
	0.6332	77.11
	0.4332	73.21
	0.2332	65.54
	0.0332	68.28
64.80	0.8332	37.93
	0.6332	36.86
	0.4332	34.17
	0.2332	31.01
	0.0332	34.05
58.02	0.8332	16.66
	0.6332	15.90
	0.4332	14.96
	0.2332	14.28
	0.0332	14.66

(cont.)

Table 3.4 (cont.)

Temperature (°C)	$[OH^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
53.77	0.8332	9.763
	0.6332	9.495
	0.4332	8.982
	0.2332	8.181
	0.0332	8.902
49.89	0.8332	6.224
	0.6332	5.852
	0.4332	5.471
	0.2332	5.107
	0.0332	5.837
45.50	0.8332	3.518
	0.6332	3.277
	0.4332	3.123
	0.2332	2.913
	0.0332	3.041

Assuming that $[OH^-] \geq 0.2332M$ the rate law is $k_{obsd} = k_1 + k_2[OH^-]$

(cont.)

Table 3.4 (cont.)

Temperature (°C)	$10^5 k_1$ (s^{-1})		$10^5 k_2$ ($M^{-1} s^{-1}$)	
75.75	91.40	±1.75	33.70	±3.18
71.80	60.49	±1.17	25.68	±2.14
64.80	28.59	±0.55	11.98	±1.01
58.02	13.30	±0.25	4.031	±0.452
53.77	7.667	±0.145	2.692	±0.263
49.89	4.669	±0.090	1.865	±0.165
45.50	2.685	±0.052	0.9807	±0.094

Standard deviation in k_{obsd} = 1.3%

$\Delta H_1^{\ddagger}$ = 25.14 ±0.15 kcal mol^{-1}

$\Delta S_1^{\ddagger}$ = -0.67 ±0.46 e.u.

$\Delta H_2^{\ddagger}$ = 25.84 ±0.70 kcal mol^{-1}

$\Delta S_2^{\ddagger}$ = -0.49 ±2.10 e.u.

Assuming that k_{obsd} at $[OH^-]$ = 0.0332M equals k_1

$\Delta H_1^{\ddagger}$ = 25.08 ±0.44 kcal mol^{-1}

$\Delta S_1^{\ddagger}$ = -0.56 ±1.33 e.u.

Standard deviation in k_{obsd} = 5.7%

Table 3.5

Kinetic data for the reaction of trans-$[Rhen_2Cl_2]^+$ with OH^-

$[cmx] = 5.5 \times 10^{-4}M$ $I = 1.00M$

Temperature (°C)	$[OH^-]$ (M)	$10^6 k_{obsd}$ (s^{-1})
77.70	1.00	76.17
	0.800	62.22
	0.550	51.58
	0.200	39.60
	0.010	33.12
74.62	1.00	50.07
	0.750	41.75
	0.500	36.67
	0.250	29.20
	0.010	23.92
71.74	1.00	34.15
	0.750	29.43
	0.500	23.17
	0.250	19.34
	0.010	17.02
67.95	1.00	22.47
	0.750	18.61
	0.500	15.53
	0.250	13.67
	0.010	11.91

(cont.)

Table 3.5 (cont.)

Temperature (°C)	$[OH^-]$ (M)	$10^6 k_{obsd}$ (s^{-1})
64.86	1.00	13.26
	0.750	11.03
	0.500	9.610
	0.250	8.181
	0.010	7.358
64.33	1.00	13.36
	0.750	11.73
	0.500	9.731
	0.250	8.736
	0.010	8.083
62.21	1.00	9.458
	0.750	8.247
	0.500	7.039
	0.250	6.108
	0.010	5.549

Temperature (°C)	$10^6 k_1$ (s^{-1})	$10^6 k_2$ (M^{-1} s^{-1})
77.70	32.12 ±1.28	40.31 ±2.91
74.62	23.38 ±0.79	25.70 ±2.07
71.74	16.04 ±0.67	16.83 ±1.44
67.95	11.43 ±0.46	9.843 ±0.963
64.86	7.047 ±0.284	5.595 ±0.570
64.33	7.696 ±0.308	5.165 ±0.611
62.21	5.330 ±0.213	3.853 ±0.427

(cont.)

Table 3.5 (cont.)

Standard deviation of k_{obsd} = 4.6%

$\Delta H_1^{\ddagger}$ = 26.06 ±0.63 kcal mol^{-1}

$\Delta S_1^{\ddagger}$ = -5.14 ±1.84 e.u.

$\Delta H_2^{\ddagger}$ = 35.07 ±1.42 kcal mol^{-1}

$\Delta S_2^{\ddagger}$ = 21.00 ±4.14 e.u.

Experiments at varying perchlorate concentrations

[cmx] = 5.3×10^{-4}M Temperature = 80.36°C

$[ClO_4^-]$ (M)	$[OH^-]$ (M)	$10^6 k_{obsd}$ (s^{-1})
0.906	0.0100	40.65
0.604	0.0100	42.07
0.302	0.0100	41.95
0.000	0.0100	41.69

Table 3.6

Kinetic data for the reaction of trans-$[Rhen_2Br_2]^+$ with OH^-

[cmx] = 1.2×10^{-4}M I = 1.00M

Temperature (°C)	$[OH^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
80.2	1.00	51.4
	0.900	47.1
	0.800	40.8
	0.700	37.1
	0.600	35.1
	0.500	30.8
	0.400	27.2
	0.300	26.0
	0.200	22.6
	0.100	19.7
	0.0100	18.3, 17.9, 17.3
75.2	1.00	27.0
	0.900	23.9
	0.800	21.9
	0.700	20.2
	0.600	17.8
	0.500	16.4
	0.400	15.0
	0.300	13.1
	0.200	12.0
	0.100	10.9
	0.0100	9.86

(cont.)

Table 3.6 (cont.)

Temperature	$[OH^-]$	$10^5 k_{obsd}$
70.0	1.00	13.1
	0.900	12.4
	0.800	11.3
	0.700	10.5
	0.600	9.52
	0.500	8.72
	0.400	8.15
	0.300	7.53
	0.200	6.84
	0.100	6.08
	0.0100	5.86
64.8	1.00	6.67
	0.900	6.24
	0.800	5.55
	0.700	5.24
	0.600	4.89
	0.500	4.48
	0.400	4.06
	0.300	3.80
	0.200	3.55
	0.100	3.31
	0.0100	3.12, 3.24

(cont.)

Table 3.6 (cont.)

Temperature	$[OH^-]$	$10^5 k_{obsd}$
60.4	1.00	3.48
	0.900	3.48
	0.800	3.09
	0.700	3.03
	0.600	2.77
	0.500	2.52
	0.400	2.46
	0.300	2.32
	0.200	2.08
	0.100	1.97
	0.0100	1.83, 1.84

Temperature (°C)	$10^5 k_1$ (s^{-1})	$10^5 k_2$ ($M^{-1} s^{-1}$)
80.2	17.07 ±0.36	30.13 ±1.03
75.2	9.136 ±0.270	15.67 ±0.64
70.0	5.466 ±0.150	7.183 ±0.343
64.8	3.001 ±0.069	3.238 ±0.162
60.4	1.794 ±0.040	1.683 ±0.091

Standard deviation of k_{obsd} = 4.0%

$\Delta H_1^{\ddagger}$ = 25.78 ±0.33 kcal mol^{-1}

$\Delta S_1^{\ddagger}$ = -3.21 ±0.96 e.u.

$\Delta H_2^{\ddagger}$ = 33.65 ±0.64 kcal mol^{-1}

$\Delta S_2^{\ddagger}$ = 20.26 ±1.84 e.u.

Table 3.7

Kinetic data for the reaction of trans-$[Rhen_2I_2]^+$ with OH^-

[cmx] = 6×10^{-5}M I = 1.00M

Temperature (°C)	$[OH^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
65.06	1.00	100.5
	0.750	89.02
	0.500	80.26
	0.250	71.32
	0.010	67.11
59.60	1.00	56.99
	0.750	51.95
	0.500	47.18
	0.250	42.44
	0.010	39.05
55.07	1.00	31.74
	0.750	28.76
	0.500	26.28
	0.250	24.28
	0.010	22.65
50.18	1.00	17.12
	0.750	15.83
	0.500	14.68
	0.250	13.65
	0.010	12.80

(cont.)

Table 3.7 (cont.)

Temperature	$[OH^-]$	$10^5 k_{obsd}$
45.96	1.00	9.745
	0.750	9.272
	0.500	8.383
	0.250	8.071
	0.010	7.523
41.10	1.00	5.065
	0.750	4.714
	0.500	4.494
	0.250	4.290
	0.010	4.078
36.35	1.00	2.416
	0.750	2.432
	0.500	2.298
	0.250	2.222
	0.010	2.100

Temperature (°C)	$10^5 k_1$ (s^{-1})		$10^5 k_2$ ($M^{-1} s^{-1}$)	
65.05	64.97	±1.00	33.00	±1.90
59.60	38.43	±0.58	18.08	±1.10
55.07	22.24	±0.34	8.939	±0.622
50.18	12.65	±0.19	4.312	±0.343
45.96	7.464	±0.111	2.254	±0.199
41.10	4.048	±0.060	0.9549	±0.1051
36.35	2.120	±0.031	0.3437	±0.0525

(cont.)

Table 3.7 (cont.)

Standard deviation of k_{obsd} = 1.8%

$\Delta H_1^{\ddagger}$ = 24.33 ±0.12 kcal mol^{-1}

$\Delta S_1^{\ddagger}$ = -1.35 ±0.38 e.u.

$\Delta H_2^{\ddagger}$ = 31.18 ±0.71 kcal mol^{-1}

$\Delta S_2^{\ddagger}$ = 17.66 ±2.16 e.u.

Table 3.8

Spectroscopic data for the dihydroxy-products of base hydrolysis of trans-$[Rhen_2LX]^+$

L	X	$[OH^-]$ (M)	Temperature (°C)	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})
OH	I	1.00	80.0	297, 347	133, 102
OH	I	0.100	80.0	297, 348	133, 100
OH	Br	0.732	80.13	296, 346	128, 97.7
OH	Br	0.065	80.13	297, 346	129, 97.0
OH	Cl	0.734	80.16	297, 346	131, 99.0
OH	Cl	0.067	80.16	298, 347	130, 96.6
Cl	Cl	1.00	80.58	287, 336	149, 142
Cl	Cl	0.100	80.58	296, 343	138, 110
Br	Br	1.00	80.09	286, 334	147, 141
Br	Br	0.100	80.09	296, 344	135, 110
I	I	1.00	80.27	294, 345	138, 108
I	I	0.100	80.27	297, 347	132, 100

Table 3.9. Spectra of dihalobisethylenediaminerhodium(III) complexes

(A) Spectra of cis- and trans-$[Rhen_2Cl_2]^+$

λ (nm)	ϵ_c from Method A	ϵ_c from Method B	ϵ_t
280	150.1	198.6	127.4
285	173.1	229.9	126.4
290	190.0	248.4	127.7
295	198.7	257.6	125.7
300	195.9	259.7	117.6
305	180.7	236.6	108.3
310	159.2	187.7	100.0
315	140.1	168.2	89.26
320	132.8	157.7	78.50
325	131.4	154.7	66.28
330	140.1	171.4	52.58
335	155.1	188.8	41.82
340	173.4	219.1	31.79
345	187.5	240.8	24.21
350	195.9	253.3	19.32
360	194.6	256.9	16.63
370	170.4	243.4	20.05
380	141.7	213.2	35.22
390	113.6	165.6	56.00
400	85.3	103.6	78.26
410	56.8	51.4	86.57
420	36.0	-10.1	81.93
430	22.4	-34.8	63.59

ϵ_c = extinction coefficient of cis-$[Rhen_2Cl_2]^+$ in M^{-1} cm^{-1}

ϵ_t = extinction coefficient of trans-$[Rhen_2Cl_2]^+$ in M^{-1} cm^{-1}

Table 3.9 (contd.)

(B) Spectra of cis- and trans-$[Rhen_2Br_2]^+$

λ (nm)	ϵ_c from Method A	ϵ_c from Method B	ϵ_t
330	167.5	230.1	84.31
335	153.8	221.3	66.82
340	153.2	229.2	53.05
345	160.0	245.5	41.58
350	174.9	267.8	30.97
360	197.9	304.0	17.49
370	214.0	314.1	12.04
380	206.6	296.6	12.91
390	185.5	261.9	22.37
400	160.0	225.3	44.16
410	135.2	189.2	70.83
420	110.4	148.8	100.1
430	86.2	112.7	115.6
440	66.4	72.6	113.0
450	50.2	43.8	90.05

ϵ_c = extinction coefficient of cis-$[Rhen_2Br_2]^+$ in M^{-1} cm^{-1}

ϵ_t = extinction coefficient of trans-$[Rhen_2Br_2]^+$ in M^{-1} cm^{-1}

Table 3.10

Specimen calculations for the determination of X_c from the dihydroxy-products of base hydrolysis of <u>trans</u>-$[Rhen_2X_2]^+$ (X = Cl, Br, I) and from the dihalo-products of anation of these dihydroxy-complexes

(A) From the $[Rhen_2Cl_2]^+$ product of anation of the dihydroxy-product (Data for the reaction of <u>trans</u>-$[Rhen_2Cl_2]^+$ with 1.00M hydroxide at 80.58°C)

λ (nm)	ϵ_{app} (M^{-1} cm^{-1})	ϵ_c (M^{-1} cm^{-1})	ϵ_t (M^{-1} cm^{-1})	x_c	ϵ_{calc}[a] (M^{-1} cm^{-1})
285	162	173	126	0.77	155
290	170	190	128	0.67	166
295	172	199	126	0.63	171
300	168	196	118	0.64	166
305	159	181	108	0.70	153
310	146	159	100	0.77	136
315	133	140	89.3	0.85	120
320	121	133	78.5	0.79	112
325	115	131	66.3	0.75	106
330	113	140	52.6	0.69	106
335	112	155	41.8	0.62	111
340	113	173	31.8	0.58	118
345	116	188	24.2	0.56	124
350	117	196	19.3	0.55	127
360	117	195	16.6	0.56	126
370	113	170	20.1	0.62	112

[a] ϵ_{calc} is the value of ϵ_{app} calculated from equation 3.42 taking $X_c = \bar{X}_c$.

(cont.)

Table 3.10 (cont.)

380	106	142	35.2	0.67	100
390	102	114	56.0	0.80	91

Weighted average of $X_c = \bar{X}_c = 0.61$.

(B) From the $[Rhen_2Br_2]^+$ product of anation of the dihydroxy-product (Data for the base hydrolysis of <u>trans</u>-$[Rhen_2Br_2]^+$ in 1.00M hydroxide at 80.09°C)

λ (nm)	ϵ_{app} (M^{-1} cm^{-1})	ϵ_c (M^{-1} cm^{-1})	ϵ_t (M^{-1} cm^{-1})	X_c	ϵ_{calc} [a] (M^{-1} cm^{-1})
330	155	176	81.5	0.85	145
335	135	161	64.8	0.78	130
340	128	161	51.6	0.75	126
345	127	168	40.4	0.72	127
350	129	184	30.4	0.68	134
360	139	208	18.1	0.67	146
370	142	225	12.6	0.65	156
380	136	217	13.2	0.64	151
390	126	195	22.9	0.64	139
400	121	168	44.7	0.67	128
410	119	142	73.1	0.75	120

Weighted mean value of $X_c = \bar{X}_c = 0.68$.

[a] ϵ_{calc} is the value of ϵ_{app} calculated from equation 3.42 taking $X_c = \bar{X}_c$.

(cont.)

Table 3.10 (cont.)

(C) From the $[Rhen_2(OH)_2]^+$ product. (Data for the base hydrolysis of trans-$[Rhen_2I_2]^+$ in 1.00M hydroxide at 80.29°C)

λ (nm)	ϵ_{app} (M^{-1} cm^{-1})	ϵ_c (M^{-1} cm^{-1})	ϵ_t (M^{-1} cm^{-1})	X_c	ϵ_{calc} [a] (M^{-1} cm^{-1})
270	118	141	95.7	-	105
275	121	155	102	0.37	113
280	128	163	110	0.34	121
285	133	163	118	0.34	128
290	136	161	126	0.29	133
295	138	155	130	0.30	136
300	136	150	130	0.30	135
305	132	146	125	0.31	130
310	123	150	114	0.25	122
315	115	154	106	0.18	116
320	109	159	98.3	0.17	111
325	106	165	93.7	0.17	109
330	105	168	92.4	0.17	109
335	106	168	94.0	0.17	110
340	108	164	96.6	0.16	111
345	109	156	98.3	0.18	111
350	107	142	98.1	0.21	107
360	93.1	111	88.2	0.22	93.0
370	72.5	78.4	69.8	-	71.7
380	52.2	51.7	51.0	-	51.2

Weighted average value of $X_c = \overline{X}_c = 0.21$.

[a] ϵ_{calc} is the value of ϵ_{app} calculated from equation 3.42 taking $X_c = \overline{X}_c$.

Table 3.11

Stereochemical rearrangement during the hydroxide-dependent pathway for base hydrolysis of trans-$[Rhen_2LX]^+$

L	X	$[OH^-]$ (M)	Temperature (°C)	X_c [a]	P.R. [b]
Cl	Cl	1.00	80.58	0.61 [c]	100
Cl	Cl	0.10	80.58	0.20 [c,d]	
Br	Br	1.00	80.09	0.68 [c]	100
Br	Br	0.10	80.09	0.20 [c,d]	
I	I	1.00	80.27	0.21 [d]	46
I	I	0.10	80.27	0 [d]	
OH	Cl	0.73	80.16	0 [c,d]	
OH	Br	0.73	80.13	0 [c,d]	
OH	I	1.00	80.0	0 [d]	

[a] Uncertainty in X_c estimated as ±0.1

[b] P.R. = Percentage rearrangement occurring in the second-order pathway

[c] from dihalo-products of anation of the dihydroxy-complexes

[d] from dihydroxy-products

Table 3.12

Kinetic data for the reaction of trans-$[Rhen_2I_2]^+$ with Cl^-

[cmx] = ca. 6×10^{-5} M I = 1.00 M

Temperature (°C)	$[Cl^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
55.0	1.00	26.93
	0.800	26.20
	0.550	25.03
	0.300	23.20
	0.100	22.94
49.9	1.00	15.10
	0.800	14.33
	0.550	13.83
	0.300	13.17
	0.100	12.63
45.4	1.00	8.206
	0.800	7.893
	0.550	7.593
	0.300	7.211
	0.100	6.966
42.0	1.00	5.323
	0.800	5.121
	0.550	5.036
	0.300	4.812
	0.100	4.663

(cont.)

Table 3.12 (cont.)

Temperature (°C)	$[Cl^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
34.8	1.00	1.990
	0.800	1.981
	0.550	1.908
	0.300	1.850
	0.100	1.788

Temperature (°C)	$10^5 k_1$ (s^{-1})	$10^5 k_2$ ($M^{-1}\ s^{-1}$)
55.0	22.21 ±0.20	4.802 ±0.327
49.9	12.36 ±0.11	2.633 ±0.182
45.4	6.819 ±0.060	1.373 ±0.095
42.0	4.602 ±0.040	0.7070 ±0.0655
34.8	1.774 ±0.015	0.2349 ±0.0249

Standard deviation of k_{obsd} = 0.96%

$$\Delta H_1^{\ddagger} = 24.54 \pm 0.11 \text{ kcal mol}^{-1}$$
$$\Delta S_1^{\ddagger} = -0.66 \pm 0.36 \text{ e.u.}$$
$$\Delta H_2^{\ddagger} = 29.57 \pm 1.08 \text{ kcal mol}^{-1}$$
$$\Delta S_2^{\ddagger} = 11.75 \pm 3.37 \text{ e.u.}$$

Table 3.13. Kinetic data for the reaction of trans-$[Rhen_2I_2]^+$ with Cl^- at varying ionic strengths

(A) Experiments at varying ionic strength and varying $[Cl^-]$

[cmx] = ca. 6×10^{-5} M I = $[Cl^-]$ temperature = 55.0°C

$[Cl^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
1.00	27.43, 27.11
0.700	26.53, 26.08
0.300	25.57, 24.22
0.200	24.63
0.100	24.25, 23.68, 23.30
0.0700	23.60
0.0500	23.74
0.0200	23.30
0.0100	23.64, 22.86

(B) Experiments at varying ionic strength and constant $[Cl^-]$

[cmx] = ca. 6×10^{-5} M I = $[ClO_4^-]$ temperature = 55.25°C

$[Cl^-]$ = 0.0502 M

$[ClO_4^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
0.906	23.13
0.604	23.28
0.302	23.26
0.000	23.38

Table 3.14

Kinetic data for the reaction of trans-$[Rhen_2I_2]^+$ with Br^-

[cmx] = 6×10^{-5} M I = 1.00 M

Temperature (°C)	$[Br^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
54.2	1.00	25.73
	0.800	25.54
	0.550	24.12
	0.300	23.11
	0.100	21.65
50.0	1.00	15.38
	0.800	15.00
	0.550	14.46
	0.300	13.77
	0.100	12.83
45.3	1.00	8.283
	0.800	8.136
	0.550	7.766
	0.300	7.216
	0.100	6.961
42.0	1.00	5.403
	0.800	5.205
	0.550	5.000
	0.300	4.683
	0.100	4.571

(cont.)

Table 3.14 (cont.)

Temperature (°C)	$[Br^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
35.5	1.00	2.458
	0.800	2.341
	0.550	2.259
	0.300	2.128
	0.100	2.105

Temperature (°C)	$10^5 k_1$ (s^{-1})	$10^5 k_2$ ($M^{-1} s^{-1}$)
54.2	21.45 ±0.28	4.678 ±0.458
50.0	12.75 ±0.16	2.797 ±0.272
45.3	6.808 ±0.088	1.569 ±0.147
42.0	4.449 ±0.058	0.9513 ±0.0957
35.5	2.040 ±0.026	0.3964 ±0.0437

Standard deviation of k_{obsd} = 1.4%

$\Delta H_1^{\ddagger}$ = 24.78 ±0.18 kcal mol^{-1}

$\Delta S_1^{\ddagger}$ = 0.15 ±0.56 e.u.

$\Delta H_2^{\ddagger}$ = 25.98 ±1.37 kcal mol^{-1}

$\Delta S_2^{\ddagger}$ = 0.85 ±4.31 e.u.

Table 3.15

Kinetic data for the reaction of <u>trans</u>-$[Rhen_2I_2]^+$ with OH^- in the presence of other anions, Y^{n-}

$[cmx] = 7.1 \times 10^{-5}M$ $I = 1.01M$

$[OH^-] = 0.010M$ Temperature = 53.78°C

Y^{n-}	$[Y^{n-}]$	$10^5 k_{obsd}$ (s^{-1})	$10^5 k_2$ ($M^{-1} s^{-1}$)
PO_4^{3-}	0.167	23.12	23
SO_4^{2-}	0.333	23.63	13
F^- [a]	0.200	19.87	ca. 3
ClO_4^-	1.00	19.32	-

[a] $[ClO_4^-] = 0.800M$

Table 3.16. Kinetic data for the reaction of trans-$[Rhen_2Cl_2]^+$ with OH^- in the presence of Br^-

[cmx] = 5.4×10^{-4}M I = 1.00M

$[OH^-]$ = 0.100M Temperature = 77.87°C

$[Br^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
0.900	3.704
0.700	3.728
0.500	3.684
0.200	3.545
0.000	3.555

$10^5 k_1' = 3.543 \pm 0.051\ s^{-1}$ $10^5 k_1 = 3.143\ s^{-1}$

$10^5 k_2 = 0.217 \pm 0.092\ M^{-1} s^{-1}$ Standard deviation of k_{obsd} = 1.85%

Table 3.17. Kinetic data for the reaction of trans-$[Rhen_2Cl_2]^+$ with OH^- in the presence of SO_4^{2-}

[cmx] = 5.8×10^{-4}M I = 1.01

$[OH^-]$ = 0.01M Temperature = 77.22°C

$[SO_4^{2-}]$ (M)	$10^5 k_{obsd}$ (s^{-1})
0.333	4.226
0.120*	3.460
0.0334	3.271
0.00334	3.235

*I = 0.87M

$10^5 k_1' = 3.175 \pm 0.104\ s^{-1}$ $10^5 k_1 = 3.137\ s^{-1}$

$10^5 k_2 = 3.03 \pm 0.69\ M^{-1} s^{-1}$ Standard deviation of k_{obsd} = 4.5%

Table 3.18. Kinetic data for the reaction of trans-$[Rhen_2Cl_2]^+$ with OH^- in the presence of PO_4^{3-}

[cmx] = 6.0×10^{-4}M I = 1.01M

$[OH^-]$ = 0.01M Temperature = 79.44°C

$[PO_4^{3-}]$ (M)	$10^5 k_{obsd}$ (s^{-1})
0.167	5.973
0.0833	4.787
0.0167	4.066
0.00167	3.860

$10^5 k_1' = 3.832 \pm 0.095\ s^{-1}$ $10^5 k_1 = 3.780\ s^{-1}$

$10^5 k_2 = 12.5 \pm 1.3\ M^{-1} s^{-1}$ Standard deviation of k_{obsd} = 3.3%

Table 3.19. Kinetic data for the reaction of trans-$[Rhen_2Cl_2]^+$ with OH^- in the presence of F^-

[cmx] = 5.8×10^{-4}M I = 1.01M

$[OH^-]$ = 0.01M Temperature = 77.82°C

$[F^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
0.200	3.474
0.100	3.324
0.050	3.194
0.000	3.220

$10^5 k_1' = 3.180 \pm 0.085\ s^{-1}$ $10^5 k_1 = 3.140\ s^{-1}$

$10^5 k_2 = 1.40 \pm 0.77\ M^{-1} s^{-1}$ Standard deviation of k_{obsd} = 3.4%

Table 3.20

Kinetic data for the reaction of trans-$[Rhen_2Br_2]^+$ with F^-

[cmx] = 3.5×10^{-4}M I = 1.00M Temperature = 80.4°C

$[F^-]$ (M)	$10^5 k_{obsd}$ (s^{-1})
1.00	20.23
0.70	19.19
0.40	17.01

Table 3.21

Spectroscopic interaction between trans-$[Rhen_2Cl_2]^+$ and iodide

[cmx] = 2.412×10^{-3}M I = $[I^-]$

$[I^-]$	Absorbance at 285 nm
0	0.2919
0.2140	0.4460
0.3817	0.4967
0.6047	0.6249
0.7993	0.6921
1.032	0.7837
1.205	0.8330
1.398	0.9148
1.603	0.9780
1.799	1.0532
2.004	1.1160
2.230	1.1604
2.404	1.2489
2.611	1.3206
2.808	1.3796
3.005	1.4486

Table 3.22

Spectroscopic interaction between trans-$[Rhen_2Cl_2]^+$ and bromide

$[cmx] = 2.661 \times 10^{-4}M$ $I = [Br^-]$

Absorbance at λ =

$[Br^-]$ (M)	235 nm	240 nm	245 nm	250 nm
0	0.492	0.471	0.418	0.312
0.200	0.496	0.473	0.407	0.302
0.400	0.526	0.490	0.430	0.321
0.600	0.538	0.488	0.429	0.324
0.800	0.543	0.486	0.423	0.320
1.00	0.572	0.513	0.449	0.340

$[cmx] = 2.309 \times 10^{-3}M$ $I = [Br^-]$

Absorbance at λ =

$[Br^-]$ (M)	260 nm	270 nm	280 nm	290 nm	300 nm
0	0.863	0.312	0.260	0.270	0.252
0.200	0.910	0.337	0.275	0.280	0.256
0.400	0.965	0.362	0.287	0.291	0.269
0.600	0.983	0.374	0.294	0.297	0.270
0.800	1.040	0.385	0.291	0.291	0.267
1.00	1.075	0.408	0.302	0.301	0.274

Table 3.23

Spectroscopic interaction between trans-$[Rhen_2Cl_2]^+$ in iodide in the presence of other anions, Y^{n-}

	Y^{n-}	$[Y^{n-}]$	ϵ_{app} at 285 nm (M^{-1} cm^{-1})	ϵ_{app} at 290 nm (M^{-1} cm^{-1})
(a)	-	-	115	116
(b)	-	-	234	206
(b)	F^-	0.149	233	205
(b)	Cl^-	1.00	221	198
(b)	Br^-	1.00	218	195
(b)	OH^-	0.400	229	203
(b)	SO_4^{2-}	0.334	226	202
(b)	PO_4^{3-}	0.167	233	204

(a) no iodide added

(b) $[I^-]$ = 0.500M

Table 3.24

Spectroscopic interaction between trans-$[Rhen_2I_2]^+$ and iodide in the presence of other anions, Y^{n-}

Y^{n-}	$[Y^{n-}]$ (M)	ϵ_{app} at 300 nm (M^{-1} cm^{-1})
(a) ClO_4^-	1.50	3330
(b) ClO_4^-	1.00	4980, 5300
(b) F^-	0.997	5020
(b) Cl^-	1.00	5430
(b) Br^-	1.00	5510
(b) OH^-	0.400	4440
(b) SO_4^{2-}	0.334	5490
(b) PO_4^{3-}	0.167	5280

Ionic strength = 1.50M

(a) no iodide added

(b) $[I^-]$ = 0.500M

Table 3.25

Calculation of the ion-association constant for the ion-pair {trans-[$Rhen_2I_2$],Cl} using equation 3.85 and the results in Table 3.13

$[Cl^-]$ (M)	$10^5 (k_{obsd} - k_0)$ (s^{-1})	$10^5 y$ ($M^{-1} s^{-1}$)	$10^5 \sigma_y$ ($M^{-1} s^{-1}$)	$10^5 k_{obsd}$ (s^{-1})
1.00	4.33	6.863	1.58	27.43
	4.01	6.354	1.70	27.11
0.700	3.43	8.626	2.51	26.53
	2.98	7.494	2.50	26.08
0.300	2.47	15.12	6.1	25.57
	1.12	6.86	6.2	24.22
0.200	1.53	13.60	8.8	24.63
0.100	1.15	18.7	16.2	24.25
	0.58	9.4	16.2	23.68
	0.20	3.2	16.2	23.30

$$k_0 = 2.310 \times 10^{-4}\ s^{-1}$$

Table 3.26

Calculation of the ion-association constant for the ion-pair {trans-[$Rhen_2Cl_2$],Br} using equation 3.87 and the results in Table 3.22 for λ = 260 nm

$[Br^-]$ (M)	$\epsilon_{app} - \epsilon_0$ (M^{-1} cm^{-1})	z (M^{-2} cm^{-1})	ϵ_{app} (M^{-1} cm^{-1})
0.200	20.4	193.8	394.1
0.400	44.2	204.4	417.9
0.600	52.0	156.3	425.7
0.800	76.7	163.6	450.4
1.00	91.8	145.5	465.6

Table 3.27

Calculation of the ion-association constant for the ion-pair {trans-$[Rhen_2Cl_2]$,I} using equation 3.89 and the results in Table 3.21

$[I^-]$ (M^{-1})	Y	$\epsilon_{app} - \epsilon_0$ (M^{-1} cm^{-1})	w (M^{-2} cm^{-1})	ϵ_{app} (M^{-1} cm^{-1})
0.6047	0.704	138.1	461.0	259.1
0.7993	0.690	165.9	436.2	286.9
1.032	0.679	203.9	428.3	324.9
1.205	0.675	224.3	408.8	345.4
1.398	0.673	258.3	408.2	379.3
1.603	0.671	284.5	393.7	405.5
1.799	0.671	315.6	389.3	436.7
2.004	0.672	341.7	377.4	462.7
2.230	0.677	360.1	352.4	481.1
2.404	0.682	396.8	354.6	517.8
2.611	0.689	426.6	344.1	547.5
2.808	0.696	451.1	331.6	572.0
3.005	0.703	479.7	323.1	600.6

Table 3.28

Calculation of ion-association constants at zero ionic strength (K_Y^0) for the ion-pairs $\{Rhen_2LX,Y\}^{m+}$ using the Fuoss equation

Y^{n-}	K_Y^0 (M^{-1}) for association with		
	$[Rhen_2LX]^+$	$[Rhen_2LX]^{2+}$	$[Rhen_2LX]^{3+}$
F^-	1.4	5.2	19
Cl^-	1.7	5.5	18
Br^-	1.8	5.6	18
I^-	1.9	5.7	17
OH^-	1.3	5.1	20
ClO_4^-	2.3	6.3	17
SO_4^{2-}	6.3	46	340
PO_4^{3-}	17	340	6700

Ionic radii used

trans-$[Rhen_2LX]^{n+}$	4.1 Å
F^-	1.3 Å
Cl^-	1.8 Å
Br^-	2.0 Å
I^-	2.2 Å
OH^-	1.0 Å
ClO_4^-	2.9 Å
SO_4^{2-}	2.9 Å
PO_4^{3-}	2.9 Å

Table 3.29

Upper limits for ion-association constants of trans-$[Rhen_2Cl_2]^+$ and Y^{n-}

Y^{n-}	K_Y (M^{-1})	K_Y^0 (M^{-1})	K_Y at I = 1.0M (M^{-1})
F^-	< 2.4 at I = 0.65M	< 4.3	< 2.7
Cl^-	< 0.35 at I = 1.50M	< 0.44	< 0.28
Br^-	< 0.35 at I = 1.50M	< 0.44	< 0.28
OH^-	< 0.88 at I = 0.90M	< 1.5	< 0.95
SO_4^{2-}	< 1.0 at I = 1.50M	< 4.5	< 0.90
PO_4^{3-}	< 2.1 at I = 1.50M	< 33	< 2.1

Table 3.30

Calculation of the association constant for the ion-pair

{trans-$[Rhen_2I_2]$, ClO_4}

Temperature = 55.0°C

$K^\circ_{Cl} = 1.2\ M^{-1}$

$k_0 = 2.310 \times 10^{-4}\ s^{-1}$

$k_{Cl} = 3.313 \times 10^{-4}\ s^{-1}$

$[Cl^-]$ (M)	$10^4\ k_{obsd}$ (s^{-1})	K_{ClO_4} (a) (M^{-1})	$K^\circ_{ClO_4}$ (b) (M^{-1})
0.100	2.294	-6.5	-10
0.300	2.320	30.9	49
0.550	2.503	1.7	2.7
0.800	2.620	1.8	2.9

(a) At I = 1.0M

(b) corrected to zero ionic strength using equations 3.81 and 3.84

Table 3.31

Relative reactivities k_Y/k_0 of the ion-pairs $\{\underline{trans}\text{-}[Rhen_2LX],Y\}^{(1-n)+}$ and the free ions $\underline{trans}\text{-}[Rhen_2LX]^+$

L	X	Y^{n-}	k_Y/k_0	Temperature (°C)
Cl	Cl	F^-	> 1.09	77.82
Cl	Cl	Br^-	> 1.16	77.14
Cl	Cl	SO_4^{2-}	> 1.36	77.22
Cl	Cl	PO_4^{3-}	> 1.51	79.44
Br	Br	F^-	∿ 1.0	80.4
I	I	F^-	> 1.03	53.78
I	I	Cl^-	> 1.22	55.0
I	I	Br^-	> 1.22	54.2
I	I	SO_4^{2-}	> 1.22	53.78
I	I	PO_4^{3-}	> 1.39	53.78

Table 3.32

Effect of ionic strength on the theoretical association constants calculated from the Fuoss equation for the ion-pair $\{\underline{trans}\text{-}[Rhen_2LX],Y\}^{(1-n)+}$

Y^{n-}	K_Y^0 (M^{-1})	K_Y at I = 1.0M (M^{-1})
F^-	1.4	0.9
Cl^-	1.7	1.1
Br^-	1.8	1.1
SO_4^{2-}	6.3	1.3
PO_4^{3-}	17	1.1

Table 3.33

Relative reactivities, R, of the ion-pairs $\{\underline{trans}\text{-}[Rhen_2Cl_2],Y\}^{(1-n)+}$ and $\{\underline{trans}\text{-}[Rhen_2I_2],Y\}^{(1-n)+}$

(a) $\{\underline{trans}\text{-}[Rhen_2Cl_2],Y\}^{(1-n)+}$

Y^{n-}	k_2/k_1 (M^{-1})	R
F^-	0.44	2.8
Br^-	0.16	1
SO_4^{2-}	1.07	6.7
PO_4^{3-}	3.06	19

(b) $\{\underline{trans}\text{-}[Rhen_2I_2],Y\}^{(1-n)+}$

Y^{n-}	k_2/k_1 (M^{-1})	R
F^-	0.14	0.64
Cl^-	0.22	1
Br^-	0.22	1
SO_4^{2-}	0.67	3.1
PO_4^{3-}	1.18	5.4

Table 3.34

Base hydrolysis of rhodium(III) complexes

trans-$[Rhen_2LX]^{n+}$

L	X	$\Delta H_2^{\ddagger}$ (kcal mol^{-1})	$\Delta S_2^{\ddagger}$ (e.u.)	k_2/k_1 at 80°C (M^{-1})	PR[a]	reference
OH	Cl	25.84	-0.49	0.39	0%	This work
OH	Br	25.08	-3.11	0.29	0%	This work
OH	I	29.34	7.93	0.49	0%	This work
Cl	Cl	35.07	21.00	1.4	100%	This work
Br	Br	33.65	20.26	1.8	100%	This work
I	I	31.18	17.66	0.82	46%	This work
py	Cl	35	25		64%	59

cis-$[Rhen_2LX]^{+}$

L	X	$\Delta H_2^{\ddagger}$ (kcal mol^{-1})	$\Delta S_2^{\ddagger}$ (e.u.)	k_2/k_1 at 80°C (M^{-1})	PR[a]	reference
Cl	Cl	24.5	10	2×10^3[b]	0%	57,59
OH	Cl	25.0	13	470	0%	59
NO_2	Cl	25.4	12	1.4×10^4	0%	59

$[Rh(NH_3)_5X]^{2+}$

X	$\Delta H_2^{\ddagger}$ (kcal mol^{-1})	$\Delta S_2^{\ddagger}$ (e.u.)	k_2/k_1 at 80°C (M^{-1})	PR[a]	reference
Cl	27.8	19.3	2×10^5	-	67, 126
Br	29.9	25.8	5×10^4	-	67, 126
I	32.2	30.7	5×10^4	-	67, 126

(a) PR = percentage rearrangement occurring during the second-order pathway.

(b) at 55°C

Table 3.35

Relative activation parameters for base hydrolysis of rhodium(III) complexes

trans-$[Rhen_2LX]^+$

L	X	$\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ (kcal mol^{-1})	$\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ (e.u.)	PR[a]	reference
Cl	Cl	9.0 ±1.6	26 ±5	100%	This work
Br	Br	7.9 ±0.7	23 ±2	100%	This work
I	I	6.9 ±0.7	19 ±2	46%	This work
OH	Cl	0.7 ±0.7	0 ±2	0%	This work
OH	Br	-0.9 ±1.3	-5 ±4	0%	This work
OH	I	1.5 ±0.9	3 ±3	0%	This work

cis-$[Rhen_2LX]^+$

L	X	$\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ (kcal mol^{-1})	$\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ (e.u.)	PR[a]	reference
OH	Cl	3.8	23	0%	59
NO_2	Cl	0.7	21	0%	59

$Rh(NH_3)_5X$

X	$\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ (kcal mol^{-1})	$\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ (e.u.)	PR[a]	reference
Cl	3.6	34.4	-	67, 126
Br	5.4	36.7	-	67, 126
I	6.0	38.5	-	67, 126

(a) PR = Percentage rearrangement occurring during the second-order pathway.

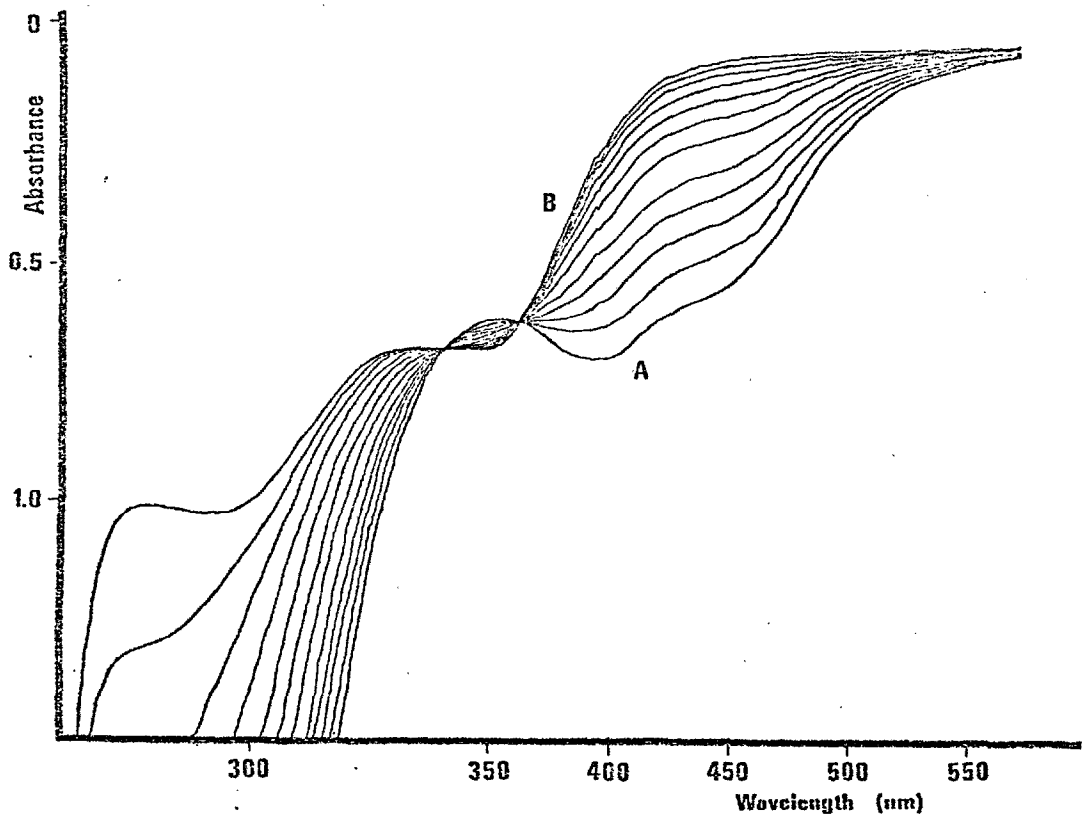


Fig. 3.1 Spectroscopic changes occurring during the reaction of <u>trans</u>-$[Rhen_2IOH]^+$ with hydroxide

temperature = 80.0 °C
[complex] = 6.42×10^{-3} M
$[OH^-]$ = 0.100 M
A = substrate B = product

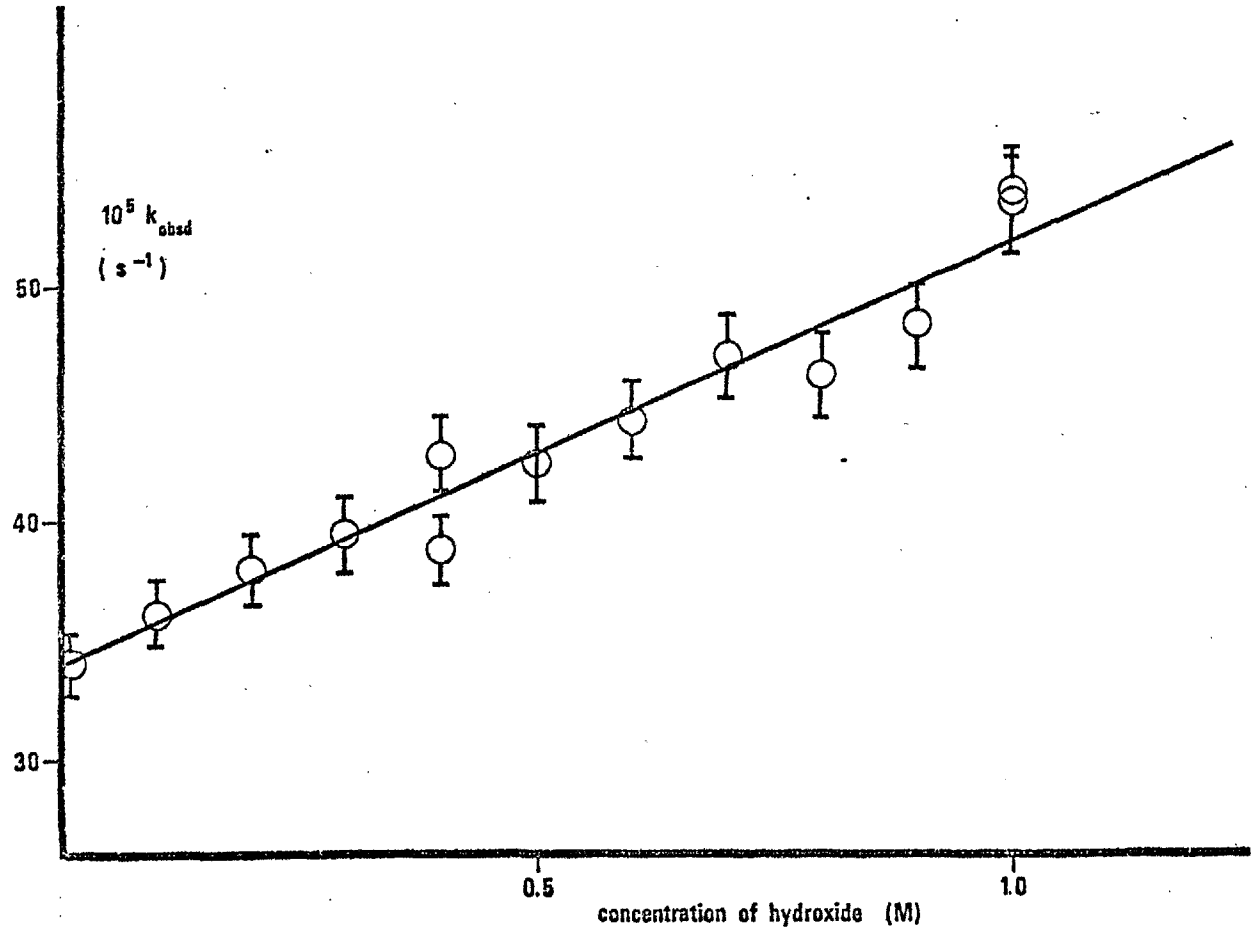


Fig. 3.2 The dependence of the pseudo-first-order rate constant for substitution of <u>trans</u>-$[Rhen_2IOH]^+$ on the concentration of added hydroxide at 75.7 °C

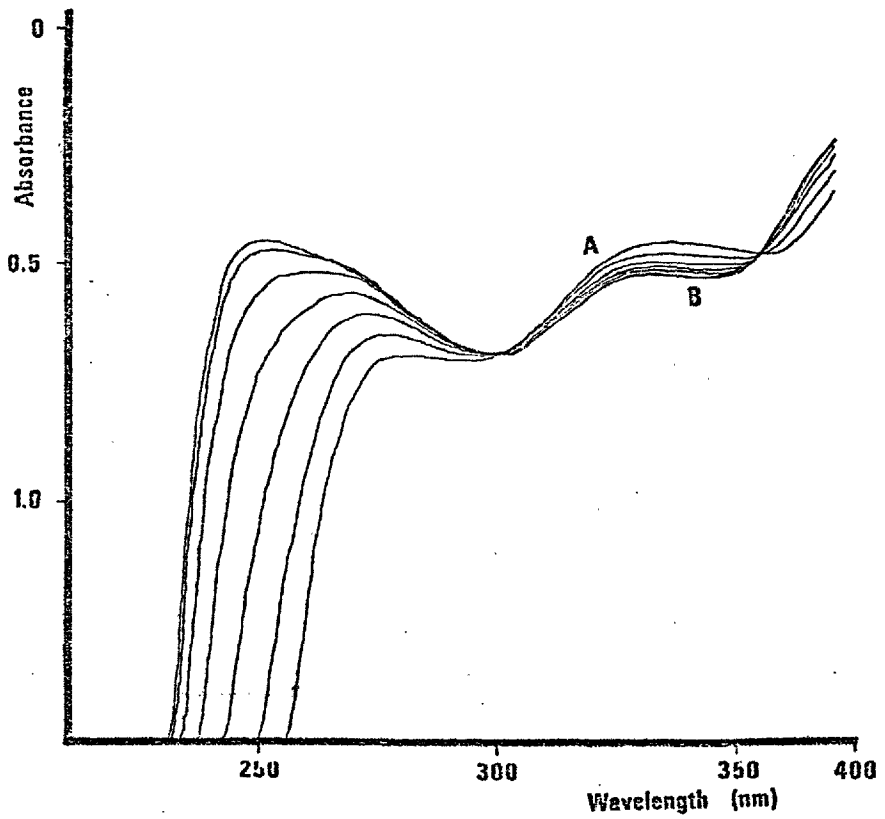


Fig. 3.3 Spectroscopic changes occurring during the reaction of <u>trans</u>-$[Rhen_2BrOH]^+$ with hydroxide

temperature = 79.95 °C
[complex] = 4.42×10^{-3} M
$[OH^-]$ = 0.097 M
A = substrate B = product

Fig. 3.4A is given overleaf on page 187a

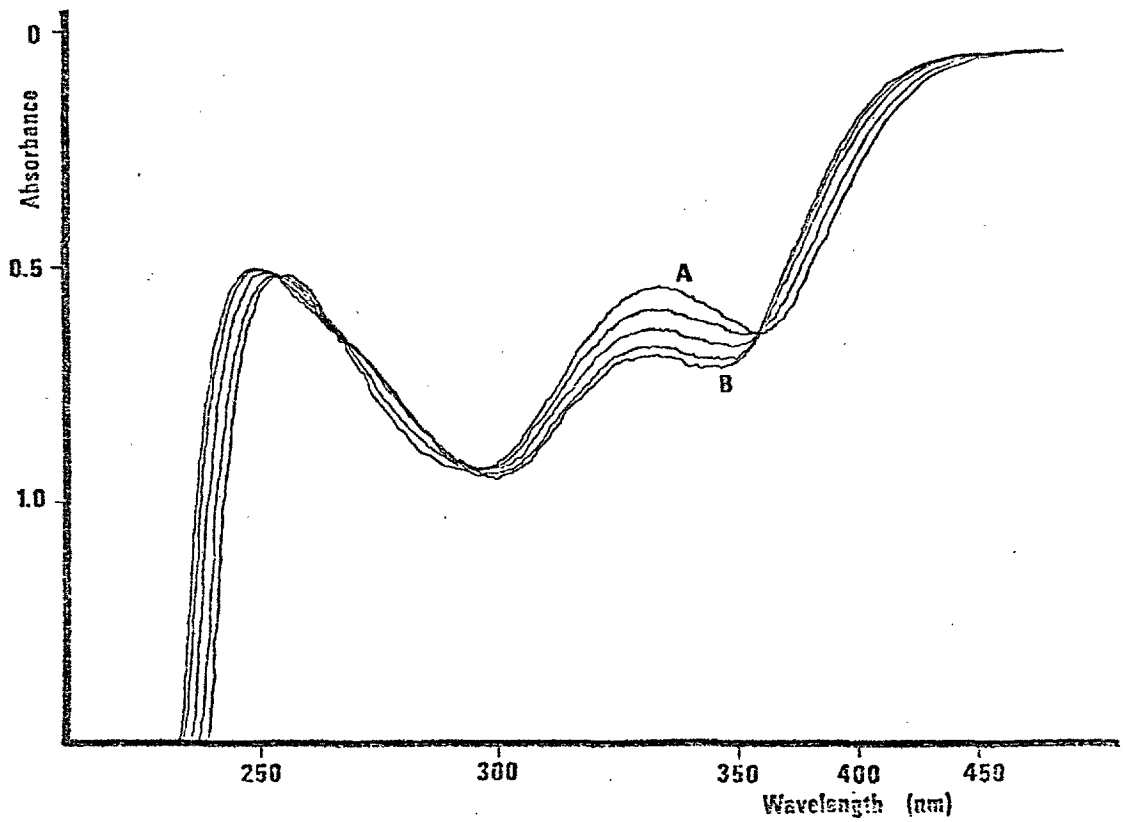


Fig. 3.4 B Spectroscopic changes occurring during the reaction of <u>trans</u>-$[Rhen_2ClOH]^+$ with hydroxide

temperature = 71.04 °C
[complex] = 6.48×10^{-3} M
$[OH^-]$ = 0.067 M
A = substrate B = product

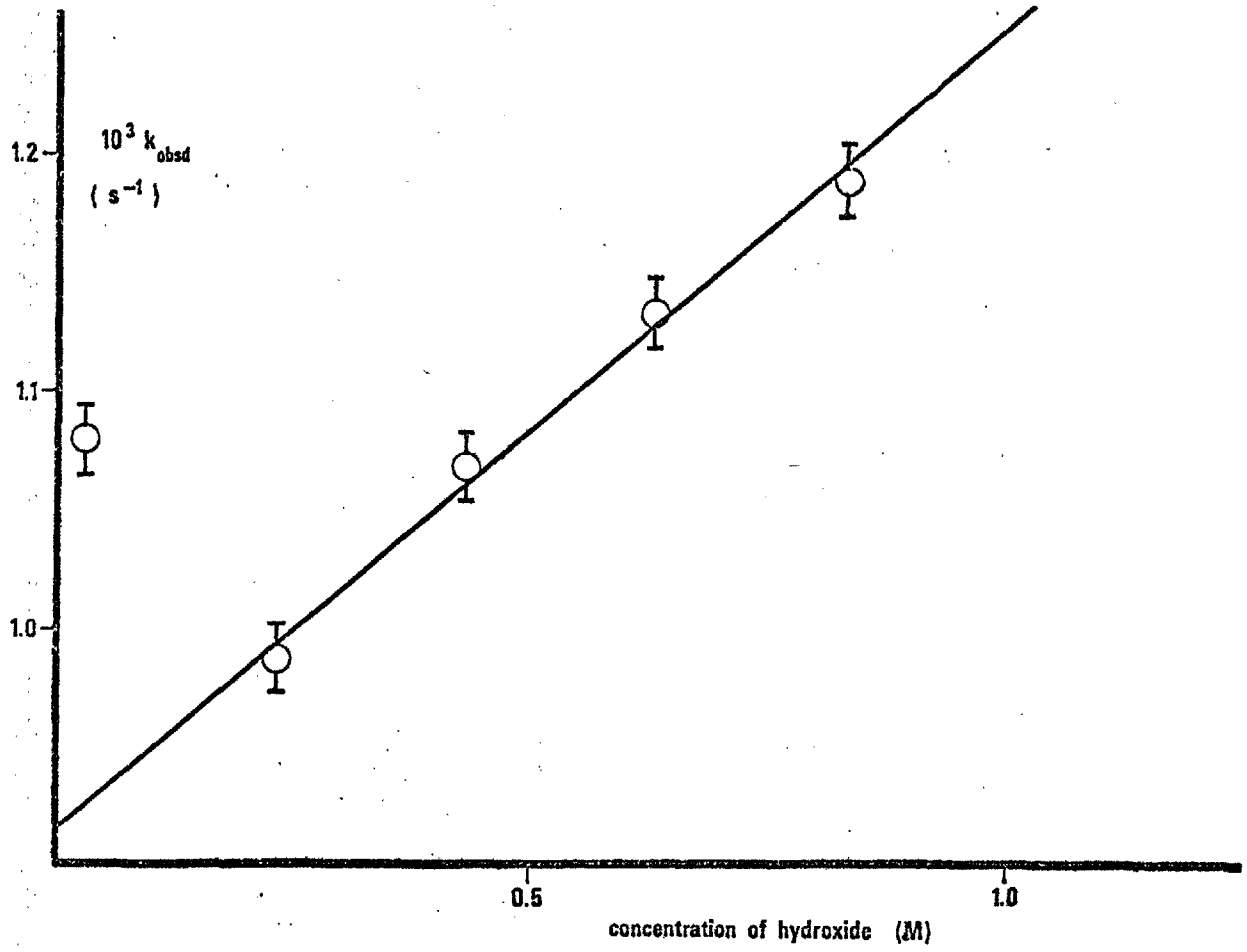


Fig. 3.5 The dependence of the pseudo-first-order rate constant for substitution of <u>trans</u>-$[Rhen_2ClOH]^+$ on the concentration of added hydroxide at 75.75 °C

Fig. 3.6A is given overleaf on page 190a

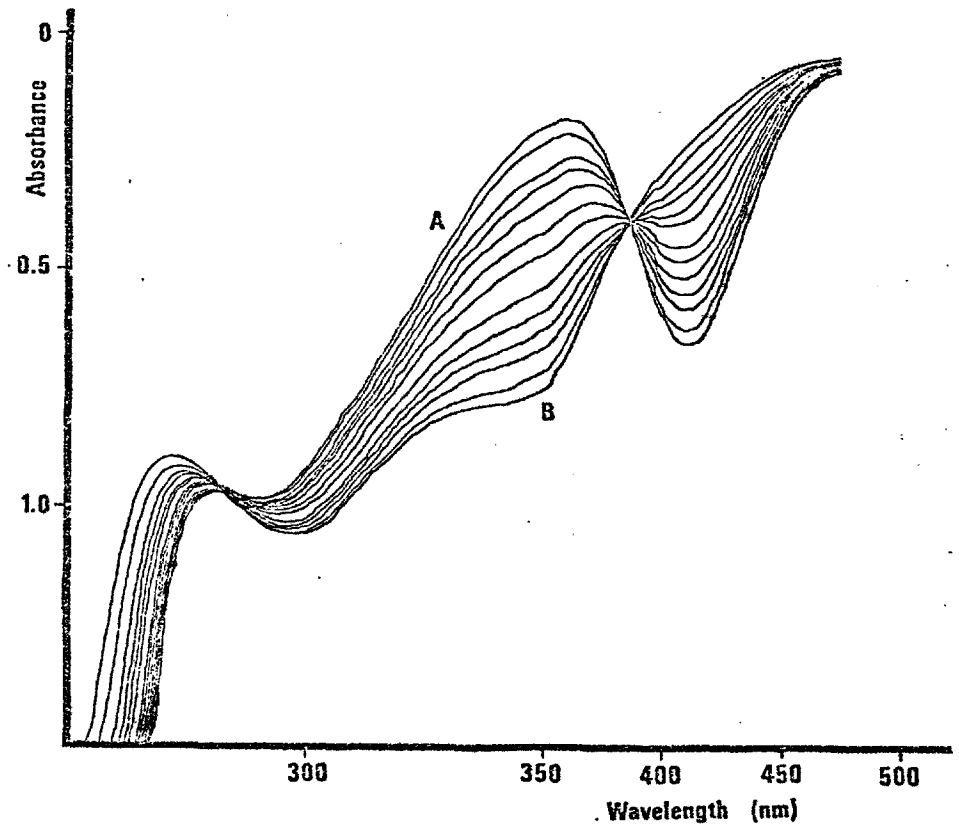


Fig. 3.6B Spectroscopic changes occurring during the reaction of <u>trans</u>-$[Rhen_2Cl_2]^+$ with hydroxide

temperature = 80.58 ^{o}C
[complex] = 7.50×10^{-3} M
$[OH^-]$ = 0.100 M
A = substrate B = product

Fig. 3.7A is given overleaf on page 192a

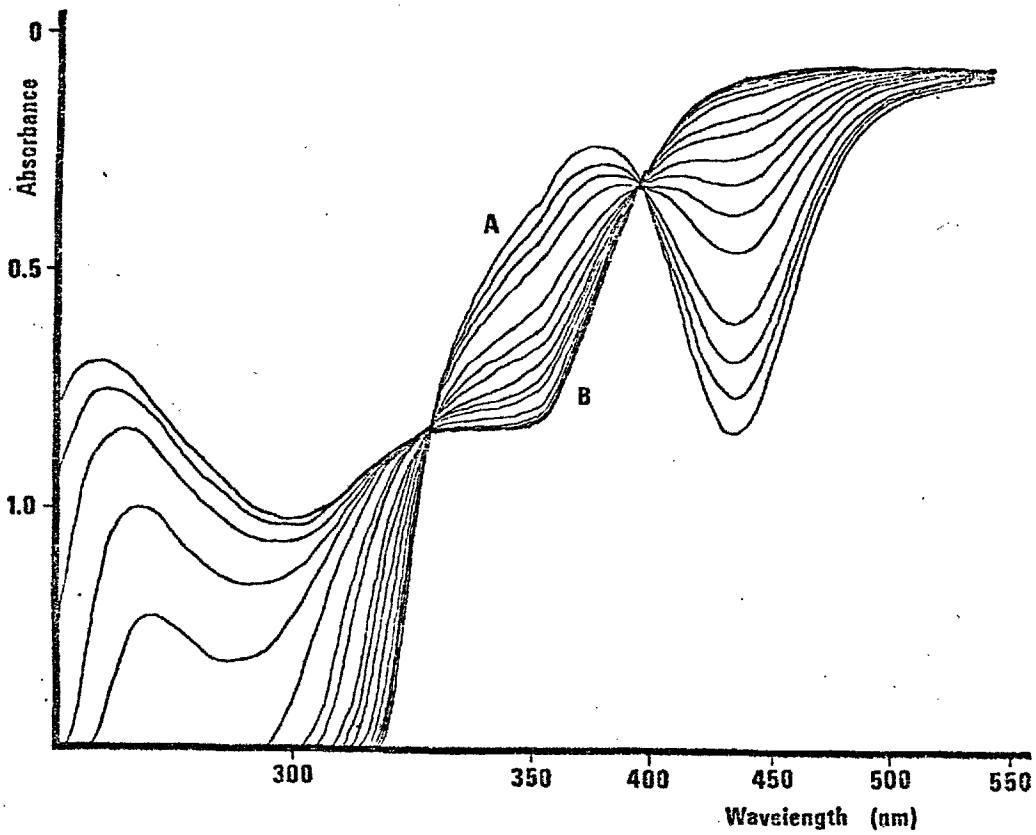


Fig. 3.7 B Spectroscopic changes occurring during the reaction of <u>trans</u>-$[Rhen_2Br_2]^+$ with hydroxide

temperature = 80.09 °C
[complex] = 6.95×10^{-3} M
$[OH^-]$ = 0.100 M
A = substrate B = product

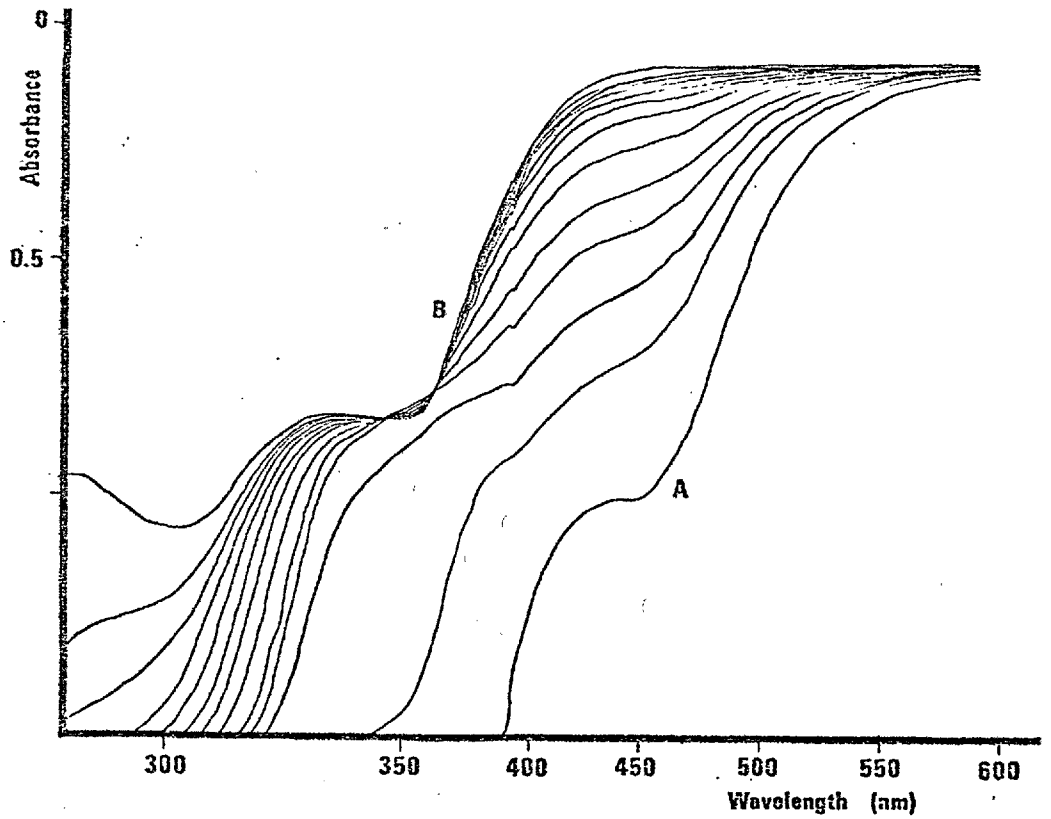


Fig. 3.8 Spectroscopic changes occurring during the reaction of trans-$[Rhen_2I_2]^+$ with hydroxide

temperature = 80.27 °C
[complex] = 7.36×10^{-3} M
$[OH^-]$ = 0.100 M
A = substrate B = product

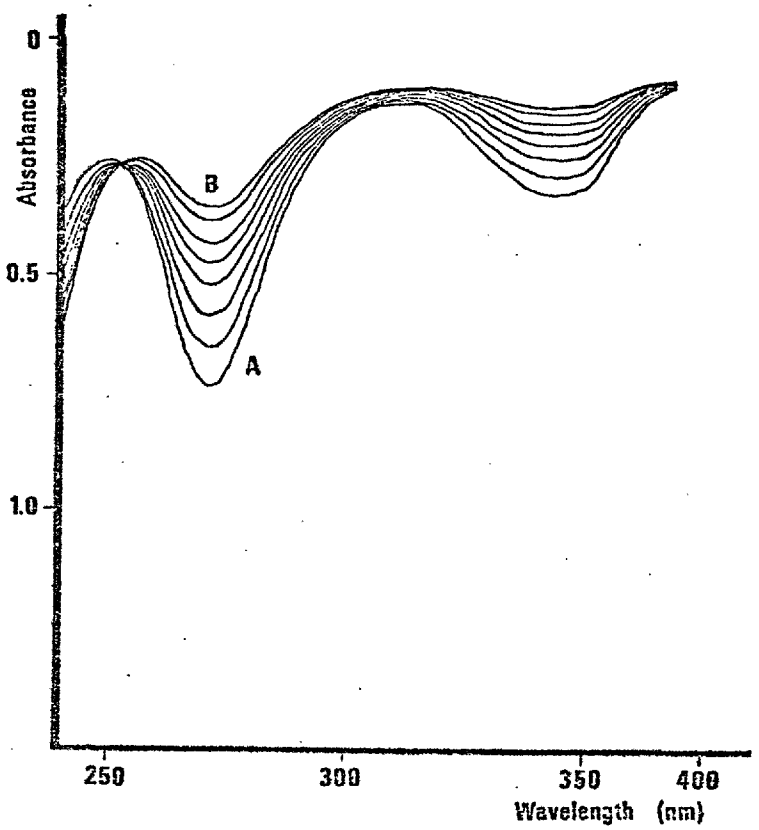


Fig. 3.9 Spectroscopic changes occurring during the first stage of the reaction of <u>trans</u>-$[Rhen_2I_2]^+$ with hydroxide

temperature = 60.57 °C
[complex] = 2.17×10^{-5} M
$[OH^-]$ = 1.00M
A = substrate B = product

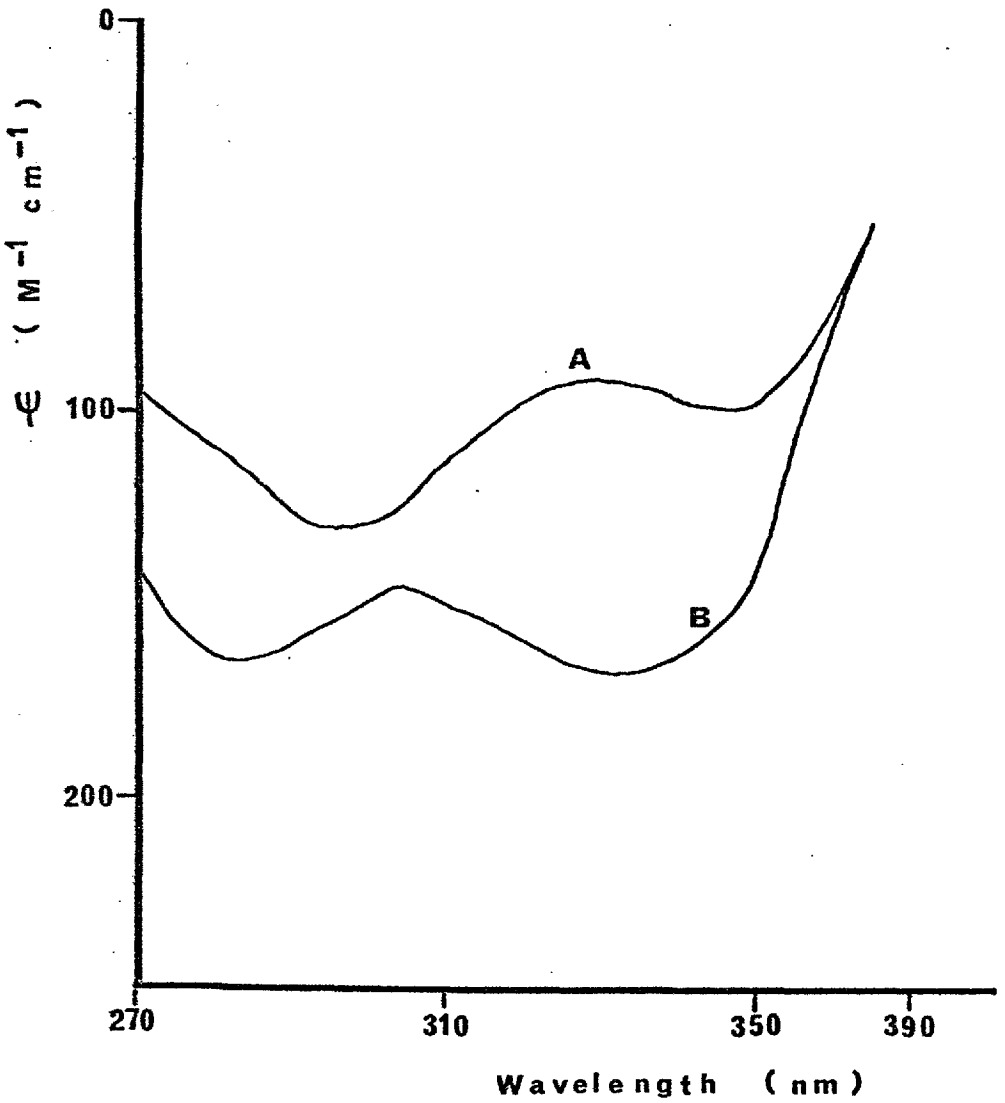


Fig. 3.10 Spectra of dihydroxybisethylenediaminerhodium(III) complexes

A <u>trans</u>-$[Rhen_2(OH)_2]^+$ B <u>cis</u>-$[Rhen_2(OH)_2]^+$

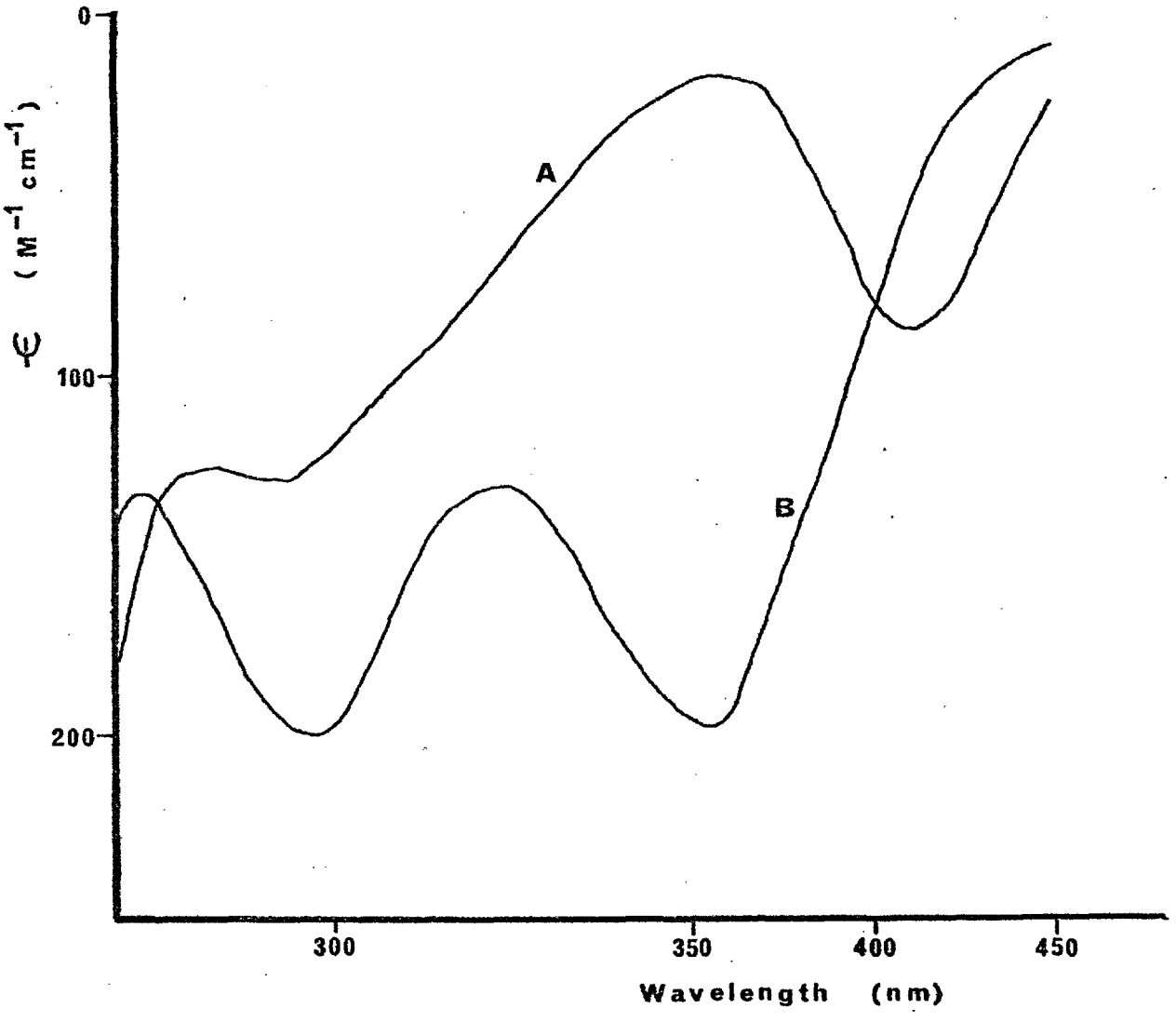


Fig. 3.11 Spectra of dichlorobisethylenediaminerhodium(III) complexes

A <u>trans</u>-$[Rhen_2Cl_2]^+$ B <u>cis</u>-$[Rhen_2Cl_2]^+$

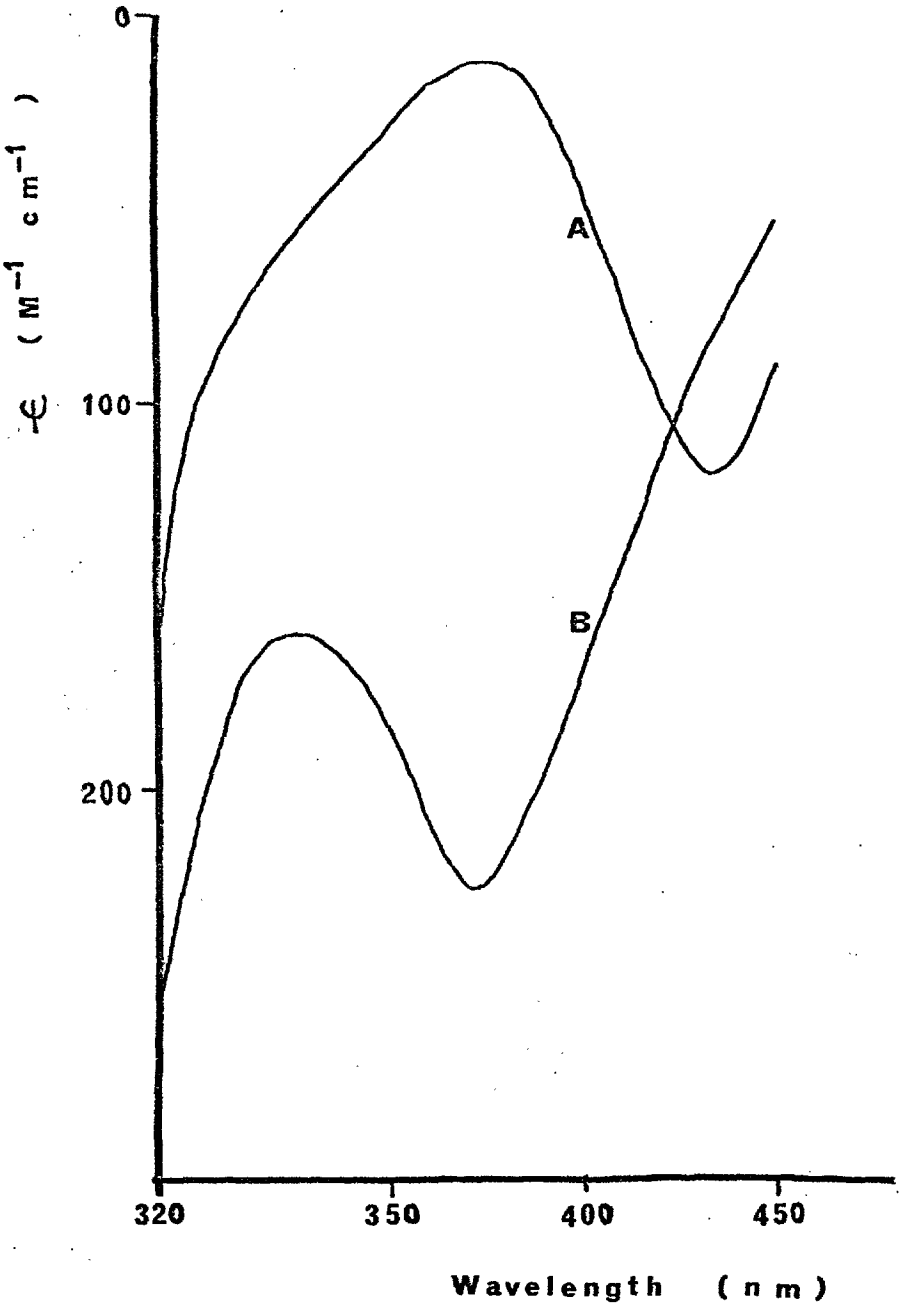


Fig. 3.12 Spectra of dibromobisethylenediaminerhodium(III) complexes

A <u>trans</u>-[$Rhen_2Br_2$]$^+$ B <u>cis</u>-[$Rhen_2Br_2$]$^+$

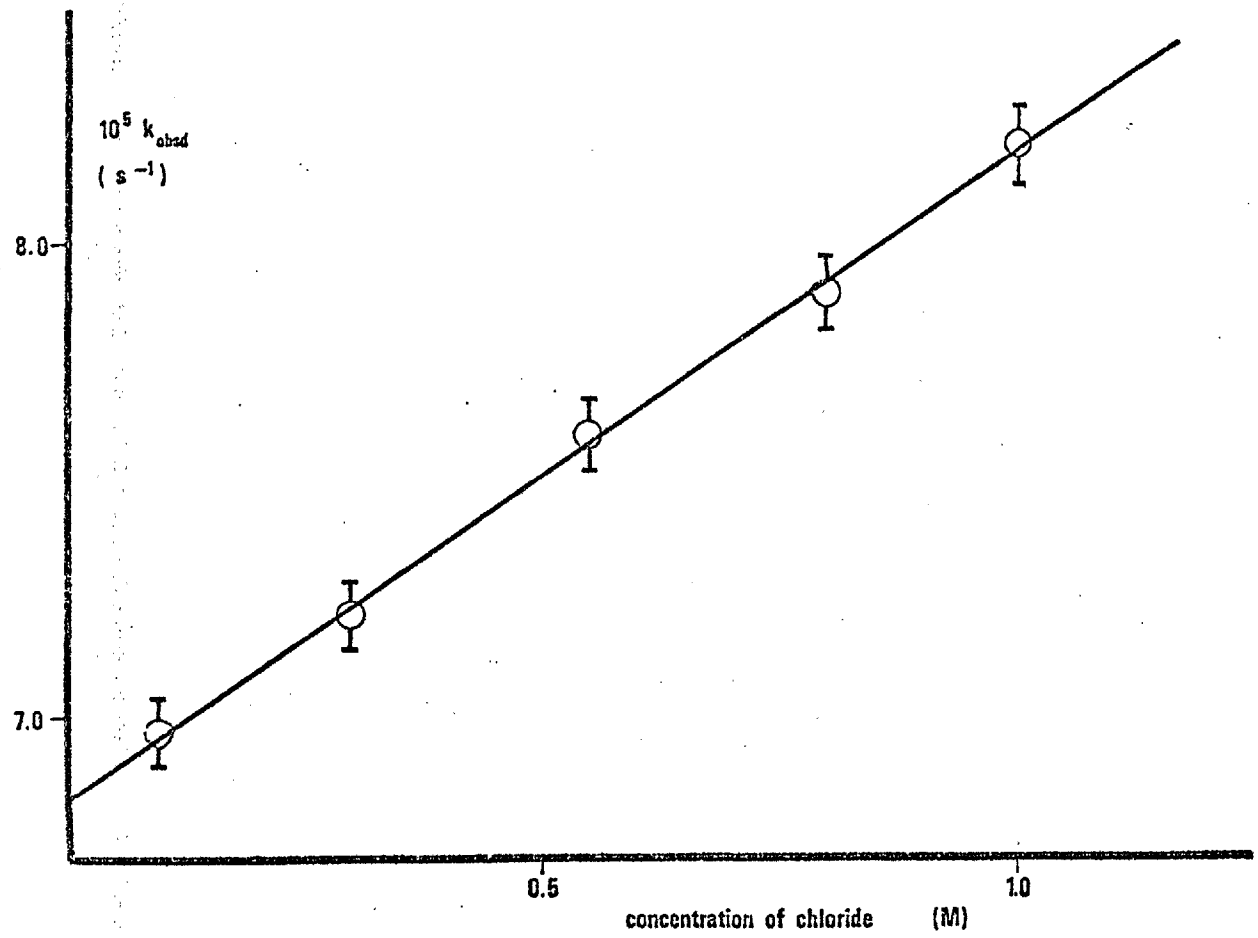


Fig. 3.13 The dependence of the pseudo-first-order rate constant for substitution of <u>trans</u>-$[Rhen_2I_2]^+$ on the concentration of added chloride ion at 45.4 °C

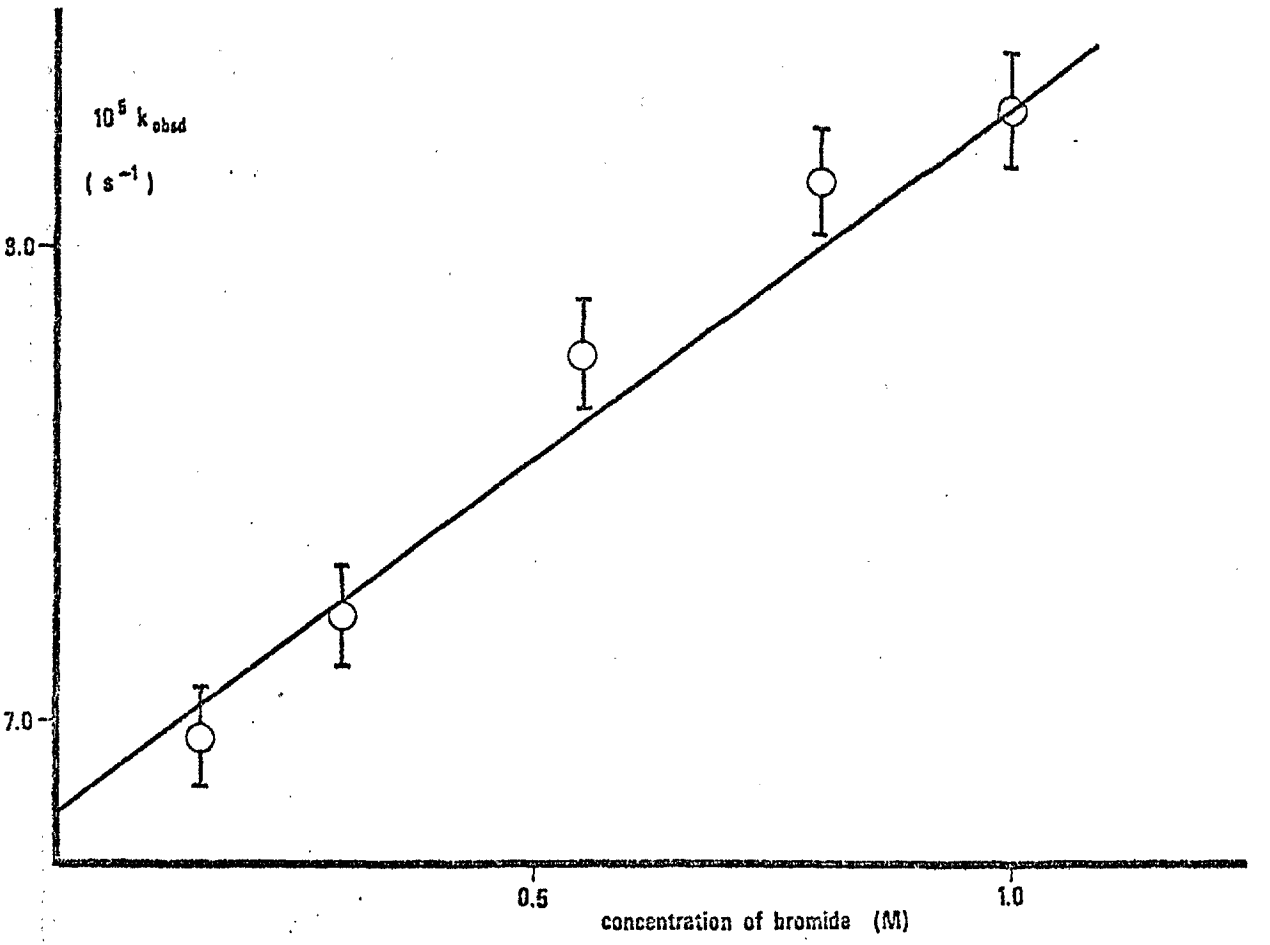


Fig. 3.14 The dependence of the pseudo-first-order rate constant for substitution of <u>trans</u>-$[Rhen_2I_2]^+$ on the concentration of added bromide ion at 45.3 °C

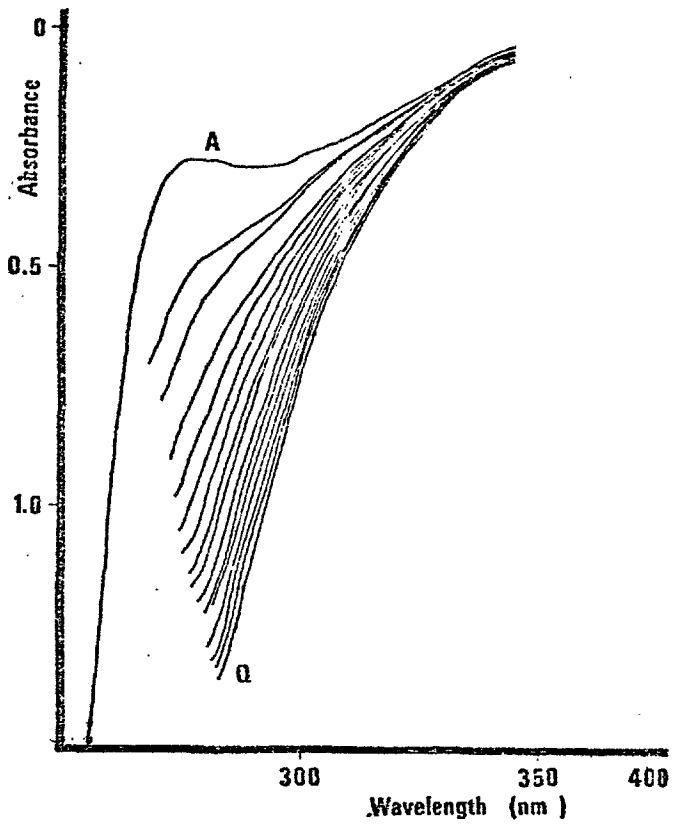


Fig. 3.15 The spectroscopic interaction between <u>trans</u>-$[Rhen_2Cl_2]^+$ and iodide

[complex] = 2.412×10^{-3} M

Spectra from A to Q are of increasingly more concentrated iodide solutions

For A $[I^-] = 0$

For Q $[I^-] = 3.005$ M

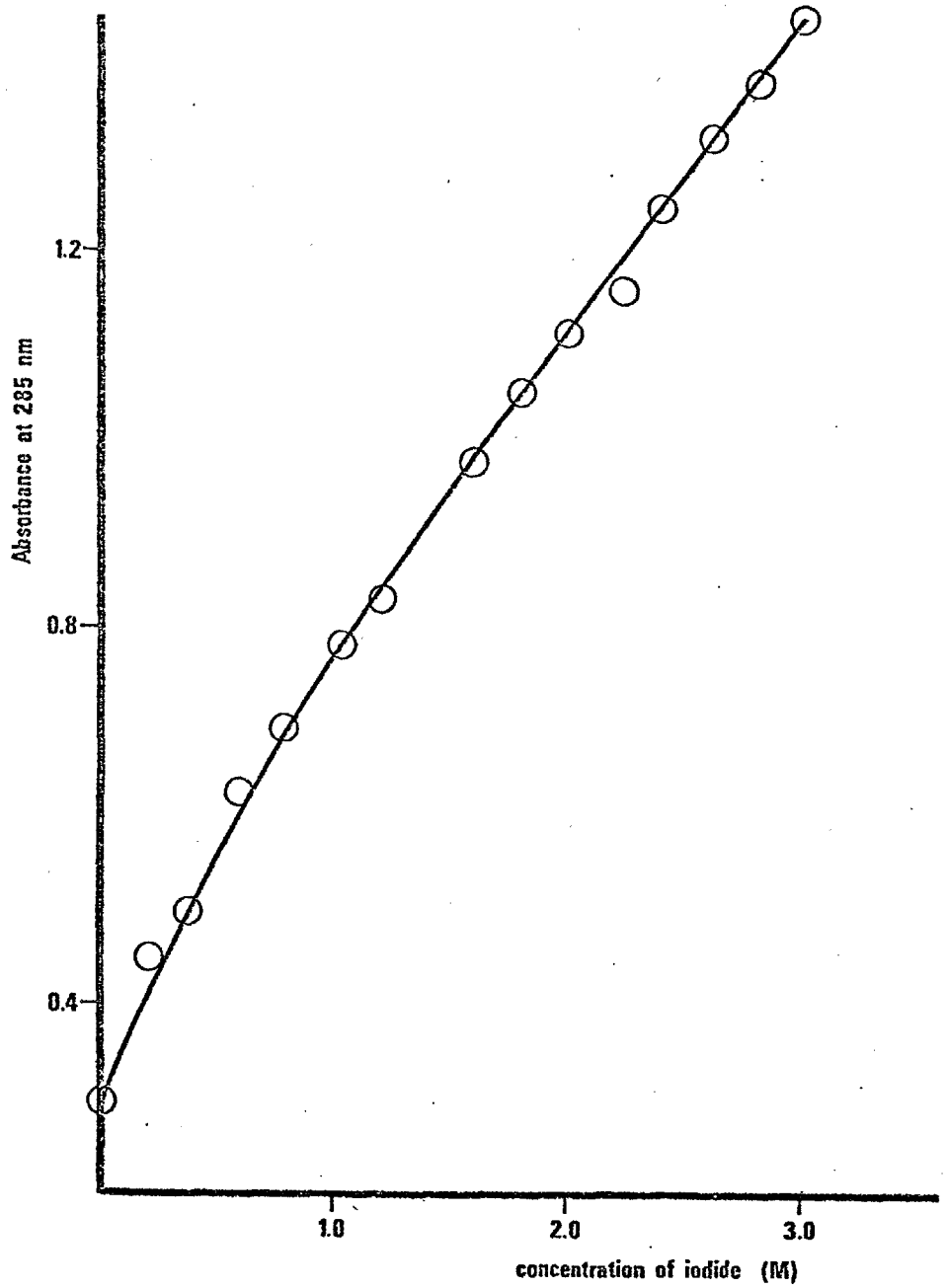


Fig. 3.16 The absorbance at 285 nm of <u>trans</u>-$[Rhen_2Cl_2]^+$ solutions as a function of added iodide ion

[complex] = 2.412×10^{-3} M

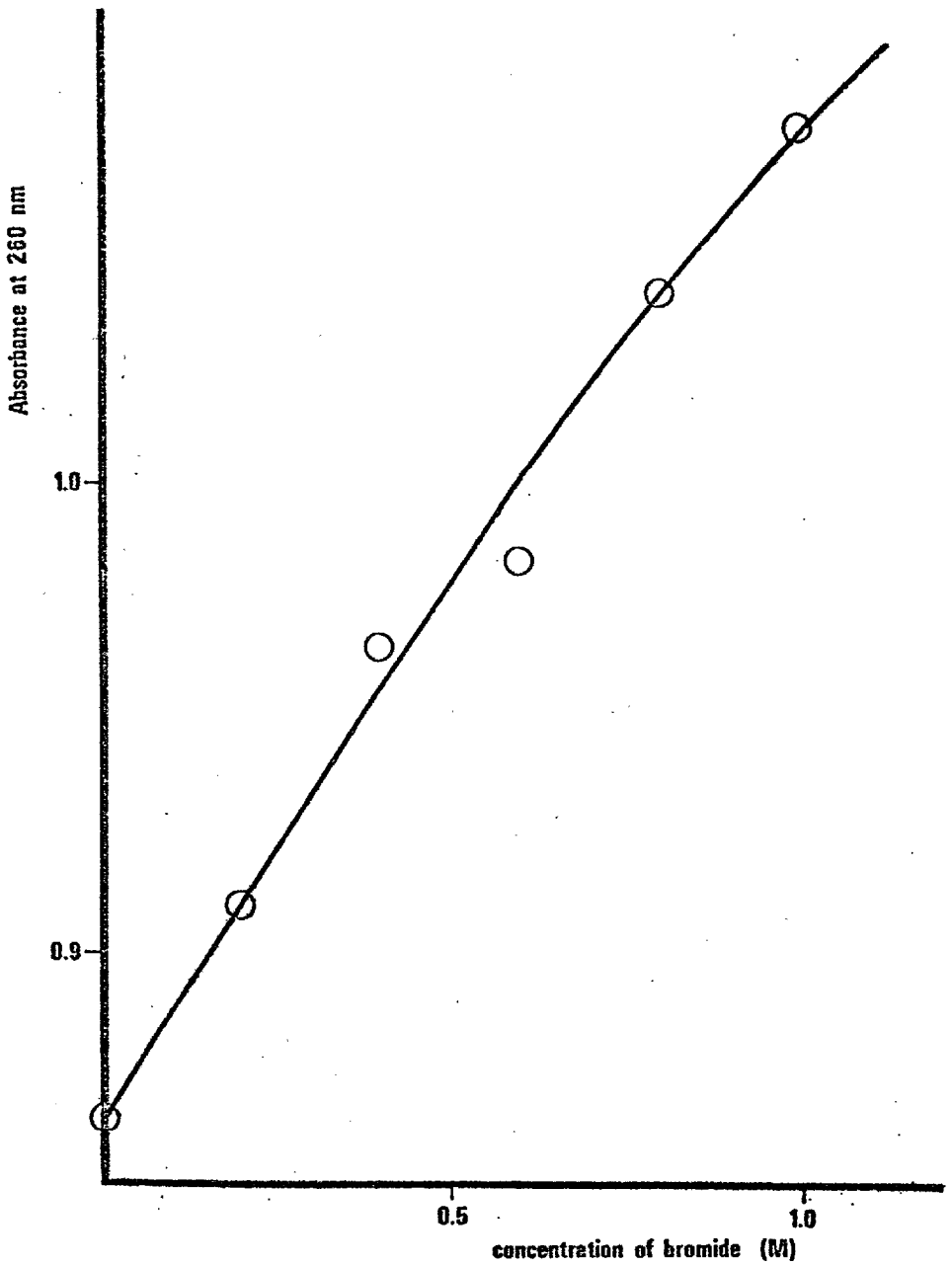


Fig. 3.17 The absorbance at 260 nm of <u>trans</u>-$[Rhen_2Cl_2]^+$ solutions as a function of added bromide ion

[complex] = 2.309×10^{-3} M

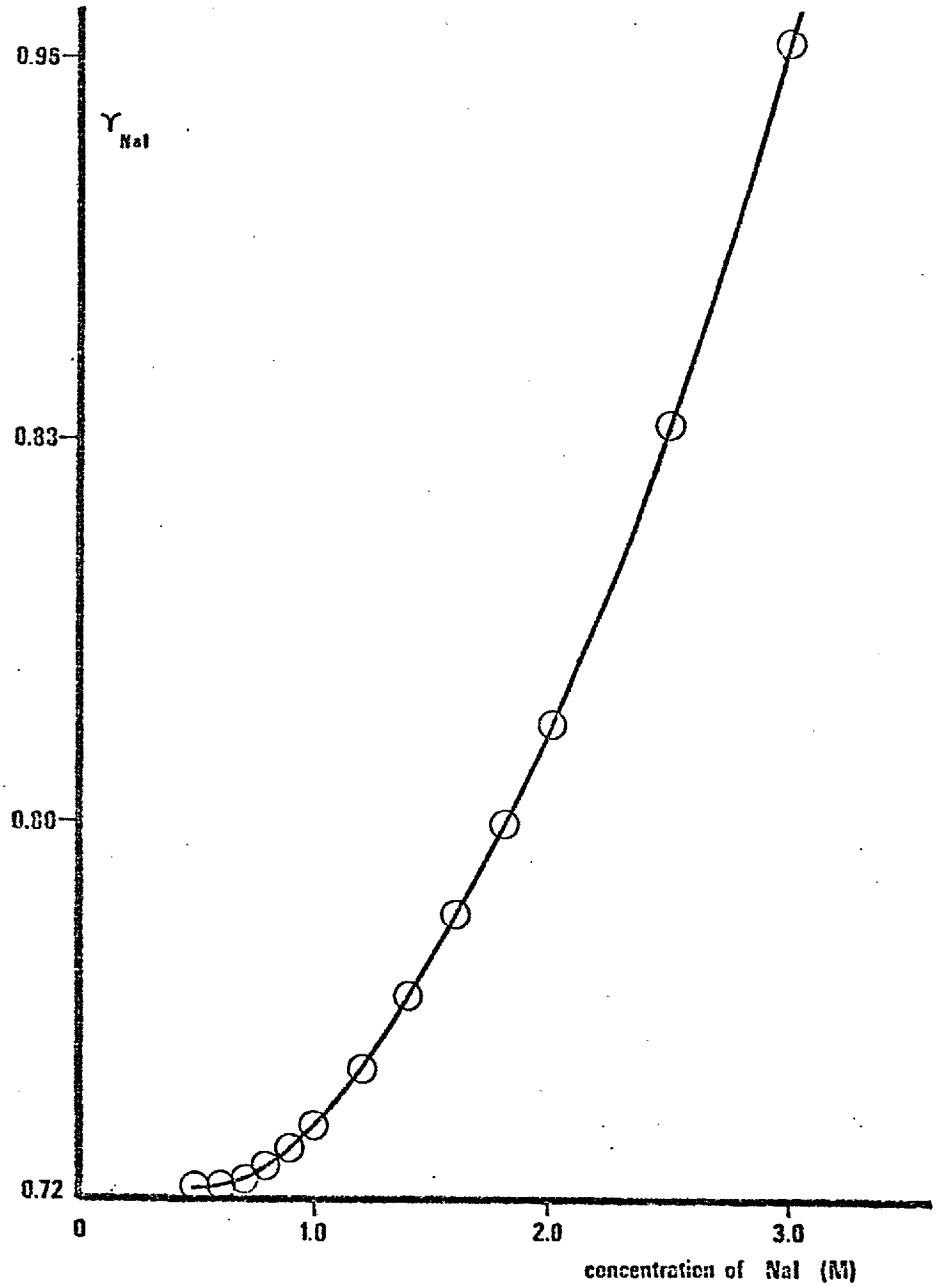


Fig. 3.18 The activity coefficient of sodium iodide as a function of ionic strength

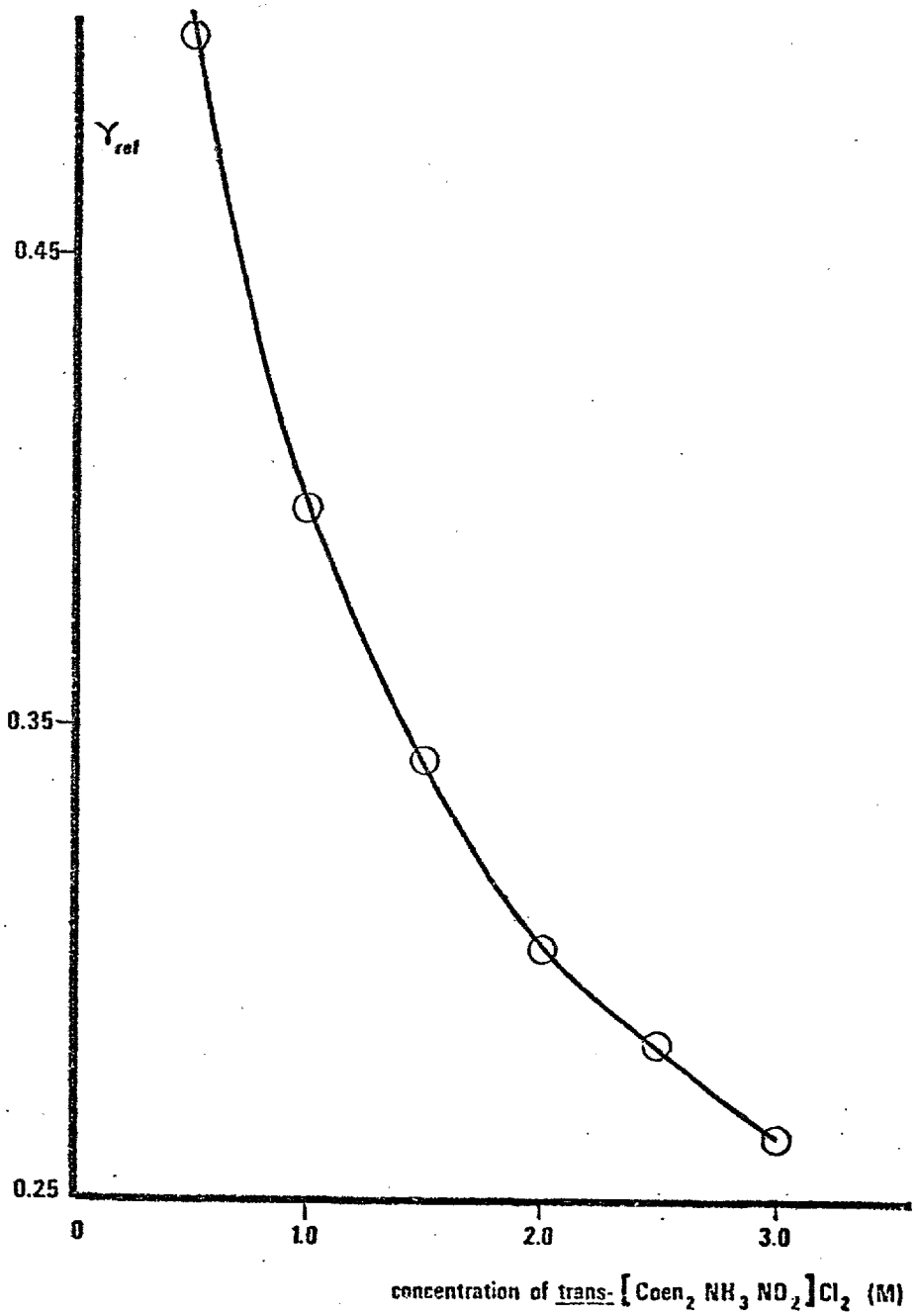
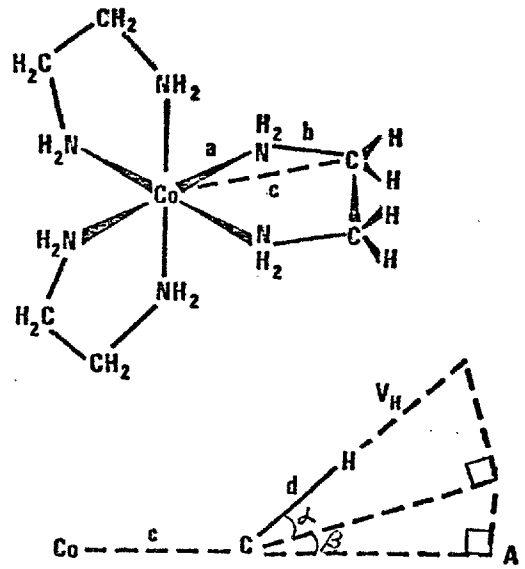


Fig. 3.19 The activity coefficient of the salt trans-$[Coen_2NH_3NO_2]Cl_2$ as a function of ionic strength



$$c^2 = a^2 + b^2 - 2ab \cos \angle CoNC$$

$$\cos \angle CoCN = (b^2 + c^2 - a^2) / 2bc$$

$$\beta = (\angle NCC) / 2 - \angle CoCN$$

$$r_+ = CoA = c + (d + V_H) \cos\alpha \cos\beta$$

From reference 19

$a = 1.96$ Å ; $b = 1.48$ Å

$\angle CoNC = 112°$; $\angle NCC = 107°$

From references 101 and 135

d = sum of covalent radii of C and H = 1.05 Å

V_H = Van de Waals radius of H = 1.2 Å

α = one half the Tetrahedral angle = 55°

Fig. 3.20 The molecular dimensions of the $[Coen_3]^{3+}$ cation and the estimation of its ionic radius

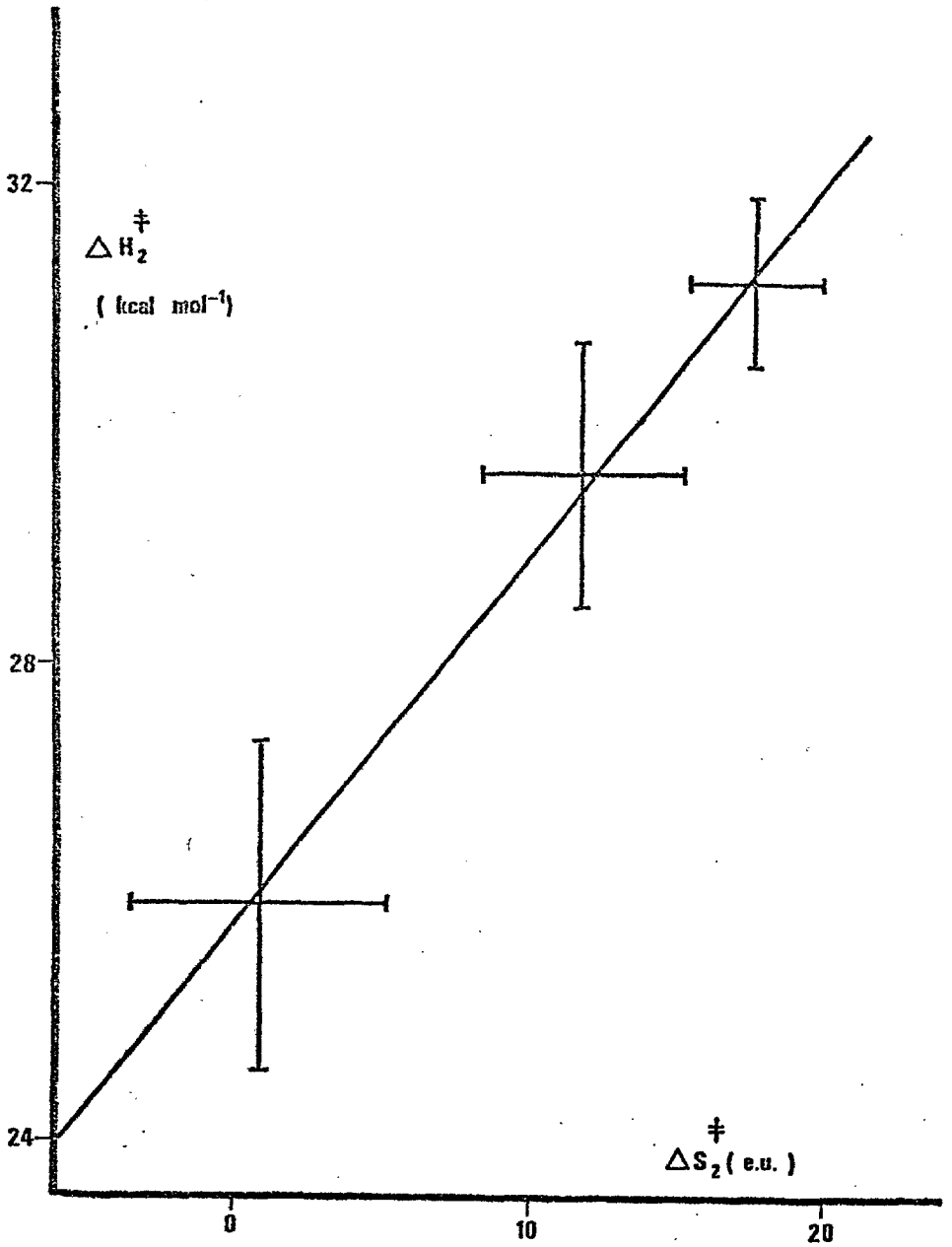


Fig. 3.21 Isokinetic relationship for ligand-dependent pathways in the substitution reactions of <u>trans</u>-$[Rhen_2I_2]^+$

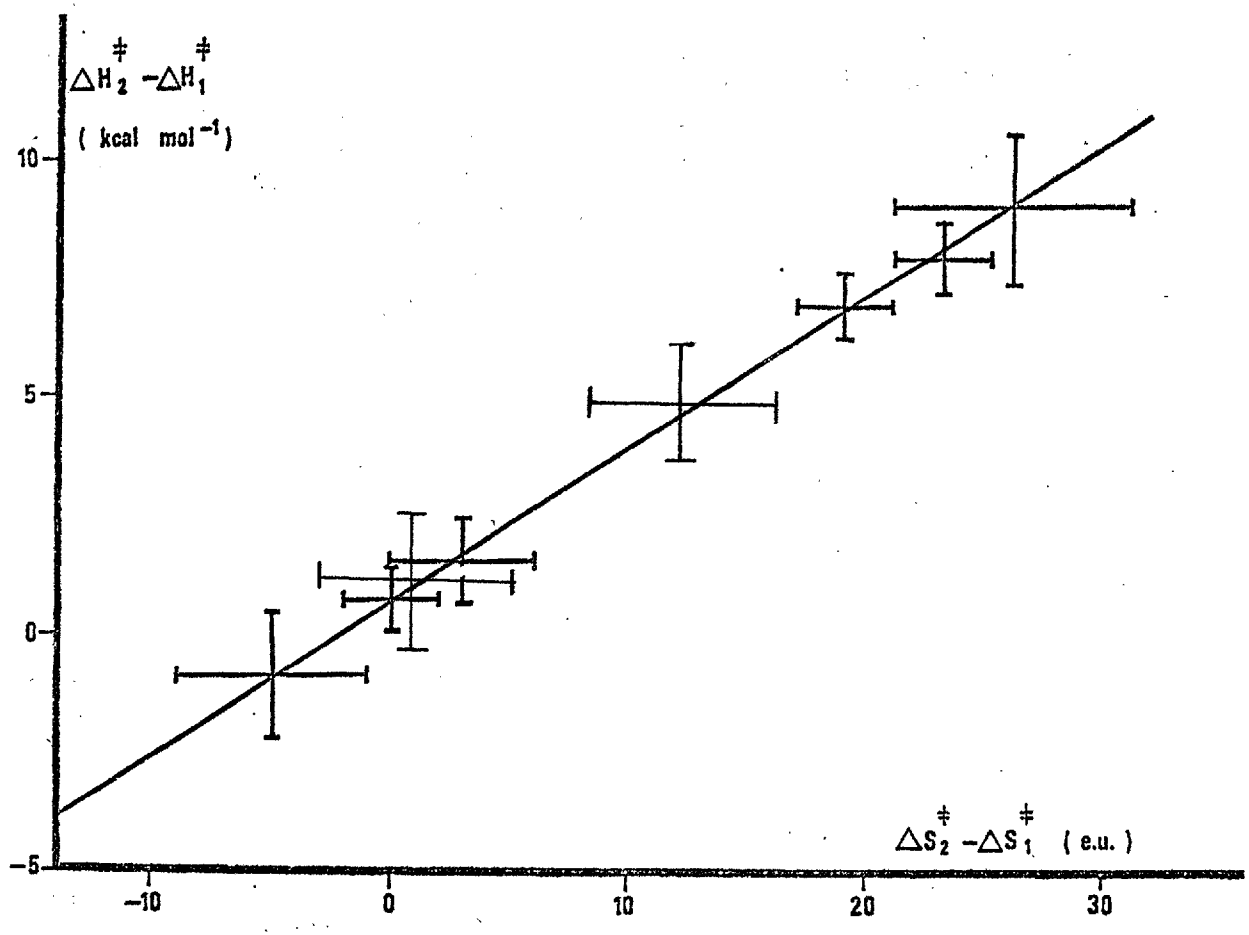


Fig. 3.2 2 Pseuo-isokinetic relationship for ligand-dependent pathways in the substitution reactions of <u>trans</u>-[Rhen$_2$LX]$^+$

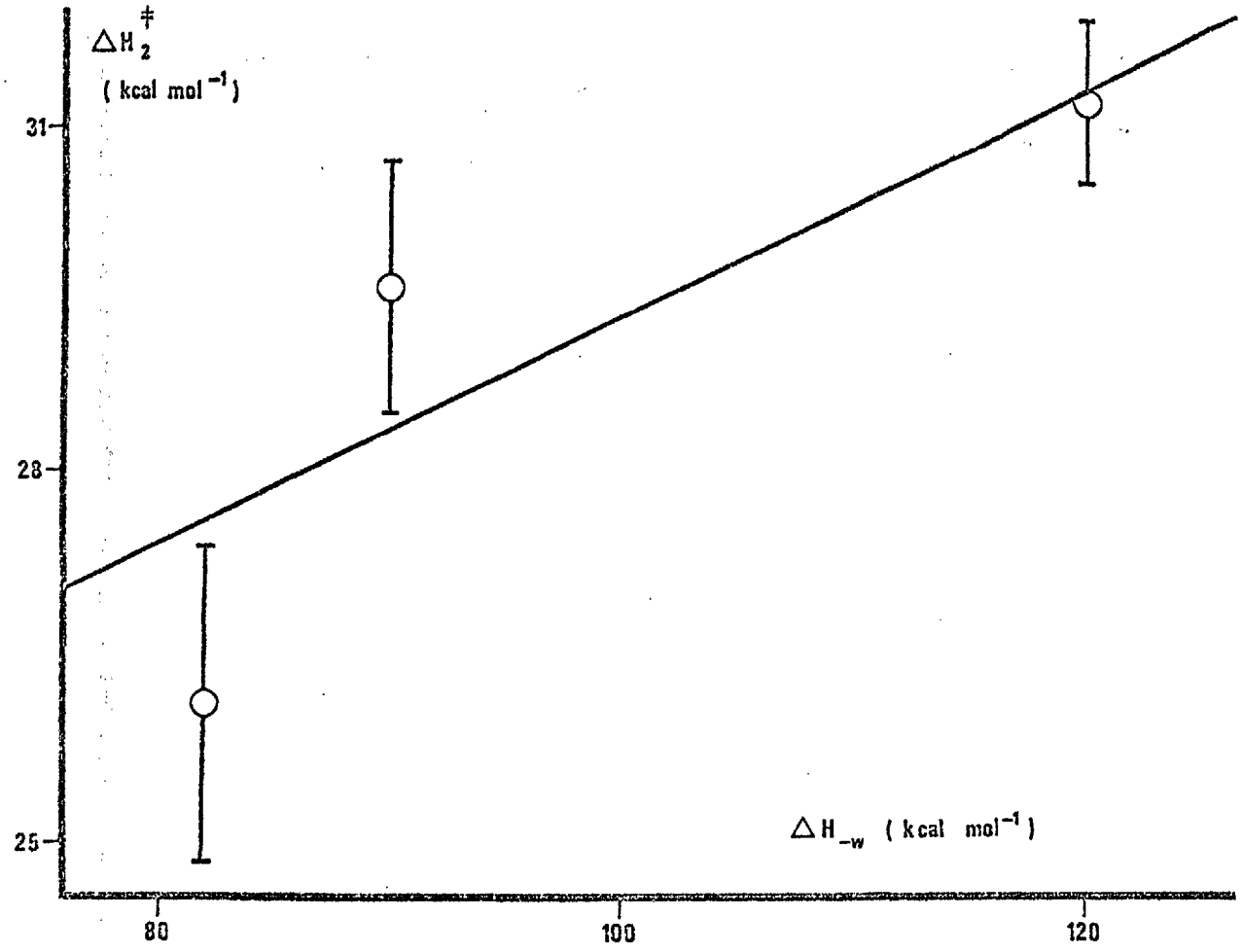


Fig. 3.23 The relationship between the enthalpy of activation of the ligand-dependent pathways for substitution in <u>trans</u>-$[Rhen_2I_2]^+$ and the enthalpy of desolvation of the entering ligand

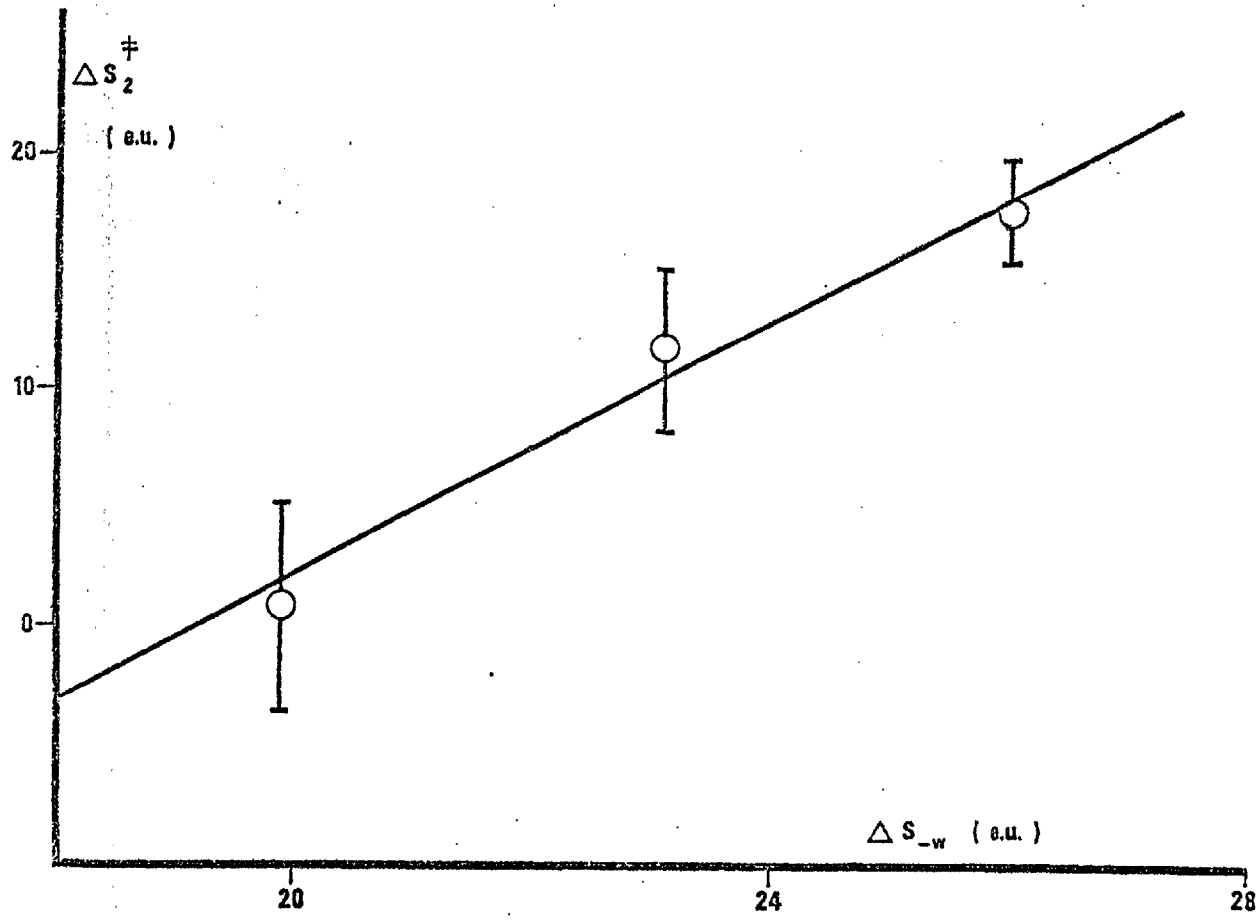
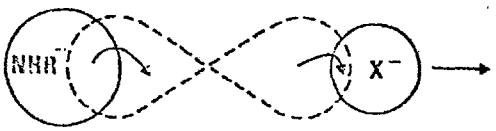
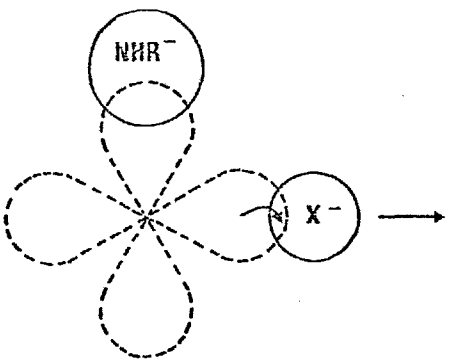


Fig. 3.24 The relationship between the entropy of activation of the ligand-dependent pathways for substitution in <u>trans</u>-$[Rhen_2I_2]^+$ and the entropy of desolvation of the entering ligand

Case A — The amido-group is trans to the leaving group in an incipient square pyramidal transition state



Case B — The amido-group is cis to the leaving group in an incipient square pyramidal transition state



Case C — The amido-group, the original trans-ligand and the leaving group form the trigonal plane of an incipient trigonal bipyramidal transition state

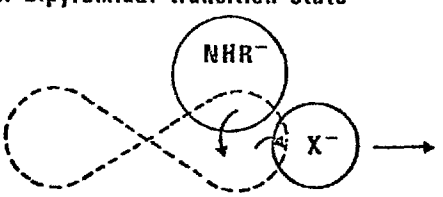


Fig. 3.25 Movements of electron density, indicated by arrows (↷), in the dissociative substitution of the conjugate base $[Rhen(en\text{-}H)LX]^{n+}$

CHAPTER 4

The Trans-Effect of Hydroxide

Introduction

Basolo and Pearson[1] have defined the trans-effect of the ligand L in the complex trans-$[MA_4LX]^{n+}$ as the effect of L on the rate of loss of X; the complex is considered to show a trans-effect if the effect of changing L is greater than the effect of changing the cis-ligands, A. Similarly, if the ligand L weakens the M-X bond in the ground-state complex trans-$[MA_4LX]^{n+}$ more than it does in the complex cis-$[MA_4LX]^{n+}$, L can be said to exhibit a trans-influence. Not all workers have agreed with these definitions, and the condition that trans-effects and trans-influences be greater than the corresponding cis-effects and cis-influences has often been omitted.[2][3]

The trans-influence of L is measured by the effect of changing L on an equilibrium property (such as i.r. stretching frequency, bond length, n.m.r. parameters) of the M-X bond. Appleton et al.[3] have compared the various methods for measuring the trans-influence; both the effect of L on the hybridisation of the M-X bond, and the net charge transfer by σ- and π-bonding from L to M appear to be important in determining the magnitude of the trans-influence. The various methods differ in their relative sensitivities to these two factors, so that no unambiguous estimate of the effect of L on the strength of the M-X bond can be obtained from the physical properties of the complexes.

The Thermodynamic Trans-Effect

Poë and his co-workers[4]-[6] have discussed the effect of L in

trans-$[Rhen_2LX]^{n+}$ (X = a halide) on the softness, or class (b) character, of the $\{Rhen_2L\}^{(n+1)+}$ moiety. This is formally a trans-influence, but Poë et al. have called it the thermodynamic trans-effect (TTE). Because it is measured by truly thermodynamic quantities, and because the concept of the TTE is intimately related to studies on the kinetic trans-effect, the distinction of the TTE from other trans-influences seems justified. The relative enthalpies of the complex ions are much more sensitive than their free energies to the nature of L,[4] and the TTE is more usefully defined in terms of enthalpies, rather than equilibrium constants. The TTE of L is measured by the slope dH^0_{LX}/dH^0_{ClX} of the graph of H^0_{LX} against H^0_{ClX}, where H^0_{LX}, H^0_{ClX} are the relative enthalpies of trans-$[Rhen_2LX]^{n+}$ and trans-$[Rhen_2ClX]^{+}$ respectively (X = Cl , Br , I). The enthalpy of trans-$[Rhen_2LI]^{n+}$ is invariably greater than that of trans-$[Rhen_2LCl]^{n+}$, but as the $\{Rhen_2L\}^{(n+1)+}$ moiety becomes softer (in the Pearson[7] sense) the enthalpy of trans-$[Rhen_2LI]^{n+}$ decreases relative to that of trans-$[Rhen_2LCl]^{n+}$. Thus a small value of dH^0_{LX}/dH^0_{ClX} corresponds to a large thermodynamic trans-effect of L. When L is H_2O, dH^0_{LX}/dH^0_{ClX} cannot be measured directly, because the graph of $H^0_{H_2OX}$ against H^0_{ClX} is not linear.[5] However, $H^0_{H_2OI} - H^0_{H_2OCl}$ can be calculated by the equation

$$(H^0_{H_2OI} - H^0_{H_2OCl}) - (H^0_{ClI} - H^0_{ClCl}) = \Delta H^{\ddagger}_{ClOH_2/Cl} - \Delta H^{\ddagger}_{IOH_2/Cl} - (\Delta H^{\ddagger}_{ClCl/H_2O} - \Delta H^{\ddagger}_{ICl/H_2O}) \qquad (4.1)$$

where $\Delta H^{\ddagger}_{LX/Y}$ is the enthalpy of activation for the reaction

$$\text{trans-}[Rhen_2LX]^{n+} + Y \longrightarrow \text{trans-}[Rhen_2LY]^{n+} + X \qquad (4.2)$$

In this way $H^0_{H_2OI} - H^0_{H_2OCl}$ was found to be 21.0 ±1.2 kcal mol^{-1}: division

of this value by $H^0_{ClI} - H^0_{ClCl}$ gives $dH^0_{H_2OX}/dH^0_{ClX}$ as 1.12 ±0.06 kcal mol^{-1}. The TTE of L decreases in the order[4]-[6]

$$L = I^- > NH_3 \sim Br^- > Cl^- > H_2O \qquad (4.3)$$

$$dH^0_{LX}/dH^0_{ClX} = 0.66; \quad 0.81; \quad 0.85; \quad 1.00; \quad 1.12 \qquad (4.4)$$

In their discussion of the TTE, Poë and Bounsall[4] pointed out that in comparing the thermodynamic trans-effects of two halide ligands L and L' on the same Rh-X indicator bond, it was necessary to also consider the thermodynamic trans-effect of X on the Rh-L and Rh-L' bonds. If we consider the case where L, L' and X are all halide ions, we can assume that the TTE of a ligand L on the trans Rh-X bond is due to the product of two terms: the trans-bond weakening effect (TBWE) of L, and the susceptibility to trans-bond weakening (STBW) of X. If H^0(Rh-I) and H^0(Rh-Cl) are the bond energies of isolated Rh-I and Rh-Cl bonds, α and β are the TBWE of I^- and Cl^-, and a and b are the STBW of I^- and Cl^- respectively, then

$$H^0_{II} - H^0_{ICl} = H^0(Rh\text{-}I) - H^0(Rh\text{-}Cl) + 2\alpha a - (\alpha b + \beta a) \qquad (4.5)$$

$$H^0_{ICl} - H^0_{ClCl} = H^0(Rh\text{-}I) - H^0(Rh\text{-}Cl) + (\alpha b + \beta a) - 2\beta b \qquad (4.6)$$

Experimentally the TTE of iodide is greater than that of chloride,[4] i.e.

$$H^0_{II} - H^0_{ICl} < H^0_{ICl} - H^0_{ClCl} \qquad (4.7)$$

Rearrangement of equation 4.7 gives

$$2H^0_{ICl} - H^0_{II} - H^0_{ClCl} > 0 \qquad (4.8)$$

and substitution of equations 4.5 and 4.6 in equation 4.8 gives

$$\alpha b + \beta a - \beta b - \alpha a > 0 \qquad (4.9)$$

i.e.,

$$(\alpha-\beta)(b-a) > 0 \qquad (4.10)$$

From the inequality 4.10, either $\alpha > \beta$ and $b > a$ or $\alpha < \beta$ and $b < a$. The i.r. stretching frequency ν_{Rh-Br} of the Rh-Br bond in trans-$[Rhen_2IBr]^+$ is lower than ν_{Rh-Br} for trans-$[Rhen_2ClBr]^+$,[4] which indicates that in fact α is greater than β and therefore b is greater than a. The rhodium-chloride bond is stronger than the rhodium-iodide bond,[8] so it appears that the susceptibility to trans-bond weakening is directly related to the strength of the rhodium-halide bond, stronger bonds being more susceptible to trans-bond weakening. This postulate explains the very high thermodynamic trans-effects found for the partially dissociated chloride and bromide ligands in the transition states $\{Rhen_2X...Cl\}^+$ and $\{Rhen_2X...Br\}^+$ (X = Cl, Br, I).[2] If $Cl^{\ddagger}$ and $Br^{\ddagger}$ represent the partially dissociated chloro- and bromo-ligands respectively, then $H^0_{Cl^{\ddagger}I} - H^0_{Cl^{\ddagger}Cl}$ is 15.1 kcal mol^{-1} and $H^0_{Br^{\ddagger}I} - H^0_{Br^{\ddagger}Cl}$ is 11.4 kcal mol^{-1}. This gives the TTE of $Cl^{\ddagger}$ as 0.81, approximately equal to the TTE of NH_3, whereas the TTE of $Br^{\ddagger}$ is 0.61, greater even than that of I^-. The high values obtained for the TTE of $Cl^{\ddagger}$ and $Br^{\ddagger}$ need not imply that the trans-bond weaking effects of these ligands are high. If γ is the TBWE of $Cl^{\ddagger}$ and c the STBW of the Rh-$Cl^{\ddagger}$ bond, then

$$H^0_{Cl^{\ddagger}I} - H^0_{Cl^{\ddagger}Cl} = H^0(Rh-I) - H^0(Rh-Cl) + (\gamma a+\alpha c) - (\gamma b+\beta c) \qquad (4.11)$$

Experimentally, it is found that[2]

$$H^0_{Cl^{\ddagger}I} - H^0_{Cl^{\ddagger}Cl} < H^0_{ClI} - H^0_{ClCl} \qquad (4.12)$$

Substituting equations 4.11 and 4.6 in equation 4.12 gives

$$\gamma a + \alpha c - \gamma b - \beta c < \alpha b + \beta a - 2\beta b \qquad (4.13)$$

Rearrangement of equation 4.13 gives

$$(b-c)(\alpha-\beta) + (\gamma-\beta)(b-a) > 0 \qquad (4.14)$$

From equation 4.14 it can be seen that the high TTE of $Cl^{\ddagger}$ may be due to the susceptibility to trans-bond weakening of Cl^{-} being very much less than that of a "normal" chloride ligand: this factor could completely outweigh the effect of the differing trans-bond weakening effects of $Cl^{\ddagger}$ and Cl. Thus care must be exercised in deducing relative trans-bond weakening effects from relative thermodynamic trans-effects.

The Kinetic Trans-Effect

In octahedral complexes the kinetic trans-effect (KTE) is by no means as well documented as the trans-influence. There are a few isolated examples of the KTE reported for complexes of iridium(III),[9][10] chromium(III)[11] and rhenium(V),[12] and more extensive studies have been made of the KTE in cobalt(III)[13]-[16] and rhodium(III)[2][5][6][17]-[19] complexes. For the amine complexes of cobalt(III), large trans-effects exist in the sense that the nature of the ligand L has a profound effect on the rate of loss of X from trans-$[Coen_2LX]^{n+}$: however, this trans-effect is generally similar in magnitude to the cis-effect of L in cis-$[Coen_2LX]^{n+}$.[20] In tetramine complexes of cobalt(III) ligand effects are therefore predominantly non-directional. The exceptions to this rule are sulphite, and alkyl ligands, which have very specific trans-labilising properties.[15]

In the cobalamin complexes, and in the cobalamin "model" complexes of dimethylglyoxime and its analogues, there has been much investigation

of kinetic trans-effects. Since the cis-isomers of these complexes do not exist, there is no possibility of measuring the corresponding cis-effects, but Pratt and Thorp[13] have suggested that there is little difference between the cobalamins or glyoxime complexes and the "normal" amine complexes of cobalt(III), ligand-effects being non-directional in both cases.

For rhodium(III) complexes, however, it appears that specific kinetic trans-effects do indeed exist. The rate of chloride loss from trans-$[Rhen_2NO_2Cl]^+$ is 75 times greater than the rate of chloride loss from cis-$[Rhen_2NO_2Cl]^+$, indicating that NO_2^- has a high KTE.[19] Chloride and hydroxide appear to have low kinetic trans-effects, comparable to that of ethylenediamine, when measured by the relative rates of chloride loss from cis- and trans-$[Rhen_2LCl]^+$ ($L = Cl^-, OH^-$).[19][21]

There has been some speculation about the cause of this difference between rhodium(III) and cobalt(III) complexes. Pearson and Basolo[16] suggested that the failure to observe a specific trans-effect in $[Coen_2LX]^+$ was due to opposing σ- and π-donor effects of L on the energy of the transition state. The transition state is most effectively stabilised by σ-donation from L when L is trans to the leaving group, and by π-donation when L is cis to the leaving group. In rhodium(III) complexes π-bonding seems to be relatively unimportant, and a specific trans-effect is observed. Langford,[22] however, feels that the difference between rhodium(III) and cobalt(III) complexes can be explained if in forming σ-bonds rhodium(III) uses p-orbitals, and cobalt(III) uses d-orbitals. p-Orbitals specifically connect trans-ligands, whereas d-orbitals connect both cis- and trans-ligands.

Poë and his co-workers[2][5][6][17] have carried out systematic

studies on the trans-effect of L in trans-$[Rhen_2LX]^+$; these provide information about the nature of the interaction between trans-ligands, although since detailed studies of the cis-complexes are lacking, it is not clear whether the effects observed are specific trans-effects. The kinetic trans-effect (KTE) of L can be measured by the quantity Δ_L, which is defined as

$$\Delta_L = \Delta H^{\ddagger}_{LX/Y} - \Delta H^{\ddagger}_{IX/Y} \qquad (4.15)$$

$\Delta H^{\ddagger}_{LX/Y}$ and $\Delta H^{\ddagger}_{IX/Y}$ are the enthalpies of activation for reactions 4.16 and 4.17 respectively.

$$\text{trans-}[Rhen_2LX]^{n+} + Y \rightarrow \text{trans-}[Rhen_2LY]^{n+} + X \qquad (4.16)$$

$$\text{trans-}[Rhen_2IX]^{n+} + Y \rightarrow \text{trans-}[Rhen_2IY]^{n+} + X \qquad (4.17)$$

(Since substitution reactions of rhodium(III) complexes occur by an aquo-intermediate[36], either X or Y in equations 4.15 to 4.17 must be H_2O). Small values of Δ_L correspond to large kinetic trans-effects[2]. However, using the definition of equation 4.15, the magnitude of the KTE of L depends on the nature of X,[5][6] softer leaving groups giving smaller values of Δ_L, and hence larger values of the KTE. This can be understood by considering the enthalpy changes occurring during the reactions

$$\text{trans-}[Rhen_2LX]^{n+} + H_2O \rightleftharpoons \text{trans-}[Rhen_2LOH_2]^{(n+1)+} + X^- \qquad (4.18)$$

$$\text{trans-}[Rhen_2IX]^{+} + H_2O \rightleftharpoons \text{trans-}[Rhen_2IOH_2]^{2+} + X^- \qquad (4.19)$$

$\Delta H^{\ddagger}_{LX/H_2O}$ and $\Delta H^{\ddagger}_{IX/H_2O}$ are the enthalpies of activation for reactions 4.18 and 4.19 proceeding from left to right; $\Delta H^{\ddagger}_{LOH_2/X}$ and $\Delta H^{\ddagger}_{IOH_2/X}$ are the enthalpies of activation for the reverse reactions.

From equation 4.15

$$\Delta_L = \Delta H^{\ddagger}_{LX/H_2O} - \Delta H^{\ddagger}_{IX/H_2O} \quad (4.20)$$

But

$$H^0_{LX^{\ddagger}} = \Delta H^{\ddagger}_{LX/H_2O} + H^0_{LX} + H^0_{H_2O} \quad (4.21)$$

$$H^0_{IX^{\ddagger}} = \Delta H^{\ddagger}_{IX/H_2O} + H^0_{IX} + H^0_{H_2O} \quad (4.22)$$

where $H^0_{LX^{\ddagger}}$ and $H^0_{IX^{\ddagger}}$ are the enthalpies of the transition states for reactions 4.18 and 4.19 respectively.

Substituting equations 4.22 and 4.21 in equation 4.20 gives

$$\Delta_L = H^0_{LX^{\ddagger}} - H^0_{IX^{\ddagger}} + (H^0_{IX} - H^0_{LX}) \quad (4.23)$$

Similarly, from equation 4.15

$$\Delta_L = \Delta H^{\ddagger}_{LOH_2/X} - \Delta H^{\ddagger}_{IOH_2/X} \quad (4.24)$$

But

$$H^0_{LX^{\ddagger}} = \Delta H^{\ddagger}_{LOH_2/X} + H^0_{LOH_2} + H^0_X \quad (4.25)$$

$$H^0_{IX^{\ddagger}} = \Delta H^{\ddagger}_{IOH_2/X} + H^0_{IOH_2} + H^0_X \quad (4.26)$$

Substituting equations 4.25 and 4.26 in equation 4.24 gives

$$\Delta_L = H^0_{LX^{\ddagger}} - H^0_{IX^{\ddagger}} + (H^0_{IOH_2} - H^0_{LOH_2}) \quad (4.27)$$

Comparison of equations 4.23 and 4.27 shows that the KTE will only be a constant if

$$H^0_{IX} - H^0_{LX} = H^0_{IOH_2} - H^0_{LOH_2} \quad (4.28)$$

Since the thermodynamic trans-effect of L will not necessarily equal that of iodide, equation 4.28 will not generally be true, and the kinetic trans-effect of L will depend on the reaction used to measure it.

The condition that the KTE of L be independent of the leaving group can be obtained in a different form by adding the quantity $H^0_X - H^0_{H_2O}$ to both sides of equation 4.28, then rearranging to give equation 4.29

$$H^0_{LOH_2} + H^0_X - H^0_{LX} - H^0_{H_2O} = H^0_{IOH_2} + H^0_X - H^0_{IX} - H^0_{H_2O} \qquad (4.29)$$

Thus the KTE of L will be independent of the leaving roup if the molar enthalpy changes ΔH^0 for reactions 4.18 and 4.19 are the same. In order to achieve this condition, Poë et al.[6] constructed curves of $\Delta H^{\ddagger}$ against ΔH^0 for the reactions

$$\underline{\text{trans}}\text{-}[Rhen_2LX]^{n+} + H_2O \longrightarrow \underline{\text{trans}}\text{-}[Rhen_2LOH_2]^{(n+1)+} + X^- \qquad (4.30)$$

$$\underline{\text{trans}}\text{-}[Rhen_2LOH_2]^{(n+1)+} + X^- \longrightarrow \underline{\text{trans}}\text{-}[Rhen_2LX]^{n+} + H_2O \qquad (4.31)$$

These curves are shown in Fig. 4.1. The intrinsic kinetic <u>trans</u>-effect (IKTE) of L is now measured by Δ^0_L, which is defined as the vertical distance between the curve obtained when the <u>trans</u>-ligand is L, and the curve for the <u>trans</u>-iodo-ligand; this distance corresponds to the difference in $\Delta H^{\ddagger}$ for reaction 4.18 and the corresponding reaction 4.19a of the hypothetical complex <u>trans</u>-$[Rhen_2IZ]^+$ which proceeds with the same value of ΔH^0 as reaction 4.18

$$\underline{\text{trans}}\text{-}[Rhen_2IZ]^+ + H_2O \rightleftharpoons \underline{\text{trans}}\text{-}[Rhen_2IOH_2]^{2+} + Z^- \qquad (4.19a)$$

The IKTE series obtained by Poë, Shaw and Wendt[6] was

$$L = I^- > Br^- > NH_3 \geq Cl^- \qquad (4.32)$$

Values of Δ^0_L increase along this series.

The IKTE of hydroxide has not been studied, but estimates of its kinetic <u>trans</u>-effect (uncorrected for thermodynamic effects) can be obtained using equation 4.15 and the reactions

$$\underline{\text{trans}}\text{-}[Rhen_2LCl]^{n+} + H_2O \longrightarrow \underline{\text{trans}}\text{-}[Rhen_2LOH_2]^{(n+1)+} + Cl^- \qquad (4.33)$$

$$\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{LBr}]^{n+} + H_2O \longrightarrow \underline{\text{trans}}\text{-}[\text{Rhen}_2\text{LOH}_2]^{(n+1)+} + Br^- \quad (4.34)$$

$$\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{LOH}_2]^{(n+1)+} + I^- \longrightarrow \underline{\text{trans}}\text{-}[\text{Rhen}_2\text{LI}]^{n+} + H_2O \quad (4.35)$$

However, if the KTE of hydroxide is determined in this way not only the magnitude of the KTE but also the position of hydroxide in the trans-effect series depends on the reaction used. Thus using reaction 4.33 and data from references 2, 6 and 19, the KTE series is

$$L = I^- > OH^- > Br^- > NH_3 > Cl \quad (4.36)$$

$$\Delta H^{\ddagger}_{LCl} - \Delta H^{\ddagger}_{ICl} = 0; \quad 1.2; \quad 2.1; \quad 3.1; \quad 3.8 \text{ kcal mol}^{-1} \quad (4.37)$$

Reaction 4.34 and data from references 2, 6 and 23 give the KTE series

$$L = I^- > NH_3 > Br^- \geq OH^- > Cl^- \quad (4.38)$$

$$\Delta H^{\ddagger}_{LBr} - \Delta H^{\ddagger}_{IBr} = 0; \quad 1.5; \quad 2.1; \quad 2.4; \quad 4.5 \text{ kcal mol}^{-1} \quad (4.39)$$

Finally, reaction 4.35 and data from references 2, 6 and 17 give the KTE series

$$L = I^- > Br^- > OH^- \sim Cl^- > NH_3 \quad (4.40)$$

$$\Delta H^{\ddagger}_{LOH_2} - \Delta H^{\ddagger}_{IOH_2} = 0; \quad 3.2; \quad 5.8; \quad 5.9; \quad 6.4 \text{ kcal mol}^{-1} \quad (4.41)$$

A similar situation occurs when L is NH_3, but in this case the difficulties are removed by using the intrinsic kinetic trans-effect.[6] The aim of the present research was therefore to measure the IKTE of hydroxide and so determine unambiguously the position of hydroxide in the kinetic trans-effect series.

Results

Calculation of the Intrinsic Kinetic Trans-Effect of Hydroxide

(a) From the aquation of trans-$[Rhen_2IOH]^+$ and the iodide anation of trans-$[Rhen_2(OH)OH_2]^{2+}$

As discussed in chapter 3, the base hydrolysis of trans-$[Rhen_2IOH]^+$ obeys the rate law

$$k_{obsd} = k_1 + k_2[OH^-] \qquad (4.42)$$

the term which is independent of the hydroxide concentration corresponding to the reaction

$$\text{trans-}[Rhen_2IOH]^+ + H_2O \longrightarrow \text{trans-}[Rhen_2(OH)OH_2]^{2+} + I^- \qquad (4.43)$$

The rate constants and activation parameters for reaction 4.43 are therefore given by k_1 and the associated values of $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ which are listed in Table 4.1. Thus the enthalpy of activation of reaction 4.43 is 27.81 ±0.18 kcal mol^{-1}. Combining this value with Poë and Shaw's value[17] of 23.81 ±0.15 kcal mol^{-1} for the enthalpy of activation of the reaction

$$\text{trans-}[Rhen_2(OH)OH_2]^{2+} + I^- \longrightarrow \text{trans-}[Rhen_2IOH]^+ + H_2O \qquad (4.44)$$

gives ΔH^0 = 4.00 ±0.23 kcal mol^{-1} for reaction 4.43, and -4.00 ±0.23 kcal mol^{-1} for reaction 4.44. The IKTE of hydroxide was measured by Δ^0_{OH} which is defined as

$$\Delta^0_{OH} = \Delta H^{\ddagger}_{OHX/Y} - \Delta H^{\ddagger}_{ref} \qquad (4.45)$$

where $\Delta H^{\ddagger}_{OHX/Y}$ is the enthalpy of activation for the reaction

$$\text{trans-}[Rhen_2OHX]^{n+} + Y \longrightarrow \text{trans-}[Rhen_2OHY]^{m+} + X \qquad (4.46)$$

and $\Delta H^{\ddagger}_{ref}$ is the enthalpy of activation of the corresponding reaction

$$\underline{trans}\text{-}[Rhen_2IZ]^+ + Y \longrightarrow \underline{trans}\text{-}[Rhen_2IY] + Z \qquad (4.46a)$$

which proceeds with the same molar enthalpy change as reaction 4.46. Values of $\Delta H^{\ddagger}_{ref}$ were interpolated from the curve for $L = I^-$ given in Fig. 4.1 and were 22.69 ±0.17 kcal mol^{-1} for reaction 4.43, and 18.76 ±0.07 kcal mol^{-1} for reaction 4.44. (The error limits in $\Delta H^{\ddagger}_{ref}$ represent the uncertainty induced in the value of $\Delta H^{\ddagger}_{ref}$ by the standard deviation of ΔH^0.) The value of Δ^0_{OH} is thus 5.12 ±0.25 kcal mol^{-1} from reaction 4.43, and 5.05 ±0.17 kcal mol^{-1} from reaction 4.44.

(b) From the aquation of $\underline{trans}\text{-}[Rhen_2BrOH]^+$ and the bromide anation of $\underline{trans}\text{-}[Rhen_2(OH)OH_2]^{2+}$

The base hydrolysis of $\underline{trans}\text{-}[Rhen_2BrOH]^+$ also obeys the rate law of equation 4.42, the hydroxide-independent pathway corresponding to the reaction

$$\underline{trans}\text{-}[Rhen_2BrOH]^+ + H_2O \longrightarrow \underline{trans}\text{-}[Rhen_2(OH)OH_2]^{2+} + Br^- \qquad (4.47)$$

The enthalpy of activation for reaction 4.47 is therefore $\Delta H_1^{\ddagger}$, the enthalpy of activation associated with k_1. $\Delta H_1^{\ddagger}$ was estimated (a) from the temperature-dependence of k_1 and (b) from the temperature-dependence of k_{obsd} at $[OH^-] = 0.032M$, a concentration of hydroxide which is so low that the contribution to k_{obsd} from the term $k_2[OH^-]$ is negligible. Table 4.2 lists the rate constants used, and the enthalpies of activation calculated. The final value for the enthalpy of activation for reaction 4.47 was 26.30 ±0.09 kcal mol^{-1}; this is the weighted mean of the values calculated by methods (a) and (b). The rate of the reaction

$$\underline{trans}\text{-}[Rhen_2(OH)OH_2]^{2+} + Br^- \longrightarrow \underline{trans}\text{-}[Rhen_2BrOH]^+ + H_2O \qquad (4.48)$$

cannot be determined because the subsequent formation of trans-$[Rhen_2Br_2]^+$ complicates the kinetics of reaction 4.48.[5] However, Poë and his co-workers[5][6] have shown that the nucleophilic characters of the halide ions as measured by the relative values of the enthalpies of activation $\Delta H^{\ddagger}_{LOH_2/X}$ for the reaction

$$\text{trans-}[Rhen_2LOH_2]^{(n+1)+} + X^- \longrightarrow \text{trans-}[Rhen_2LX]^{n+} + H_2O \qquad (4.49)$$

are independent of the nature of the ligand L. This is shown clearly in Table 4.3 which lists values of $(\Delta H^{\ddagger}_{LOH_2/Cl} - \Delta H^{\ddagger}_{LOH_2/I})$, $(\Delta H^{\ddagger}_{LOH_2/Br} - \Delta H^{\ddagger}_{LOH_2/I})$ and $(\Delta H^{\ddagger}_{LOH_2/Cl} - \Delta H^{\ddagger}_{LOH_2/Br})$ for a variety of trans-ligands, L. From Table 4.3 the average value of $(\Delta H^{\ddagger}_{LOH_2/Br} - \Delta H^{\ddagger}_{LOH_2/I})$ is 0.77 ±0.27 kcal mol^{-1}. (It is assumed in this calculation that the cis-effect of four ammonia ligands is equal to that of two ethylenediamine ligands; both Shaw[17] and Twigg[24] have shown this to be justified.) The enthalpy of activation for reaction 4.48 is therefore the enthalpy of activation of reaction 4.44 plus 0.77 ±0.27 kcal mol^{-1}, i.e., 24.58 ±0.31 kcal mol^{-1}. The molar enthalpy change associated with reaction 4.47 is thus 1.72 ±0.32 kcal mol^{-1}, and for reaction 4.48 it is -1.72 ±0.32 kcal mol^{-1}. Using these values of ΔH^0, the value of $\Delta H^{\ddagger}_{ref}$ appropriate to reaction 4.47 is 21.14 ±0.20 kcal mol^{-1}, and to reaction 4.48, 19.50 ±0.12 kcal mol^{-1}. Δ^0_{OH} is thus 5.16 ±0.22 kcal mol^{-1} using reaction 4.47, and 5.08 ±0.33 kcal mol^{-1} using reaction 4.48.

(c) From the aquation of trans-$[Rhen_2ClOH]^+$ and the chloride anation of trans-$[Rhen_2(OH)OH_2]^{2+}$

The base hydrolysis of trans-$[Rhen_2ClOH]^+$ also obeys equation 4.42, and the hydroxide-independent pathway corresponds to the reaction

$$\underline{\text{trans}}\text{-}[Rhen_2ClOH]^+ + H_2O \longrightarrow \underline{\text{trans}}\text{-}[Rhen_2(OH)OH_2]^{2+} + Cl^- \qquad (4.50)$$

The enthalpy of activation for reaction is thus $\Delta H_1^{\ddagger}$, the enthalpy of activation associated with k_1, which is 25.14 ±0.15 kcal mol^{-1}. The value of k_{obsd} at 0.033M hydroxide was consistently higher than that predicted by equation 4.42; however, the enthalpy of activation (25.08 ±0.44 kcal mol^{-1}) associated with k_{obsd} at this hydroxide concentration was not distinguishably different from the value of $\Delta H_1^{\ddagger}$. The enthalpy of activation of reaction 4.50 was accordingly taken to be 25.13 ±0.14 kcal mol^{-1}, the weighted mean of the two estimates of this parameter.

The kinetics of the reaction

$$\underline{\text{trans}}\text{-}[Rhen_2(OH)OH_2]^{2+} + Cl^- \longrightarrow \underline{\text{trans}}\text{-}[Rhen_2ClOH]^+ + H_2O \qquad (4.51)$$

cannot be studied because of complications due to the subsequent formation of $\underline{\text{trans}}\text{-}[Rhen_2Cl_2]^+$. The enthalpy of activation of reaction 4.51 was calculated using the average value of $(\Delta H^{\ddagger}_{LOH_2/Cl} - \Delta H^{\ddagger}_{LOH_2/I})$ given in Table 4.2, and the enthalpy of activation of reaction 4.44. This calculation gives $\Delta H^{\ddagger}$ for reaction 4.51 as 25.13 ±0.40 kcal mol^{-1}; from these values of $\Delta H^{\ddagger}$ for reactions 4.50 and 4.51, ΔH^0 for reaction 4.50 is 0.00 ±0.42 kcal mol^{-1}, and for reaction 4.51 ΔH^0 is also 0.00 ±0.42 kcal mol^{-1}. Thus the value of $\Delta H^{\ddagger}_{ref}$ appropriate to reactions 4.50 and 4.51 is 20.20 ±0.19 kcal mol^{-1} for both cases. The value of Δ^0_{OH} is therefore 4.93 ±0.24 kcal mol^{-1} using reaction 4.50, and 4.93 ±0.44 kcal mol^{-1} using reaction 4.51.

The final value of Δ^0_{OH}

The final value of Δ^0_{OH} was taken to be the weighted average of the

values obtained from the reactions

$$\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{OHX}]^+ + \text{H}_2\text{O} \longrightarrow \underline{\text{trans}}\text{-}[\text{Rhen}_2\text{OHOH}_2]^{2+} + \text{X}^- \qquad (4.52)$$

and

$$\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{OHOH}_2]^{2+} + \text{X}^- \longrightarrow \underline{\text{trans}}\text{-}[\text{Rhen}_2\text{XOH}]^+ + \text{H}_2\text{O} \qquad (4.53)$$

(X = Cl , Br , I). This final value was found to be 5.06 ±0.10 kcal mol^{-1}.

Calculation of the Thermodynamic Trans-Effect of Hydroxide

It is possible to calculate the relative enthalpies of the halohydroxybisethylenediaminerhodium(III) complexes from the standard enthalpy changes of reactions 4.43, 4.47, and 4.50. Thus

$$H^0_{OHOH_2} - H^0_{IOH} + H^0_I - H^0_{H_2O} = 4.00 \pm 0.23 \qquad (4.54)$$

$$H^0_{OHOH_2} - H^0_{BrOH} + H^0_{Br} - H^0_{H_2O} = 1.72 \pm 0.32 \qquad (4.55)$$

$$H^0_{OHOH_2} - H^0_{ClOH} + H^0_{Cl} - H^0_{H_2O} = 0.00 \pm 0.42 \qquad (4.56)$$

where H^0_{LX} is the enthalpy of $\underline{\text{trans}}\text{-}[\text{Rhen}_2\text{LX}]^{n+}$, H^0_X is the enthalpy of solvated X^- and $H^0_{H_2O}$ is the enthalpy of water. From equations 4.54 and 4.55, and the known difference[25] (10.4 kcal mol^{-1}) between the enthalpies of solvated iodide and bromide ions we obtain

$$H^0_{IOH} - H^0_{BrOH} = 8.12 \pm 0.39 \text{ kcal mol}^{-1} \qquad (4.57)$$

Similarly, equations 4.54 and 4.56, and the difference in enthalpy (18.5 kcal mol^{-1}) of the solvated chloride and iodide ions,[25] gives

$$H^0_{IOH} - H^0_{ClOH} = 14.50 \pm 0.48 \text{ kcal mol}^{-1} \qquad (4.58)$$

If the enthalpy of the iodohydroxy-complex is arbitrarily taken as zero, then the enthalpies of trans-$[Rhen_2BrOH]^+$ and trans-$[Rhen_2ClOH]^+$ are -8.12 ± 0.39 and -14.50 ± 0.48 kcal mol^{-1} respectively.

Fig. 4.2 shows the graph of the relative enthalpy of trans-$[Rhen_2OHX]^+$ (X = Cl, Br, I) against the relative enthalpy of trans-$[Rhen_2ClX]^+$. The slope (dH^0_{OHX}/dH^0_{ClX}) of this graph, which measures the TTE of hydroxide is 0.77.

Discussion

The Intrinsic Kinetic Trans-effect of Hydroxide

The values found in this work for the enthalpies of activation of the reactions

$$\text{trans-}[Rhen_2OHX]^+ + H_2O \longrightarrow \text{trans-}[Rhen_2OHOH_2]^{2+} + X^- \qquad (4.52)$$

(X = Cl, Br) do not agree with the previous values of Klabunde[19] (X = Cl; Table 4.4) or Shaw[23] (X = Br; Table 4.2). Indeed, much of the confusion about the position of hydroxide in the kinetic trans-effect series was due to incorrect values for these enthalpies of activation. However, even using the new enthalpies of activation the relative positions of chloride and hydroxide in the KTE series still depend on the reactions used to measure the KTE. Thus reaction 4.33 gives the new series

$$\text{KTE of L} = I^- > Br > NH_3 > Cl^- \geq OH^- \qquad (4.59)$$

$$\Delta H^{\ddagger}_{LCl} - \Delta H^{\ddagger}_{ICl} = 0 \; ; \quad 2.1 \; ; \quad 3.1 \; ; \quad 3.8 \; ; \quad 4.04 \qquad (4.60)$$

reaction 4.34 the series

$$\text{KTE of L} = I^- > NH_3 > Br^- > OH^- > Cl^- \qquad (4.61)$$

$$\Delta H^{\ddagger}_{LBr} - \Delta H^{\ddagger}_{IBr} = 0 ; \quad 1.5 ; \quad 2.1 ; \quad 3.2 ; \quad 4.5 \qquad (4.62)$$

and the series derived from reaction 4.35

$$\text{KTE of L} = I^- > Br^- > OH^- \sim Cl^- > NH_3 \qquad (4.40)$$

$$\Delta H^{\ddagger}_{LOH_2} - \Delta H^{\ddagger}_{IOH_2} = 0 ; \quad 3.2 ; \quad 5.8 ; \quad 5.9 : \quad 6.4 \qquad (4.41)$$

is unchanged.

The values listed in Table 4.5 show that Δ^0_{OH}, and hence the IKTE of hydroxide, however, is a constant, regardless of the nature of the leaving group. The mean value of 5.06 ±0.10 kcal mol^{-1} obtained for Δ^0_{OH} is compared in Table 4.6 with the values of Δ^0_L found for other ligands. Since high positive numbers correspond to low kinetic trans-effects, it follows that the IKTE series is

$$L = I^- > Br^- > NH_3 \geq Cl^- \geq OH^- \qquad (4.63)$$

This order correlates qualitatively with the polarisability of the ligand L.[26] Quantitatively the agreement is not good as shown in Fig. 4.3 where Δ^0_L is plotted against the molar refraction, R, of the free ligand. There appears to be a linear correlation between Δ^0_L and R when $L = Cl^-, Br^-, I^-$, but when $L = OH^-$ or NH_3 the enthalpies of activation appear to be lower than those predicted by the polarisability of L. This can be understood by remembering that the difference in enthalpy of the ground state $[Rhen_2LX]^{n+}$ and the transition state $[Rhen_2L...X]^{n+}$ depends not only on the bonding forces within the complex

ion, but also on the difference in solvation of the ground state and the transition state. For the three halide ions these differential solvation effects are likely to be very similar, and the polarisability of L becomes the major factor in determining the relative magnitudes of the IKTE for these ligands.

However, when the trans-ligand is ammonia the ground state has a charge of +2 units, and the transition state an incipient charge of +3 units, and the differential solvation effects in this case will not be equal to those when L is a halide and the ground and transition states have charges of +1 and +2 respectively. To a first approximation, the enthalpy of solution ΔH_{solv} of the complex cation in either the ground or transition state can be calculated from the equations[27]

$$\Delta G_{solv} = -\frac{N(ze)^2}{2r}\left(1 - \frac{1}{D}\right) \qquad (4.64)$$

$$\Delta S_{solv} = \frac{N(ze)^2}{2r}\frac{1}{D^2}\left(\frac{\partial D}{\partial T}\right) \qquad (4.65)$$

$$\Delta H_{solv} = \Delta G_{solv} + T\Delta S_{solv} \qquad (4.66)$$

where N is Avogadro's number, ze is the charge, and r the radius of the complex ion, D the dielectric constant of water and T the absolute temperature. At 50°C equations 4.64 to 4.66 give

$$\Delta H_{solv} = -(ze)^2 \times 0.491 \times \frac{N}{r} \qquad (4.67)$$

If for the reaction

$$\text{trans-}[Rhen_2LX]^{n+} + H_2O \longrightarrow \text{trans-}[Rhen_2LOH_2]^{(n+1)+} + X^- \qquad (4.30)$$

it is assumed that the enthalpy of solvation ΔH_{SX} of the incipient X^-

anion is independent of L and that the transition state has the same radius, but one unit of charge more than the ground state, then the contribution $\Delta H^{\ddagger}_{solv}$ of the difference in solvation of the ground and transition states to Δ^{0}_{L} will be given by

$$\Delta H^{\ddagger}_{solv} = -(2n+1) \times \frac{e^2 N}{r} \times 0.491 + \Delta H_{SX} \qquad (4.68)$$

where n is the charge of the ground state. For univalent ground states ($L = OH^-, Cl^-, Br^-, I^-$), $\Delta H^{\ddagger}_{solv}$ is given by

$$\Delta H^{\ddagger}_{solv} = -3 \frac{e^2 N}{r} \times 0.491 + \Delta H_{SX} \qquad (4.69)$$

and for divalent ground states ($L = NH_3$)

$$\Delta H^{\ddagger}_{solv} = -5 \frac{e^2 N}{r} \times 0.491 + \Delta H_{SX} \qquad (4.70)$$

The extra stabilisation given by the more negative enthalpy of solvation of the transition state when L is ammonia is the reason why the enthalpies of activation of $[Rh(NH_3)_5X]^{2+}$ are lower than would be predicted from the polarisability of ammonia.

It might be expected that the point for $L = OH^-$ would lie on the straight line for $L = Cl^-, Br^-, I^-$, since all four complexes are univalent and $\Delta H^{\ddagger}_{solv}$ is given by equation 4.69 in each case. However, the solvation requirements of co-ordinated hydroxide differ from those of chloride, bromide and iodide because the hydroxy-ligand can participate in two kinds of hydrogen-bonding to the solvent. This is shown in Fig. 4.4. As the leaving group X departs, the <u>trans</u>-ligand L donates extra electron density into the Rh-L bonding orbital. When L is a halide ion (Fig. 4.4a) this means that less electron density is associated with L and the HOH...L-Rh hydrogen bond becomes weaker.

This effect also occurs when L is hydroxide, the HOH...O-Rh hydrogen bond becoming weaker, but inductive withdrawal of electrons through the H-O-Rh bond system makes the H_2O...H-O-Rh hydrogen bond stronger. This extra stabilisation of the transition state due to solvation effects explains the direction, if not necessarily the magnitude, of the deviation of Δ^0_{OH} from the graph of Δ^0_L against molar refraction of L.

The Thermodynamic Trans-effect of Hydroxide

The value of the TTE of hydroxide, measured by dH^0_{OHX}/dH^0_{ClX} is 0.77, which places hydroxide between iodide and ammonia in the thermodynamic trans-effect series

$$L = I^- > OH^- \geq NH_3 \geq Br^- > Cl^- > H_2O \qquad (4.71)$$

The increasing softness of the $\{Rhen_2L\}^{2+}$ moiety as L changes along the series Cl^-, Br^-, I^- has been ascribed[4] to the increasing degree of covalency of the Rh-L bond. When Bott and Poë[5] extended the TTE series to include H_2O they used the polarisability of L as a measure of the degree of covalency which could be expected for the Rh-L bond. However, the positions of NH_3 and OH^- in the fuller TTE series of equation 4.71 cannot be correlated with the polarisability of L, since the latter[26] would predict the TTE order

$$L = I^- > Br^- > Cl^- > NH_3 > OH^- > H_2O \qquad (4.72)$$

However, it has been suggested[5] that the nephelauxetic ratio, β, for the complex $[RhL_6]^{n+}$ might be a better measure than the polarisability of L of the degree of covalency of the Rh-L bond. Rhodium(III) does not form a hexaiodo- or hexahydroxy-complex,[28] but for the other

ligands of the TTE series 4.71, the nephelauxetic ratio of $[RhL_6]^{n+}$ increases in the order[29]

$$L = Br^- < Cl^- < NH_3 < H_2O \qquad (4.73)$$

The degree of covalency of the Rh-L bond in $[RhL_6]^{n+}$ therefore decreases in the order

$$L = Br^- > Cl^- > NH_3 > H_2O \qquad (4.74)$$

The order of equation 4.74 does not correspond with the observed TTE order of equation 4.71, the position of NH_3 in the TTE series being much higher than would be predicted from the nephelauxetic ratio of $[Rh(NH_3)_6]^{3+}$. Moreover, the position of OH^- in the TTE series is also hgiher than would be expected from the nephelauxetic ratios of other oxygen-donor ligands.[30][31]

Although the nephelauxetic ratio for $[RhL_6]^{n+}$ does not correlate well with the TTE of L, there is an alternative measure of the covalency of the Rh-L bond. This is the extinction coefficient, ϵ_{max}, of the first ligand field transition of the complex trans-$[Rhen_2LCl]^{n+}$. This transition is Laporte-forbidden since both the initial and final states are "gerade", but it gains intensity because the bonding molecular orbital formed by the interaction of an "ungerade" ligand p-orbital with the "gerade" metal d-orbital is somewhat unsymmetrical.[32] However, this is not the only mechanism by which the d-d transitions gain intensity,[32] and in addition the spectra of the trans-$[Rhen_2LCl]^{n+}$ complexes are more complicated than those of complexes which have simple O_h symmetry.[33] The intensity of the first d-d absorption band is thus a rather approximate measure of the degree of covalency of the Rh-L bond. Nevertheless, as shown in Table 4.7 and Fig. 4.5, there is indeed a correlation between

ϵ_{max} and the TTE of L. The value of ϵ_{max} for L = H_2O was calculated by multiplying Bott and Poë's[5] value by 1.80, the ratio of the extinction coefficients found by the present author for trans-$[Rhen_2ClOH]^+$ to those found by Bott and Poë[5] for the same complex. Multiplication by this factor corrects for the presumably too large concentrations of trans-$[Rhen_2ClOH_2]^{2+}$ assumed by Bott and Poë. The value of ϵ_{max} given for L = Br^- is for the peak at 413 nm; the shoulder quoted[34] by Bott and Poë at 486 nm with ϵ = 10 M^{-1} cm^{-1} was felt to be spurious, since the ligand field splitting of bromide is greater than that of iodide,[35] and the first d-d absorption in trans-$[Rhen_2ICl]^+$ is only at 490 nm.[4] The standard deviation of ϵ_{max} was assumed to be ±5%, except for trans-$[Rhen_2ClOH_2]^{2+}$; here the standard deviation of ϵ_{max} was assumed to be ±10%, because of the uncertainty introduced by the use of the correction factor.

From the values of ϵ_{max} given in Table 4.7, the covalency of the Rh-L bond in trans-$[Rhen_2LCl]^{n+}$ decreases in the order

$$L = I^- > NH_3 \sim Br^- \sim OH^- > Cl^- > H_2O \qquad (4.75)$$

which agrees well with the TTE series of equation 4.71. The correspondence between ϵ_{max} and the TTE of L (measured by dH^0_{LX}/dH^0_{ClX}) is also shown in Fig. 4.5. It appears that the TTE of L does indeed correlate with the covalence of the Rh-L bond, provided that the latter is measured in terms of the intensity of the ligand field bands of trans-$[Rhen_2LCl]^{n+}$.

It is at first sight surprising that this correlation should depend on the method used to estimate the covalence of the Rh-L bond. However, the TTE of a ligand depends not only on the trans-bond weakening effect (TBWE) of L, but also on the susceptibility to trans-bond

weakening (STBW) of the Rh-L bond.[4] The high thermodynamic trans-effects found for ammonia and hydroxide may be due to the combination of a moderate TBWE and a low STBW of the Rh-NH_3 and Rh-OH bonds. When the covalency of the Rh-L bond is estimated by the polarisability of L or the nephelauxetic ratio for $[RhL_6]^{n+}$ these mutual interactions are not taken into account. The intensity of the d-d transitions in trans-$[Rhen_2LCl]^{n+}$, however, gives a measure of the covalency of the Rh-L bond when it is trans to a halide ligand, i.e., in an environment which is similar to that in which the TTE of L is measured. This may well be the reason why the TTE of L correlates better with ϵ_{max} than it does with other methods of measuring the covalence of the Rh-L bond.

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Table 4.1

Kinetic data for the aquation of <u>trans</u>-$[Rhen_2 I OH]^+$

Temperature (°C)	10^5 k (s^{-1})(a)
81.0	62.18 ±0.89
75.7	33.95 ±0.57
70.3	17.99 ±0.37
65.6	10.26 ±0.20
60.9	5.573 ±0.108
55.4	2.619 ±0.045

$\Delta H^{\ddagger}$ = 27.81 ±0.18 kcal mol^{-1}

$\Delta S^{\ddagger}$ = 5.01 ±0.52 e.u.

(a) from the hydroxide-independent term in the rate law for the reaction

<u>trans</u>-$[Rhen_2IOH]^+ + OH^- \longrightarrow$ <u>trans</u>-$[Rhen_2(OH)_2]^+ + I^-$

Table 4.2

Kinetic data for the aquation of trans-$[Rhen_2BrOH]^+$

(a) from the hydroxide-independent term in the rate law for the base hydrolysis of trans-$[Rhen_2BrOH]^+$

Temperature (°C)	10^5 k (s^{-1})
78.94	141.9 ±2.7
69.72	51.28 ±1.00
63.38	24.66 ±0.48
56.51	10.60 ±0.21
50.06	4.734±0.092

$\Delta H^{\ddagger}$ = 25.99 ±0.19 kcal mol^{-1}

$\Delta S^{\ddagger}$ = 1.91 ±0.57 e.u.

(b) from the pseudo-first-order rate constant for base hydrolysis of trans-$[Rhen_2BrOH]^+$ at $[OH^-]$ = 0.032M

Temperature (°C)	10^5 k (s^{-1})
79.64	156.2 , 159.0 , 161.7
73.77	82.45 , 82.73 , 83.41
69.10	49.17 , 49.42 , 51.22
63.63	26.44 , 25.83 , 25.69
59.40	15.58 , 15.33 , 15.31
54.04	7.829, 8.041, 7.759
50.04	4.656, 4.656, 4.562

$\Delta H^{\ddagger}$ = 26.38 ±0.10 kcal mol^{-1}

$\Delta S^{\ddagger}$ = 3.11 ±0.29 e.u.

Standard deviation of k = 2.0%

From reference 23 $\Delta H^{\ddagger}$ = 25.5 kcal mol^{-1}

Table 4.3

Relative nucleophilicites towards anation of trans-$[Rhen_2LOH_2]^{n+}$

L	$\Delta H^{\ddagger}_{LOH_2/Cl} - \Delta H^{\ddagger}_{LOH_2/I}$	$\Delta H^{\ddagger}_{LOH_2/Br} - \Delta H^{\ddagger}_{LOH_2/I}$	$\Delta H^{\ddagger}_{LOH_2/Cl} - \Delta H^{\ddagger}_{LOH_2/Br}$
	(kcal mol^{-1})	(kcal mol^{-1})	(kcal mol^{-1})
Cl	-	-	0.9 ±0.42
Br	-	-	-0.3 ±0.58
I	1.5 ±0.50	0.6 ±0.42	0.9 ±0.50
NH_3	1.1 ±0.54	0.9 ±0.36	0.2 ±0.58

Average value of $\Delta H^{\ddagger}_{LOH_2/Cl} - \Delta H^{\ddagger}_{LOH_2/I}$ = 1.32 ±0.37 kcal mol^{-1}

Average value of $\Delta H^{\ddagger}_{LOH_2/Br} - \Delta H^{\ddagger}_{LOH_2/I}$ = 0.77 ±0.27 kcal mol^{-1}

Table 4.4

Kinetic data for the aquation of trans-$[Rhen_2ClOH]^+$

(a) from the hydroxide-independent term in the rate law for the base hydrolysis of trans-$[Rhen_2ClOH]^+$ at $[OH^-] \geq 0.2332M$

Temperature (°C)	10^5 k (s^{-1})
75.76	91.40 ±1.75
71.80	60.49 ±1.17
64.80	28.59 ±0.55
58.02	13.30 ±0.25
53.77	7.667 ±0.145
49.89	4.669 ±0.090
45.50	2.685 ±0.052

$\Delta H^{\ddagger}$ = 25.14 ±0.15 kcal mol^{-1}

$\Delta S^{\ddagger}$ = -0.67 ±0.46 e.u.

(b) from the pseudo-first-order rate constant for base hydrolysis of trans-$[Rhen_2ClOH]^+$ at $[OH^-]$ = 0.0332M

Temperature (°C)	10^5 k (s^{-1})
75.76	107.9
71.80	68.28
64.80	34.05
58.02	14.66
53.77	8.902
49.89	5.837
45.50	3.041

$\Delta H^{\ddagger}$ = 25.08 ±0.44 kcal mol^{-1}

$\Delta S^{\ddagger}$ = -0.56 ±1.33 e.u.

Standard deviation of k = 5.7%

From reference 19 $\Delta H^{\ddagger}$ = 22.3 kcal mol^{-1}

Table 4.5

The intrinsic kinetic trans-effect of hydroxide, measured by Δ^0_{OH}

$$\text{trans-}[Rhen_2OHX]^{n+} + Y \longrightarrow \text{trans-}[Rhen_2OHY]^{m+} + X$$

X	Y	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta H^{\ddagger}_{ref}$ (kcal mol^{-1})	Δ^0_{OH} (kcal mol^{-1})
Cl	H_2O	25.13 ±0.14	20.20 ±0.19	4.93 ±0.24
Br	H_2O	26.30 ±0.09	21.14 ±0.20	5.16 ±0.22
I	H_2O	27.81 ±0.18	22.69 ±0.17	5.12 ±0.25
H_2O	Cl	25.13 ±0.40	20.20 ±0.19	4.93 ±0.44
H_2O	Br	24.58 ±0.31	19.50 ±0.12	5.08 ±0.33
H_2O	I	23.81 ±0.15	18.76 ±0.07	5.05 ±0.17

Average value of Δ^0_{OH} = 5.06 ±0.10 kcal mol^{-1}

Table 4.6

Intrinsic kinetic trans-effects measured by Δ^0_L and the polarisability of L

L	Δ^0_L (kcal mol^{-1})	Molar Refraction[(a)] (cm^3 mol^{-1})
I^-	0.00	19.21
Br^-	3.20 ±0.20	12.66
NH_3	4.75 ±0.15	5.63
Cl^-	5.02 ±0.18	9.07
OH^-	5.06 ±0.10	4.76

(a) From reference 26

Table 4.7

Thermodynamic trans-effects (measured by dH^{0}_{LX}/dH^{0}_{C1X}) and the intensity (ϵ_{max}) of the first ligand field band of trans-$[Rhen_2LCl]^{n+}$

L	dH^{0}_{LX}/dH^{0}_{C1X}	ϵ_{max} (M^{-1} cm^{-1})
I^-	0.65	260 ±13
OH^-	0.77	93.5 ± 5
NH_3	0.81	104 ± 5
Br^-	0.85	95 ± 5
Cl^-	1.00	82 ± 4
H_2O	1.12	47 ± 5

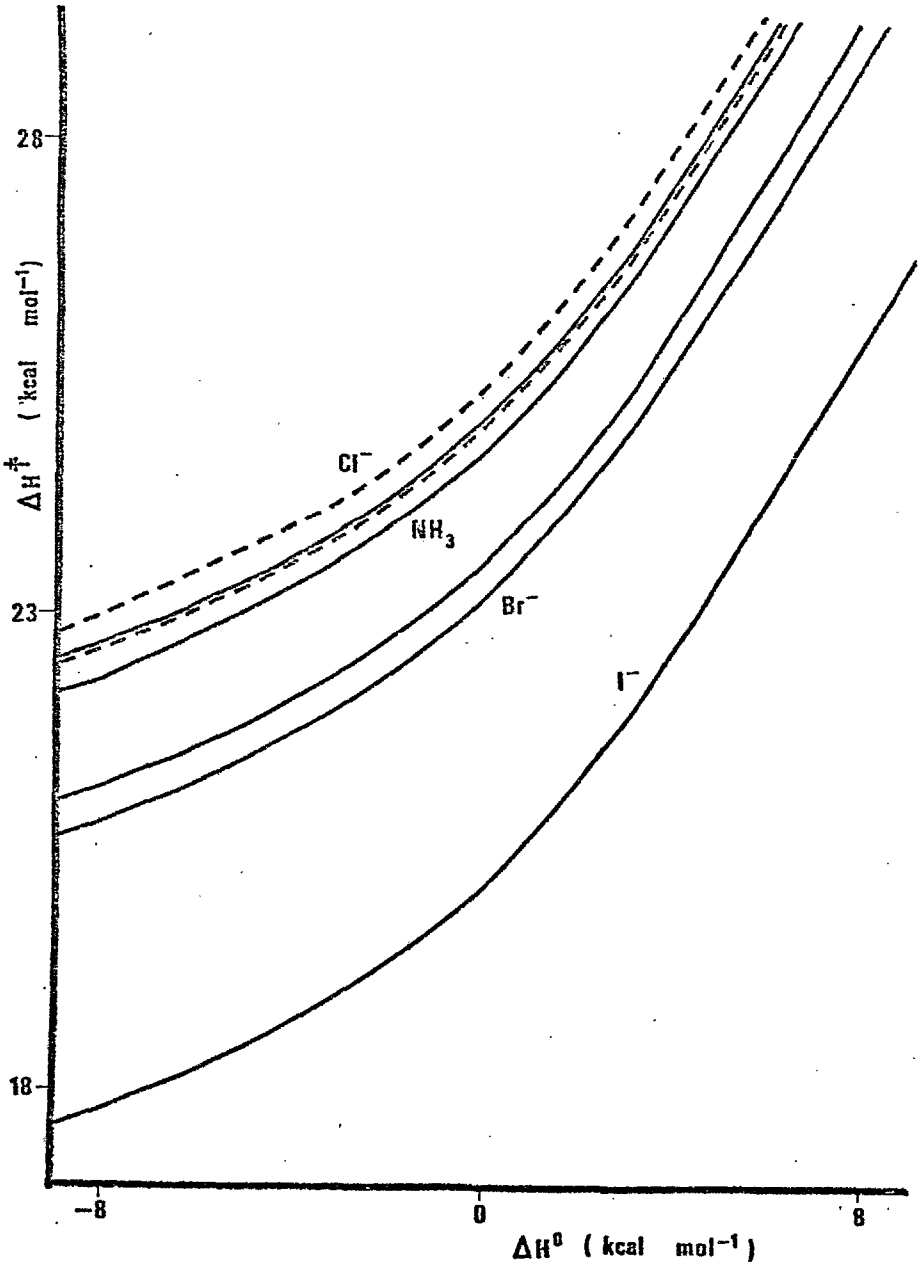


Fig. 4.1 Curves of the intrinsic kinetic <u>trans</u>-effect of L in <u>trans</u>-[Rhen$_2$LX]$^{n+}$

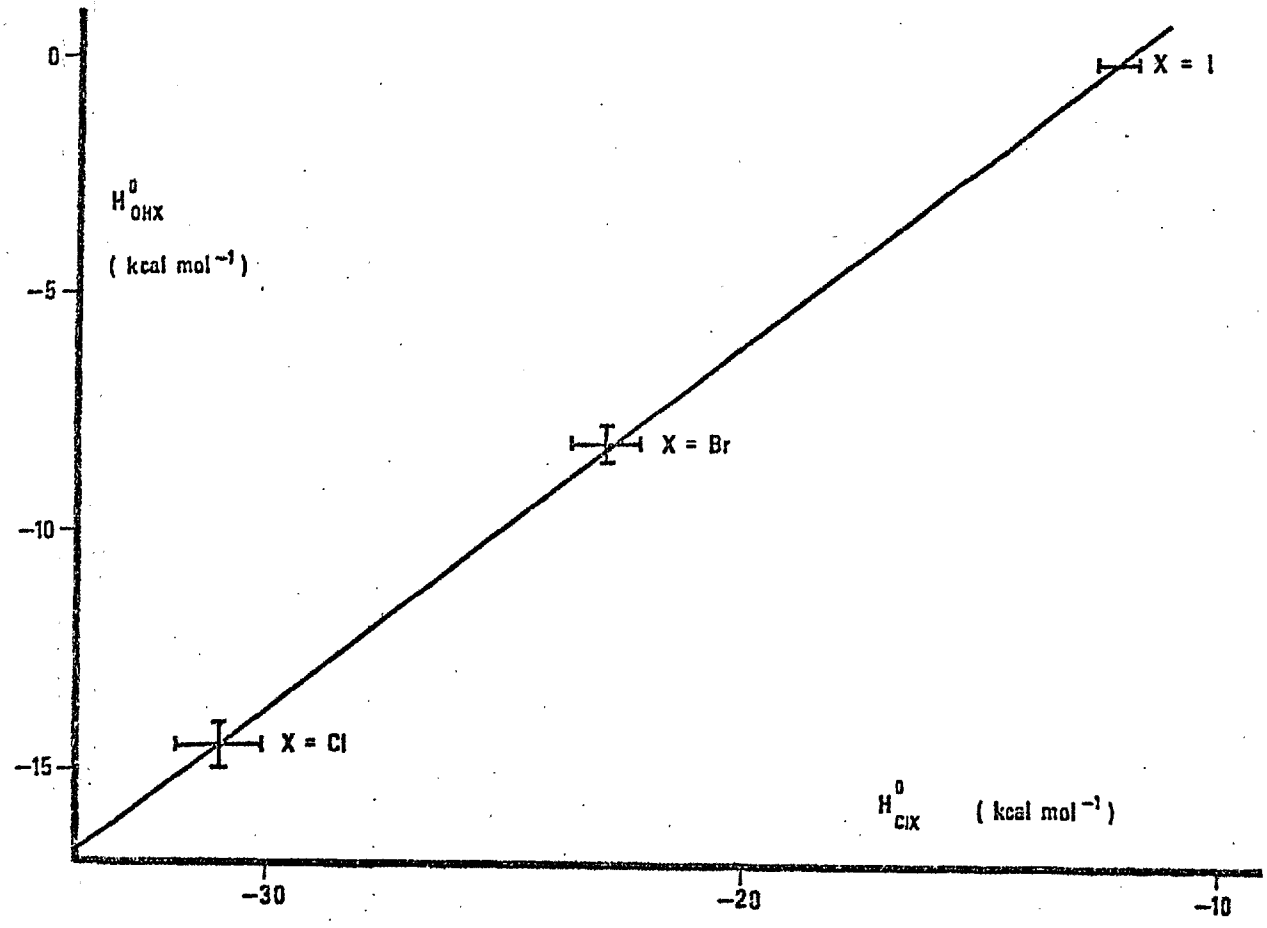


Fig. 4.2 Estimation of the thermodynamic <u>trans</u>-effect of hydroxide

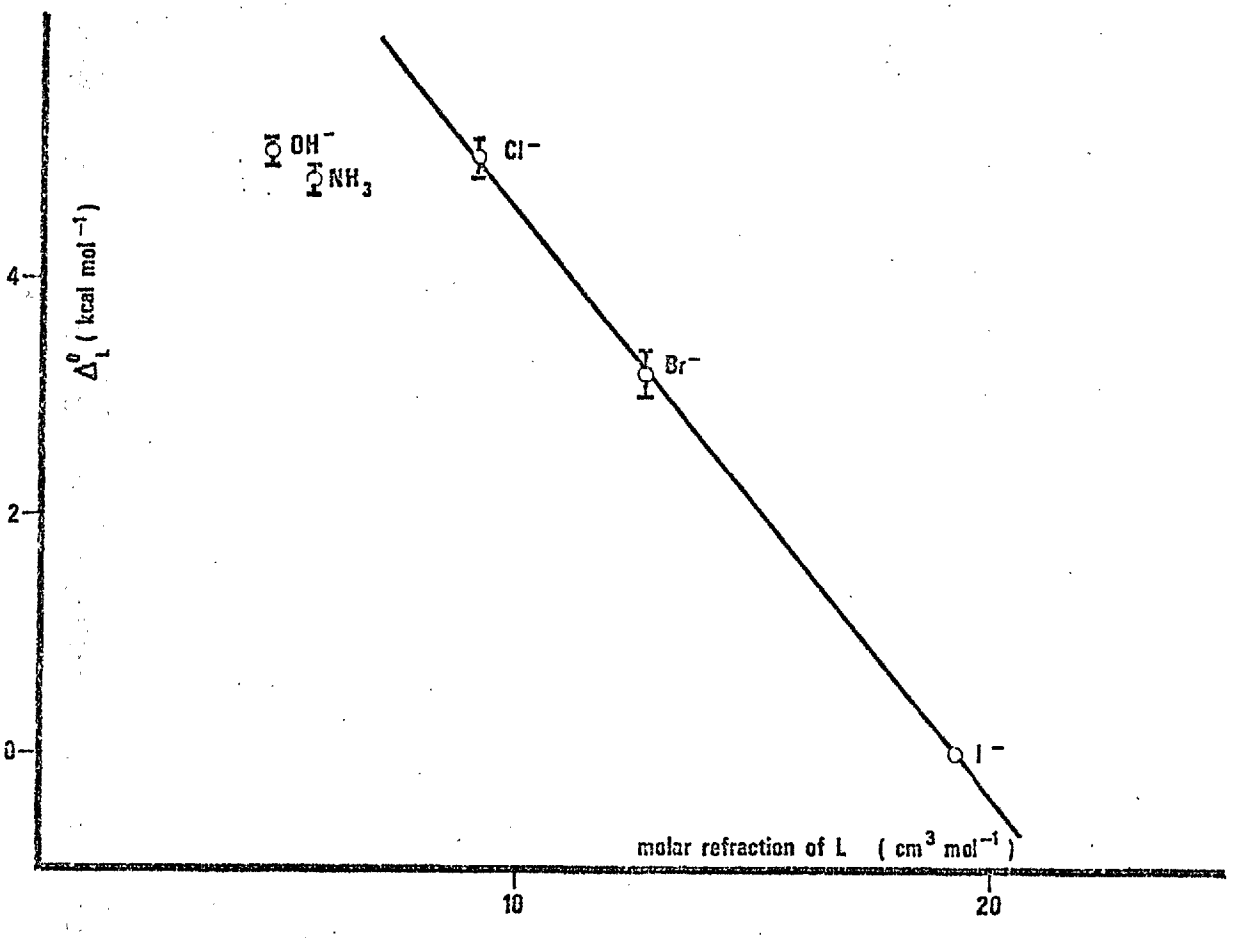
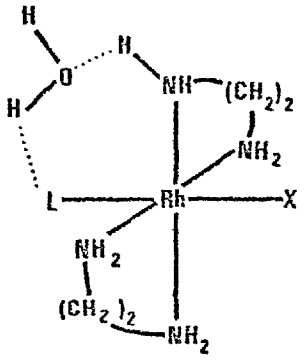
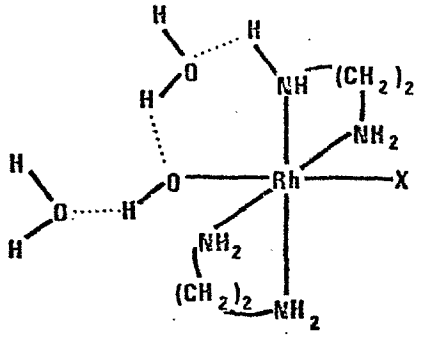


Fig. 4.3 The intrinsic kinetic <u>trans</u>-effect of L as a function of the polarisability of L



(a) Solvation of trans -[$Rhen_2LX$]$^+$ (L = Cl^-, Br^-, I^-)



Solvation of trans - [$Rhen_2OHX$]$^+$

Fig. 4.4 Solvation of trans-diacidobisethylenediamine-rhodium(III) complexes

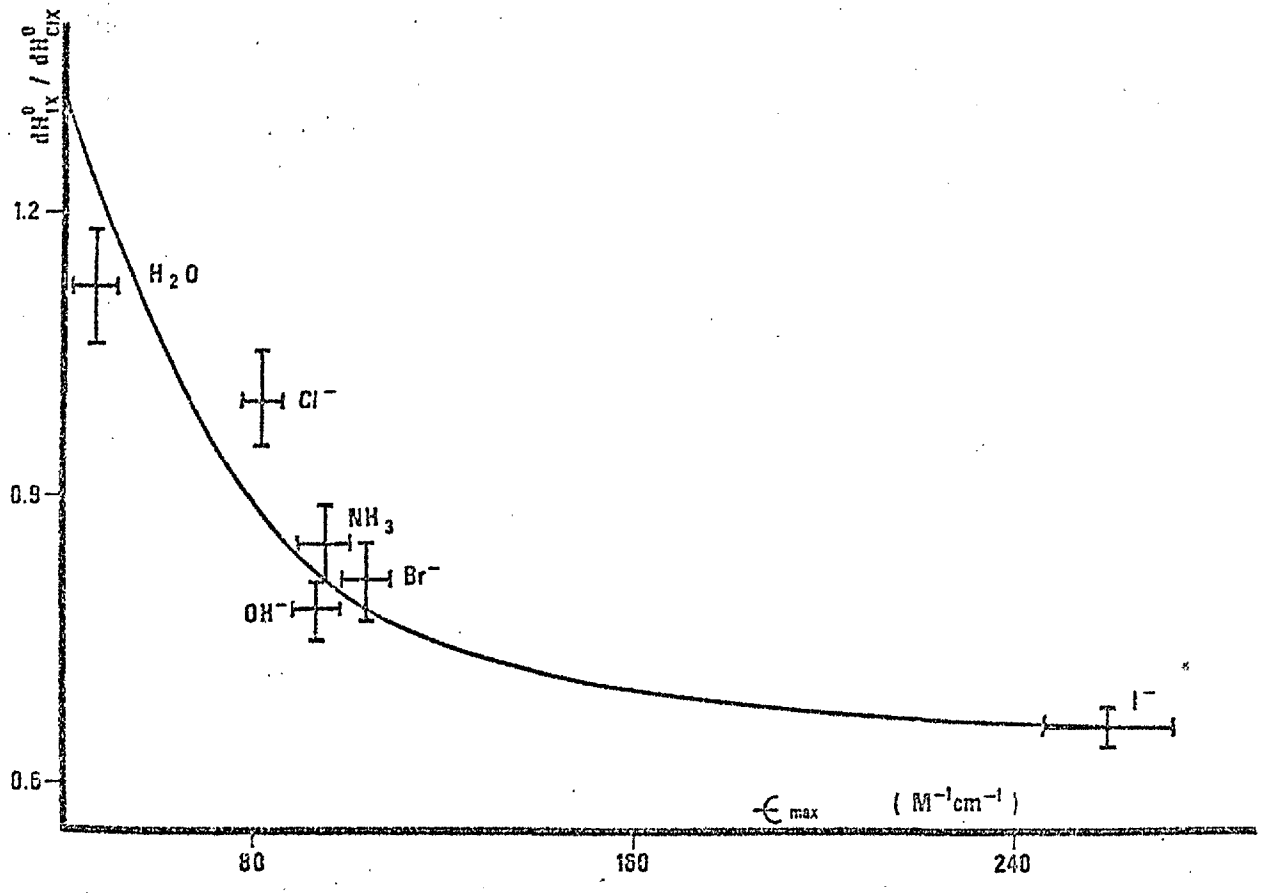


Fig. 4.5 The relationship between the thermodynamic <u>trans</u>-effect of L and the intensity of the first ligand field band of <u>trans</u>-$[Rhen_2LCl]^{n+}$

CHAPTER 5

Summary of Results Presented in Part I

The rate law for reactions 5.1 (Y^{n-} = Cl^-, Br^-) and 5.2 (Y^{n-} = Br^-, F^-, SO_4^{2-}, PO_4^{3-})

$$\underline{\text{trans}}\text{-}[Rhen_2I_2]^+ + Y^{n-} \longrightarrow \underline{\text{trans}}\text{-}[Rhen_2XY]^{(2-n)+} + I^- \qquad (5.1)$$

$$\underline{\text{trans}}\text{-}[Rhen_2Cl_2]^+ + OH^- + Y^{n-} \longrightarrow [Rhen_2ClOH]^+ + Y^{n-} + Cl^- \qquad (5.2)$$

has been found to be

$$k_{obsd} = k_1 + k_2[Y] \qquad (5.3)$$

The enhanced rate of hydrolysis of $\underline{\text{trans}}\text{-}[Rhen_2I_2]^+$ in the presence of F^-, SO_4^{2-} and PO_4^{3-} has also been interpreted in terms of equation 5.3. It is shown that a redox mechanism, involving a rhodium(I) intermediate is unlikely; instead an ion-pair interchange mechanism is suggested.

Values of the association constants, K_Y°, at zero ionic strength for the equilibrium

$$\underline{\text{trans}}\text{-}[Rhen_2X_2]^+ + Y^{n-} \overset{K_Y}{\rightleftharpoons} \{Rhen_2X_2,Y\}^{(1-n)+} \qquad (5.4)$$

have been calculated from kinetic data obtained in the absence of supporting electrolyte (X = I; Y = Cl), or from the spectroscopic interaction between $\underline{\text{trans}}\text{-}[Rhen_2X_2]^+$ and Y^{n-} (X = Cl; Y = I, Br). For the associations of $\underline{\text{trans}}\text{-}[Rhen_2I_2]^+$ with chloride, and $\underline{\text{trans}}\text{-}[Rhen_2Cl_2]^+$ with bromide, where the ionic strength, I, ranged from zero to 1.0M, the Davies equation[1] was used to calculate the changing mean activity coefficient of unassociated $\underline{\text{trans}}\text{-}[Rhen_2X_2]Y$. For the association between $\underline{\text{trans}}\text{-}[Rhen_2Cl_2]^+$ and iodide, where I ranged from 0.5 to 3.0M, the activity

coefficient of iodide was interpolated from published values, and the activity coefficient of trans-$[Rhen_2Cl_2]^+$ was assumed to be the same as γ_{SI}, the mean activity coefficient of trans-$[Coen_2NO_2X]^+$. The value of γ_{SI} was obtained from Burnett's[2] tabulation of γ_{ref}, the mean activity coefficient of trans-$[Coen_2NH_3NO_2]Cl_2$, by using the equation[2]

$$\log \gamma_{SI} = \frac{1}{2} \log \gamma_{ref} \qquad (5.5)$$

The values obtained for K_Y° by these methods were all small ($K_Y^\circ \leq 1.2 \pm 1.5\ M^{-1}$), and in reasonable agreement with the predictions of the Fuoss equation.[3] Using competition studies, limiting values of K_Y° were obtained for the interactions of trans-$[Rhen_2Cl_2]^+$ with F^-, Cl^-, Br^-, SO_4^{2-}, PO_4^{3-}; these were all slightly less than the predictions of the Fuoss equation. Finally, the rates of aquation of trans-$[Rhen_2Cl_2]^+$, trans-$[Rhen_2IOH]^+$ and trans-$[Rhen_2I_2]^+$ are all independent of the concentration of added perchlorate, indicating that either $K^\circ_{ClO_4}$ is zero, or the rate constant for aquation of the perchlorate ion-pair is equal to that for aquation of the free ion. Further evidence presented here suggests that $K^\circ_{ClO_4}$ is less than or equal to the ion association constants for other univalent anions.

Most of the kinetic experiments reported here have been performed at constant ionic strength, maintained with sodium perchlorate. Although it is not clear whether or not perchlorate ion-pairs with trans-$[Rhen_2LX]^+$, it has been shown that at I = 1.0M, the equilibrium constants for the association of trans-$[Rhen_2LX]^+$ with Y^{n-} will all be very similar, regardless of the valency of Y^{n-}. The ratio $(k_1 + k_2[Y]_{max})/k_1$, which measures the minimum value for the relative reactivity of the ion-pair and the free ion ($[Y]_{max}$ is the maximum concentration of Y^{n-} studied) is no larger

than the corresponding ratios found for the S_N1IP reactions of cobalt(III) and chromium(III) complexes. Also, the relative values of the ratio k_2/k_1 have been shown to be an approximate measure of the relative rate constants, k_Y, for reaction of the ion-pairs. The charge of the anion is the most important factor in determining the value of k_Y, and there are none of the specific effects which would be expected for an Ia mechanism. The interchange within the ion-pair is therefore assigned as Id, and the mechanism designated S_N1IP. Since substitution within $\{Rh(NH_3)_5OH_2,Y\}^{(3-n)+}$ is Ia, and within $\{Rhen_2LX,Y\}^{(1-n)+}$ it is Id, rhodium(III) appears to lie on the borderline between associative and dissociative activation, the charge on the complex deciding the intimate mechanism.

The base hydrolysis of several trans-diacidobisethylenediamine-rhodium(III) complexes has also been studied. There is an isokinetic relationship between the enthalpies ($\Delta H_2^{\ddagger}$) and entropies ($\Delta S_2^{\ddagger}$) of activation for the second-order pathways of the reaction

$$\text{trans-}[Rhen_2I_2]^+ + Y^- \longrightarrow [Rhen_2IY]^+ + I^- \qquad (5.6)$$

where Y = Cl, Br, OH. There is also a pseudo-isokinetic relationship between $\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ and $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ for the base hydrolysis of trans-$[Rhen_2LX]^+$ (L = X = Cl, Br, I; L = OH, X = Cl, Br, I) and the reactions of trans-$[Rhen_2I_2]^+$ with chloride and bromide. ($\Delta H_2^{\ddagger}$, $\Delta S_2^{\ddagger}$ are activation parameters for the second-order pathway of the reaction

$$\text{trans-}[Rhen_2LX]^+ + Y^- \longrightarrow [Rhen_2LY]^+ + X^- \qquad (5.7)$$

and $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$ are the corresponding activation parameters for the first-order pathway for reaction 5.7.) This indicates that the base hydrolysis

of the complexes trans-$[Rhen_2LX]^+$ occurs by a pathway which is energetically similar to the S_N1IP pathways found for these complexes.

Unlike the S_N1IP reactions, however, the base hydrolyses of trans-$[Rhen_2LX]^+$ often occur with extensive rearrangement. This stereomobility is best explained by the S_N1CB mechanism, if it is assumed that the amido-group has a large sigma-trans-effect which is transmitted via the rhodium p-orbitals. This hypothesis also explains the observed differences in the behaviour of cis- and trans-$[Rhen_2LX]^+$ in base hydrolysis. For cis-$[Rhen_2LX]^+$ the amido-group is generated trans to the leaving group, and the high sigma-trans-effect of NHR^-, which can operate in a square pyramidal transition state, leads to a high reactivity of the conjugate base, and to a stereoretentive reaction. In the trans-$[Rhen_2LX]^+$ complexes the amido-group is cis to the leaving group, and it can only donate electron density into the p-orbital originally used for bonding to X if the transition state is trigonal bipyramidal. Addition of water to such a transition state gives appreciable amounts of cis-$[Rhen_2LOH]^+$, and the extra crystal field activation energy (CFAE) associated with formation of a trigonal bipyramidal transition state explains the lower susceptibility of trans-$[Rhen_2LX]^+$ to base hydrolysis. It has been shown that the trans-complexes which undergo stereochemical rearrangement during base hydrolysis have large values of $\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ (in agreement with CFAE predictions), and also have large, positive values of $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$, in agreement with Tobe's correlation[4] of the entropy of activation with stereomobility. Finally, the concept of an S_N1IP/S_N1CB mechanistic spectrum cannot be discounted, and it is possible that the species responsible for base catalysis of the aquation of trans-

$[Rhen_2LX]^+$ is halfway between the conjugate base and the hydroxide ion-pair.

The first-order pathway for the base hydrolysis of trans-$[Rhen_2OHX]^+$ (X = Cl, Br, I) is the reaction

$$\text{trans-}[Rhen_2OHX]^+ + H_2O \longrightarrow \text{trans-}[Rhen_2OHOH_2]^{2+} + X^- \qquad (5.8)$$

so $\Delta H_1^{\ddagger}$ is the enthalpy of activation of reaction 5.8. From the known enthalpy of activation for the iodide anation of trans-$[Rhen_2OHOH_2]^{2+}$ and the relative nucleophilicities of the halide ions, the enthalpies of activation $\Delta H_{-1}^{\ddagger}$ for the reaction

$$\text{trans-}[Rhen_2OHOH_2]^{2+} + X^- \longrightarrow \text{trans-}[Rhen_2OHX]^+ + H_2O \qquad (5.9)$$

were calculated. The overall enthalpy changes for reactions 5.8 and 5.9 were calculated from $\Delta H_1^{\ddagger}$ and $\Delta H_{-1}^{\ddagger}$.

The kinetic trans-effect of hydroxide has been measured by the parameter Δ_{OH}, which is given by

$$\Delta_{OH} = \Delta H^{\ddagger}_{OHX/Y} - \Delta H^{\ddagger}_{IX/Y} \qquad (5.10)$$

where $\Delta H^{\ddagger}_{OHX/Y}$ is the enthalpy of activation for the reaction

$$\text{trans-}[Rhen_2OHX]^{m+} + Y^{n-} \longrightarrow \text{trans-}[Rhen_2OHY]^{(2-n)+} + X^{(2-m)-} \qquad (5.11)$$

and $\Delta H^{\ddagger}_{IX/Y}$ is the corresponding parameter for the reaction

$$\text{trans-}[Rhen_2IX]^{m+} + Y^{n-} \longrightarrow \text{trans-}[Rhen_2IY]^{(2-n)+} + X^{(2-m)-} \qquad (5.12)$$

However, both the value of Δ_{OH} and the position of hydroxide in the kinetic trans-effect series depend on the nature of the leaving group X in reactions 5.11 and 5.12, because ΔH^0 differs for the two reactions.

However, this difficulty can be completely resolved by using the intrinsic kinetic trans-effect (IKTE) of hydroxide. The IKTE of a ligand L is measured by Δ^0_L, which is given by

$$\Delta^0_L = \Delta H^{\ddagger}_{LX/Y} - \Delta H^{\ddagger}_{ref} \qquad (5.13)$$

where $\Delta H^{\ddagger}_{LX/Y}$ is the enthalpy of activation of the reaction

$$\underline{trans}\text{-}[Rhen_2LX]^{m+} + Y^{n-} \longrightarrow \underline{trans}\text{-}[Rhen_2LY]^{p+} + X^{q-} \qquad (5.14)$$

(X or Y is H_2O) and $\Delta H^{\ddagger}_{ref}$ is the enthalpy of activation for the corresponding reaction of the hypothetical complex $\underline{trans}\text{-}[Rhen_2IZ]^+$ which proceeds with the same ΔH^0 as reaction 5.14. The value of Δ^0_{OH}, and hence the IKTE of hydroxide, is a constant; using published studies of the IKTE of other ligands, the IKTE of L was found to decrease in the order

$$L = I^- > Br^- > NH_3 \geq Cl^- \geq OH^- \qquad (5.15)$$

This order correlates well with the polarisability of L, but the numerical value of Δ^0_L (and thus the IKTE of L) also depends on secondary effects such as the differential solvation of the ground state and transition state of reaction 5.14.

From the values of the over-all enthalpy changes for reaction 5.8, and the known enthalpies of solvation of X^- (X = Cl, Br, I), the relative enthalpies H^0_{OHX} of $\underline{trans}\text{-}[Rhen_2OHX]^+$ (X = Cl, Br, I) were calculated. The thermodynamic trans-effect of hydroxide was measured by the slope dH^0_{OHX}/dH^0_{ClX} of the graph of H^0_{OHX} against H^0_{ClX}, where H^0_{ClX} is the relative enthalpy of $\underline{trans}\text{-}[Rhen_2ClX]^+$. Using published values of dH^0_{LX}/dH^0_{ClX} (H^0_{LX} is the relative enthalpy of $\underline{trans}\text{-}[Rhen_2LX]^+$), the thermodynamic trans-effect of the ligand L was found to decrease in the order

$$L = I^- > OH^- \geq NH_3 \geq Br^- > Cl^- > H_2O \qquad (5.16)$$

This does not correspond with the order of either molar refraction R, or nephelauxetic ratio β, of L, but correlates well with ϵ_{max}, the intensity of the first ligand field band of trans-$[Rhen_2LCl]^{n+}$. It is postulated that ϵ_{max} is a better measure of the covalency of the Rh-L bond than either R or β, because R and β are properties of an isolated Rh-L bond, whereas ϵ_{max} refers to a Rh-L bond which is trans to a halide ligand. The thermodynamic trans-effect of a ligand L is a function of the susceptibility to trans-bond weakening of the Rh-L bond, as well as the trans-bond weakening effect of L, and it is necessary to measure the covalency of the Rh-L bond when it is in an environment similar to that used to measure the trans-effect.

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J.A.C.S. 76

PART II

THE ANATION OF

TRANS-BROMOAQUOTETRACYANOPLATINUM(IV)

BY BROMIDE

CHAPTER 6

Introduction; Substitution and Redox Reactions of Platinum(IV) Complexes

The chemistry of platinum(IV) complexes is very complicated, and the mechanisms of the substitution reactions of these compounds have been much discussed. Recently Peloso[1] has written a comprehensive review of the mechanistic studies carried out for platinum, nickel and palladium complexes, and there are several reviews[2] of the platinum(II)-catalysed reactions of platinum(IV) complexes.

Conventional substitution reactions of an octahedral complex

It was originally thought [3] that platinum(IV) complexes might undergo substitution by an I*a* process, because the crystal field activation energy of a third row transition metal is high, and also because the metal atom carries a high formal positive charge in these complexes. However, conventional substitution processes have been found for only a few reactions of platinum(IV) complexes, and there is no evidence that these reactions are associative. The reaction of $[PtF_6]^{2-}$ with iodide or bromide is independent of the concentration of the entering anion, but is acid-catalysed.[4] This behaviour is similar to that found in the dissociative reactions of cobalt(III) fluoro-complexes. Early claims that the halide interchange reactions of $[PtX_6]^{2-}$ (X = Cl, Br, I)[5][6] and the reaction of *trans*-$[Pten_2Cl_2]^{2+}$ with nitrite[7] were I*a* processes have both been withdrawn.[8][9] The first stage of the reductive elimination of C_6H_5I from *trans*-$[Pt(PEt_3)_2(C_6H_5)_2I_2]$ could be an associative or dissociative aquation of iodide,[10] but it has been claimed that the first step of the redox isomerisation of *cis*-$[Pt(C_3H_6)py_2Cl_2]$ to *trans*-$[Pt(CHEtpy)pyCl_2]$ is the dissociative loss of pyridine.[11]

Reactions involving platinum(III) intermediates

Reaction via a platinum(III) intermediate has been discussed for the light-sensitive halide exchange reactions of several platinum(IV) complexes,[5],[12]-[16] and for the allied reactions which are induced by pulse radiolysis.[17] (However, photoaquation appears to proceed by formation of a five-co-ordinate platinum(IV) species.[12][18]) Platinum-(III) intermediates are formed in non-complementary redox reactions between platinum(IV) complexes and one-electron reducing agents;[19] these reactions can be of both the inner sphere[20][21] and the outer sphere[22]-[24] type.

Platinum(II)-catalysed reactions

If the reaction

$$\underline{\text{trans}}\text{-}[PtL_4XZ]^{n+} + Y^- \longrightarrow \underline{\text{trans}}\text{-}[PtL_4XY]^{n+} + Z^- \qquad (6.1)$$

is carried out in the presence of $[PtL_4]^{n+}$, the rate law usually found is

$$k_{obsd} = k[PtL_4][Y^-] \qquad (6.2)$$

The mechanism proposed for these platinum(II)-catalysed reactions is given in equations 6.3 to 6.5.

$$Y^- + [PtL_4]^{n+} \rightleftharpoons \{Y\text{-}\underset{A}{PtL_4}\}^{(n-1)+} \qquad (6.3)$$

$$\{Y\text{-}\underset{A}{PtL_4}\}^{(n-1)+} + [X\text{-}PtL_4\text{-}Z]^{n+} \rightleftharpoons \{Y\text{-}PtL_4\text{-}\underset{B}{X}\text{-}PtL_4\text{-}Z\}^{(2n-1)+} \qquad (6.4)$$

$$\{Y\text{-}PtL_4\text{-}\underset{B}{X}\text{-}PtL_4\text{-}Z\}^{(2n-1)+} \longrightarrow [Y\text{-}PtL_4\text{-}X]^{n+} + [PtL_4]^{n+} + Z^- \qquad (6.5)$$

The most important evidence for this mechanism is that the rate of platinum-exchange is equal to the rate of ligand-exchange. This has been

shown by labelling the starting complexes with dissimilar cis-ligands,[2c][25] a radioactive cis-ligand,[2c] and with ^{195}Pt.[2c][26] Also, the bridged structure proposed for the platinum(II)/platinum(IV) intermediate, B, occurs in the solid state structure of $[PtenBr_3]$, which is composed of chains of alternate $[PtenBr_4]$ and $[PtenBr_2]$ units.[27] The platinum(II) and platinum(IV) centres of $[PtenBr_3]$ retain their identity, and there is no platinum-exchange in the solid state.[15] Finally, the accumulation of the five-co-ordinate adduct $[Ptdiars_2Y]^+$ (Y = Cl, Br, I) during the reaction

$$Y^- + [Ptdiars_2]^{2+} + [Pt(PEt_3)_2X_4] \longrightarrow [Ptdiars_2XY] + [Pt(PEt_3)_2X_2] + X^- \quad (6.6)$$

(X = Cl, Br) has been demonstrated by Peloso and Ettorre.[28]

Reduction of the platinum(IV) substrate by anions

The mechanism of equations 6.3 to 6.5 is essentially a reduction of the platinum(IV) substrate by a platinum(II) complex; the reaction is only apparently a substitution reaction if the non-labile ligands of the platinum(II) and platinum(IV) complexes are identical. In the absence of platinum(II) complexes, and in the presence of a good reducing anion, Y^-, the platinum(IV) substrate may instead be reduced by Y^-:

$$Y^- + [XPtL_4Z]^{n+} \longrightarrow YX + [PtL_4]^{n+} + Z^- \quad (6.7)$$

Peloso et al.[1][29] have studied the reduction of cis- and trans-$[PtL_2X_4]$ (L = PPh_3, P(n-Pr)$_3$, $AsEt_3$, pip, py, $MeNH_2$, $EtNH_2$; X = Cl, Br) by SCN^-, $SeCN^-$, I^-, $S_2O_3^{2-}$, and of $[Ptdiars_2X_2]^{2+}$ (X = Cl, Br) by NO_2^-, I^-, and SCN^-. The relative reactivities of the anions are independent of the substrate for all complexes except those containing methylamine or

ethylamine; and, again with the exception of the methylamine- and ethylamine-complexes, the relative reactivities of the substrates are independent of the reducing anion, Y^-. Peloso[29a] has argued that this means the contribution of Y^- to the free energy of activation is independent of the substrate, and therefore there is only slight bond-formation to Y^- in the transition state. However, Poë and Vaughan[30] pointed out that Peloso's results were consistent with a linear relationship

$$\Delta G^{\ddagger} = c\Delta G^{0} \qquad (6.8)$$

between the free energy of activation ($\Delta G^{\ddagger}$) and the standard free energy change for reaction 6.7. ΔG^{0} is given by

$$\Delta G^{0} = \Delta G_1^{0} + \Delta G_2^{0} \qquad (6.9)$$

where ΔG_1^{0} and ΔG_2^{0} are the standard free energy changes for reactions 6.10 and 6.11 respectively.

$$[PtL_4XZ]^{n+} + 2e \longrightarrow [PtL_4]^{n+} + X^- + Z^- \qquad (6.10)$$

$$Y^- + X^- \longrightarrow XY + 2e \qquad (6.11)$$

Hence

$$\Delta G^{\ddagger} = c\Delta G_1^{0} + c\Delta G_2^{0} \qquad (6.12)$$

Peloso's results follow from equation 6.12, regardless of the value of c, so his correlations give no information about the position of the transition state along the reaction co-ordinate. However, using the known reduction potentials of $[PtL_2Cl_4]$ (L = *cis*- or *trans*-P(*n*-Pr)$_3$ or *trans*-S(*n*-Pr)$_2$) and the rates of reduction of those complexes by iodide, Poë and Vaughan[30] calculated c to be approximately unity. Although they have

suggested that equation 6.12 might be better written as

$$\Delta G^{\ddagger} = c_1 \Delta G_1^{0} + c_2 \Delta G_2^{0} \qquad (6.13)$$

it appears that, at least for the phosphine and sulphide complexes, the transition state is very similar to the products.

The REOA mechanism

Poë and his co-workers have studied the substitution reactions of several anionic complexes, and shown that provided the anion is not too strong a reductant, the reductive elimination of equation 6.7 is followed by oxidative addition of YX and Y to $[PtL_4]$ to give trans-$[PtL_4XY]$. The reductive elimination-oxidative addition (REOA) mechanism is shown in equations 6.14 and 6.15.

$$Y^- + [XPtL_4X]^{n+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} YX + [PtL_4]^{n+} + X^- \qquad (6.14)$$

$$YX + [PtL_4]^{n+} + Y^- \xrightarrow{k_2} Y^- + [XPtL_4Y]^{n+} \qquad (6.15)$$

In the presence of hexachloroiridate(IV) (to prevent catalysis by platinum(III) intermediates) the reaction of iodide with $[PtBr_6]^{2-}$ proceeds in three distinct stages which have been ascribed[8] to the reaction scheme:

Stage 1

$$I^- + [PtBr_6]^- \xrightarrow{\text{slow}} IBr + [PtBr_4]^{2-} + Br^- \qquad (6.16)$$

$$BrI + [PtBr_4]^{2-} + I^- \xrightarrow{\text{fast}} Br^- + [PtBr_4I_2]^{2-} \qquad (6.17)$$

Stage 2

$$I^- + [PtBr_4I_2]^{2-} \xrightarrow{\text{slow}} IBr + [PtBr_2I_2]^{2-} + Br^- \qquad (6.18)$$

$$BrI + [PtBr_2I_2]^{2-} + I^- \xrightarrow{\text{fast}} Br^- + [PtBr_2I_4]^{2-} \qquad (6.19)$$

Stage 3

$$I^- + [PtBr_2I_4]^{2-} \xrightarrow{slow} IBr + [PtI_4]^{2-} + Br^- \quad (6.20)$$

$$BrI + [PtI_4]^{2-} + I^- \xrightarrow{fast} Br^- + [PtI_6]^{2-} \quad (6.21)$$

The rate law for all three stages is[5][8]

$$k_{obsd} = k[I^-] \quad (6.22)$$

The possibility that reaction 6.17 proceeded in three steps

$$IBr + [PtBr_4]^{2-} + I^- \xrightarrow{fast} I^- + [PtBr_5I]^{2-} \quad (6.23)$$

$$I^- + [PtBr_5I]^{2-} \xrightarrow{fast} I_2 + [PtBr_4]^{2-} + Br^- \quad (6.24)$$

$$I_2 + [PtBr_4]^{2-} + I^- \xrightarrow{fast} I^- + [PtBr_4I_2]^{2-} \quad (6.25)$$

was not excluded, nor were the analogous three-step processes for reactions 6.19 and 6.21. However, the reaction of bromide with $[PtI_6]^{2-}$ occurs by rapid replacement of three or four iodide ligands, followed by slower substitution of the others to give $[PtBr_6]^{2-}$. The intermediates observed were not those found in the reaction of $[PtBr_6]^{2-}$ with iodide, which suggested the product of the initial rapid reaction was $[PtBr_3I_3]^{2-}$ where each molecular axis had the arrangement Br-Pt-I. Poë et al.[8] explained these results by assuming that however the IBr molecule was generated, it was always the iodine atom which became attached to the platinum centre in the reoxidation step. This is consistent with the direction of polarisation of the IBr molecule, but assumes that when the IBr molecule is generated in the configuration I-Br...Pt, it is sufficiently free to rotate to the configuration Br-I...Pt.

The reaction of $[PtCl_6]^{2-}$ with iodide also obeys[5] the rate law

of equation 6.22, but in this case $[PtI_6]^{2-}$ is produced without the accumulation of any detectable intermediates. Since 1.0 M chloride does not affect the rate of production of $[PtI_6]^{2-}$, reaction 6.26 does not compete very efficiently with reaction 6.27.[31]

$$ICl + [PtCl_4]^{2-} + Cl^- \longrightarrow I^- + [PtCl_6]^{2-} \qquad (6.26)$$

$$ClI + [PtCl_4]^{2-} + I^- \longrightarrow Cl^- + [PtCl_4I_2]^{2-} \qquad (6.27)$$

The hydrolysis of $[PtI_6]^{2-}$ has also been studied,[32] but the stoichiometry and kinetics of the reaction are very complicated. The reduction of $[PtI_6]^{2-}$ by iodide to give $[PtI_4]^{2-}$ and I_3^- has been proposed as one step of the reaction

$$[PtI_6]^{2-} + H_2O \longrightarrow [PtI_5OH_2]^- + I^- \qquad (6.28)$$

This hypothesis is substantiated by the fact that the reaction of $[PtI_6]^{2-}$ with iodide or bromide in the presence of halogen scavengers gives only $[PtI_4]^{2-}$ or $[PtBr_4]^{2-}$.[8]

Although the reaction of <u>trans</u>-$[Pt(CN)_4Cl_2]^{2-}$ with bromide and of $[Pt(CN)_4BrX]^{2-}$ (X = Cl, Br) with chloride occur by predominantly $[Pt(CN)_4]^{2-}$ catalysed pathways,[39] the rate law for the reaction of <u>trans</u>-$[Pt(CN)_4X_2]^{2-}$ (X = Cl, Br) with iodide is[31]

$$k_{obsd} = k[I^-] \qquad (6.22)$$

The reaction occurs by the REOA mechanism of equations 6.29 to 6.30, as does the reaction[33] of <u>trans</u>-$[Ptox_2X_2]^{2-}$ (X = Cl, Br) with iodide, which also obeys the rate law of equation 6.22.

$$I^- + [XPtL_4X]^{2-} \xrightarrow{\text{slow}} IX + [PtL_4]^{2-} + X^- \qquad (6.29)$$

$$XI + [PtL_4]^{2-} + I^- \xrightarrow{\text{fast}} X^- + [IPtL_4I]^{2-} \qquad (6.30)$$

Reaction 6.29 is theoretically reversible, but the rate of reaction of trans-$[Pt(CN)_4Cl_2]^{2-}$ with 4.2×10^{-3} M iodide is only decreased by ca. 4% in 1.0 M chloride,[31] so reaction 6.30 is much faster than the reverse of reaction 6.29.

The rates of substitution of iodide in trans-$[PtL_4Cl_2]^{2-}$ and trans-$[PtL_4Br_2]^{2-}$ (L = CN, ½ox, I) have been compared[33] to the susceptibility of trans-$[PtL_4I_2]$ to reduction, which is given by the equilibrium constant for the reaction

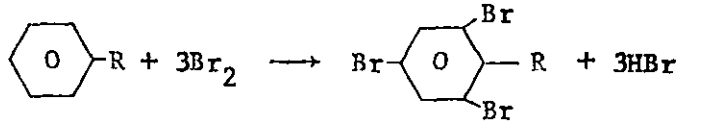
$$\text{trans-}[PtL_4I_2]^{2-} + I^- \rightleftharpoons [PtL_4]^{2-} + I_3^- \qquad (6.31)$$

The equilibrium constants for reaction 6.31 are in the ratio $10^4:10^3:1$ for L = CN, ½ox and I^- respectively, and the relative rate constants for the reaction of iodide with trans-$[PtL_4Br_2]^{2-}$ are $10^4:5 \times 10^2:1$ respectively. For the chloro-complexes the correlation is less good, the relative rate constants for reaction of iodide with trans-$[PtL_4Cl_2]^{2-}$ being $5 \times 10^4:10:1$ for L = CN, ½ox, I respectively. However, the general parallel between the equilibrium constants and the rate constants suggests that reduction is indeed the rate-determining step for these reactions. Moreover the difference in ΔG^0 for the reduction of trans-$[Pt(CN)_4Br_2]^{2-}$ and trans-$[PtBr_6]^{2-}$ by iodide is 5 kcal mol^{-1}; and the corresponding difference in $\Delta G^{\ddagger}$ is also 5 kcal mol^{-1}.[30] This implies that the transition state for the initial redox reactions of equation 6.29 lies close to the products on the reaction co-ordinate.

Skinner and Jones[34] studied the hydrolysis of trans-$[Pt(CN)_4Br_2]^{2-}$ and found the rate law

$$k_{obsd} = k_1[Br^-] + k_2[OH^-] \qquad (6.32)$$

They rejected the possibility that the first term in the rate law was due to bromide acting as the reductant in the REOA mechanism because in alkaline solution the Br_2 produced would be hydrolysed to HOBr, which they felt would be unable to oxidise the $[Pt(CN)_4]^{2-}$. (Poë and Vaughan[30] later showed that this claim was not valid.) Skinner and Jones[34] found that the rate of "decomposition" (presumably to $[Pt(CN)_4]^{2-}$) of trans-$[Pt(CN)_4Br_2]^{2-}$ is slower in the presence of 0.01 M phenol, than in the presence of 0.01 M aniline. Poë and Vaughan[30] admitted this was incompatible with a mechanism where free bromine was liberated, because bromine reacts with phenol or aniline at rates which approach diffusion control, and the reaction



(6.33)

(R = OH or NH_2) should only affect the position of equilibrium, and not the rate, of reaction 6.34

$$Br^- + [BrPt(CN)_4Br]^- \longrightarrow Br_2 + [Pt(CN)_4]^{2-} + Br^- \qquad (6.34)$$

Skinner and Jones[34] suggested that the bromide-dependent term in the rate law of equation 6.32 was due to the dissociative reaction of a $\{Br...BrPt(CN)_4Br\}^{3-}$ ion-pair. The hydroxide-dependent term was ascribed to an Id mechanism of $[Pt(CN)_4Br_2]^{2-}$; it was claimed that before fruitful reaction between trans-$[Pt(CN)_4Br_2]^{2-}$ and hydroxide could occur, the hydroxide ion must be in the second co-ordination sphere of the complex and suitably orientated to enter the vacant co-ordination site.

Poë and Vaughan[30] have reinterpreted Skinner and Jones' data according to the REOA mechanism. They showed that the graph of $\Delta G^{\ddagger}$ for the reaction

$$\underline{\text{trans}}\text{-}[Pt(CN)_4Br_2]^{2-} + Y^- \longrightarrow \underline{\text{trans}}\text{-}[Pt(CN)_4BrY]^{2-} + Br^- \qquad (6.35)$$

($Y^- = Br^-, OH^-, I^-$) against ΔG^0 for the reaction

$$Y^- + Br^- \longrightarrow YBr + 2e \qquad (6.36)$$

was linear with a slope of 0.7; this implies that the rate-determining step of reaction 6.35 is reduction of the complex by Y^-, and the transition state for this reduction is rather similar to the products. It has also been shown[31] that the rate law for the reduction of trans-$[Pt(CN)_4I_2]^{2-}$ by iodide in alkaline solution obeys the rate law

$$k_{obsd} = k_1[I^-] + k_2[OH^-] \qquad (6.37)$$

which resembles the rate law of equation 6.32 which is found for the substitution reaction

$$\underline{\text{trans}}\text{-}[Pt(CN)_4Br_2]^{2-} + OH^- \longrightarrow \underline{\text{trans}}\text{-}[Pt(CN)_4BrOH]^{2-} + Br^- \qquad (6.38)$$

Skinner and Jones[35] also studied the anation of trans-$[Pt(CN)_4BrOH_2]^-$ by bromide, and interpreted the results in terms of the rate law

$$k_{obsd} = k_1[Br^-] + k_2[Br^-]^2 \ , \qquad (6.39)$$

proposing the mechanism shown in equations 6.40 to 6.44.

Term which is first-order in $[Br^-]$

$$[PtL_4BrOH_2]^- \overset{\text{fast}}{\rightleftharpoons} \{PtL_4Br\}^- + H_2O \qquad (6.40)$$

$$\{PtL_4Br\}^- + Br^- \xrightarrow{\text{slow}} [PtL_4Br_2]^{2-} \qquad (6.41)$$

Term which is second-order in $[Br^-]$

$$Br^- + [BrPtL_4OH_2]^- \overset{\text{fast}}{\rightleftharpoons} \{Br...BrPtL_4OH_2\}^{2-} \quad (6.42)$$

$$\{Br...BrPtL_4OH_2\}^{2-} \overset{\text{fast}}{\rightleftharpoons} \{Br...BrPtL_4\}^{2-} + OH_2 \quad (6.43)$$

$$\{Br...BrPtL_4\}^{2-} + Br^- \xrightarrow{\text{slow}} Br^- + [BrPtL_4Br]^{2-} \quad (6.44)$$

where L = CN. The reaction was later studied by Mason[36] at very low bromide concentrations, and the rate law was found to be

$$k_{obsd} = k' + k[Br^-]^2 \quad (6.45)$$

The value of k' was very small, and except at very low concentrations of bromide its contribution to k_{obsd} was negligible. Mason did not discuss the difference between his rate law (equation 6.45) and that of Skinner and Jones (equation 6.39), but interpreted the rate law of equation 6.45 by the mechanism of equations 6.46 and 6.47

$$Br^- + \{BrPtL_4OH_2\}^- \overset{\text{fast}}{\rightleftharpoons} \{Br...BrPtL_4OH_2\}^{2-} \quad (6.46)$$

$$\{Br...BrPtL_4OH_2\}^{2-} + Br^- \xrightarrow{\text{slow}} Br^- + [BrPtL_4Br]^{2-} \quad (6.47)$$

where L = CN. Unlike Skinner and Jones, Mason did not feel justified in assigning the associative or dissociative nature of reaction 6.47, although he did consider it to be a normal interchange reaction. Recently, Morgan and Jones[37] re-examined the reaction, at concentrations of bromide which were intermediate between those of Mason and those of Skinner and Jones, and found the rate law

$$k_{obsd} = k[Br^-]^2 \quad (6.48)$$

They interpreted their results by the mechanism of equations 6.42 to

6.44, and claimed the term which was first-order in bromide that was found originally was due to a $[Pt(CN)_4]^{2-}$ catalysed pathway.

The anation of trans-$[Pt(CN)_4BrOH_2]^-$ by chloride has also been studied by Mason.[36] In this case the rate law was

$$k_{obsd} = k[Cl^-] \qquad (6.49)$$

and the mechanism proposed was a second-order interchange reaction between trans-$[Pt(CN)_4BrOH_2]^-$ and chloride. The non-existence of a second-order dependence on the chloride concentration was explained by the lower tendency of chloride to associate with the substrate in the equilibrium

$$Cl^- + [BrPt(CN)_4OH_2]^- \rightleftharpoons \{Cl...BrPt(CN)_4OH_2\}^{2-}$$

Skinner and Jones' original rate law (equation 6.39) has, however, been found to apply to the bromide anation of $[PtBr_5OH_2]^-$ and cis-$[PtBr_4(OH)_2]$.[38] Elding and Gustafson[38] interpreted this result in terms of the rapid pre-equilibrium between $[PtBr_4LOH_2]^{n-}$ and a $\{PtBr_4LOH_2,Br\}^{(n+1)-}$ ion-pair (L = Br^-, OH_2) and the slow, second-order reactions of both these species with bromide ions. Like Mason, Elding and Gustafson felt that no information was available on the associative or dissociative nature of these second-order reactions.

Summary

There are several pathways available for the thermal reactions of platinum(IV) complexes, and for any reaction the pathway followed is partly determined by the charge of the complex. Cationic complexes generally react by a platinum(II)-catalysed redox mechanism. Neutral complexes may also react by a platinum(II)-dependent pathway, but in the

absence of platinum(II) catalysts, they may be reduced by anions. Platinum(II)-catalysed reactions are energetically unfavourable for most anionic platinum(IV) complexes, which instead undergo substitution by the REOA mechanism. The interchange mechanism which is usually found for octahedral complexes is rather rare for platinum(IV) complexes. However, it has been claimed that the bromide-anation reactions of several anionic complexes occur by parallel pathways involving interchange reactions of the substrate and of a substrate-bromide ion-pair.

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CHAPTER 7

Anation of *trans*-$[Pt(CN)_4BrOH_2]^-$ by Bromide

Preamble

As indicated in chapter 6, the anation of trans-$[Pt(CN)_4BrOH_2]^-$ by Br^- has been studied by three groups of workers. Skinner and Jones [1] found the rate law

$$\frac{d[Pt(CN)_4Br_2]}{dt} = \frac{[H^+]}{K_A + [H^+]} (a_1[Br^-] + b_1[Br^-]^2)[Pt(CN)_4BrOH_2] \quad (7.1)$$

where K_A is the acid dissociation constant for the equilibrium

$$[Pt(CN)_4BrOH_2]^- \rightleftharpoons^{K_A} [Pt(CN)_4BrOH]^{2-} + H^+ \quad (7.2)$$

The factor $[H^+]/(K_A+[H^+])$ in equation 7.1 can be explained by assuming that the rate of Br^- anation of trans-$[Pt(CN)_4BrOH]^{2-}$ is negligible compared with that of trans-$[Pt(CN)_4BrOH_2]^-$. At a constant $[H^+]$ and with a pseudo-first order excess of Br^-, equation 7.1 reduces to

$$k_{obsd} = a[Br^-] + b[Br^-]^2 \quad (7.3)$$

where

$$a = \frac{[H^+]}{K_A + [H^+]} a_1 \quad (7.4)$$

$$b = \frac{[H^+]}{K_A + [H^+]} b_1 \quad (7.5)$$

Equation 7.3 predicts that a graph of $k_{obsd}/[Br^-]$ against $[Br^-]$ will be a straight line with a non-zero intercept. This graph was drawn using Skinner and Jones' data [1] at pH = 1.00, and is shown in Fig. 7.1. The dotted line, A, represents the equation

$$\frac{k_{obsd}}{[Br^-]} = a + b[Br^-] \qquad (7.6)$$

in which values of a and b were calculated from equations 7.4 and 7.5 respectively, using Skinner and Jones' values of a_1, b_1 and K_A.

However, Mason's results[2] at very low $[Br^-]$ obey the rate law

$$k_{obsd} = \frac{[H^+]}{K_A + [H^+]} k[Br^-]^2 + k' \qquad (7.7)$$

where k' is very small, and except at very low $[Br^-]$, negligible. For concentrations of Br^- that are sufficiently large that k' is negligible, equation 7.7 becomes

$$\frac{k_{obsd}}{[Br^-]} = \frac{[H^+]}{K_A + [H^+]} k[Br^-] \qquad (7.8)$$

Using Mason's value[2] for k and Skinner and Jones' value[1] for K_A, the dependence of $k_{obsd}/[Br^-]$ on $[Br^-]$ at pH = 1.00 was calculated. The dependence is shown in Fig. 7.1 as the full line B.

The results of Morgan and Jones[3] are not strictly comparable with those of Skinner and Jones[1] or with Mason's,[2] because the last two investigations were performed at an ionic strength, I, of 1.0 M, and Morgan and Jones' work was carried out at I = 0.5 M. For this reason, Morgan and Jones' results are shown separately in Fig. 7.2. Morgan and Jones claim that their results obey the rate law

$$k_{obsd} = \frac{[H^+]}{K_A + [H^+]} k'_3[Br^-]^2 \qquad (7.9)$$

but their tabulated values of $k_{obsd}/f[Br^-]^2$ where

$$f = \frac{[H^+]}{K_A + [H^+]} \qquad (7.10)$$

which should equal the constant, k'_3, decrease systematically by 16% over the concentration range 7.5×10^{-3} M $\leq [Br^-] \leq 2.5 \times 10^{-2}$ M (see reference 3, Table 8). Moreover, the linear graph of k_{obsd} against $[Br^-]^2$ from which k'_3 is calculated, has a non-zero intercept, in spite of the fact that equation 7.9 requires that the line pass through the origin (see reference 1, Fig. 1). Fig. 7.2 shows the graph of $k_{obsd}/[Br^-]$ against $[Br^-]$ for Morgan and Jones' data; the dotted line C was drawn by using Morgan and Jones' value of k'_3, and judging by inspection the best straight line through the points which had the required slope. The intercept of this line is ca. 25 M^{-1} s^{-1}, indicating that Morgan and Jones' interpretation of their results would in fact require the rate law

$$k_{obsd} = \frac{[H^+]}{K_A + [H^+]} \{3.23 \times 10^4 [Br^-]^2 + 25[Br^-]\} \qquad (7.11)$$

The term that is first order in $[Br^-]$ is in complete disagreement with Mason's results at very low $[Br^-]$.

However, the apparent conflict between the results of the three sets of workers seems to be resolved by the redox mechanism of Poë and co-workers.[4]-[7] This predicts the reaction sequence

$$Br^- + [BrPtL_4OH_2]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br_2 + [PtL_4]^{2-} + OH_2 \qquad (7.12)$$

$$Br_2 + [PtL_4]^{2-} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (7.13)$$

where $L^- = CN^-$. The steady state assumption applied to the concentration of $[PtL_4]^{2-}$ gives the rate law

$$k_{obsd} = \frac{k_1 k_2 [Br^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} \frac{[H^+]}{(K_A + [H^+])} \qquad (7.14)$$

Analysis of Skinner and Jones' data[1] at pH = 1.00 according to equation 7.14, and assuming a constant percentage error in k_{obsd}, gave $k_1k_2[H^+]/k_{-1}(K_A + [H^+]) = (3.5 \pm 0.3) \times 10^5\ M^{-2}s^{-1}$ and $k_2/k_{-1} = 52 \pm 8\ M^{-1}$; these values were used to draw curve D in Fig. 7.1. Similar analysis of Morgan and Jones' data[2] gave $k_1k_2[H^+]/k_{-1}(K_A + [H^+]) = (4.1 \pm 0.2) \times 10^4\ M^{-2}s^{-1}$ at pH = 1.88 and $k_2/k_{-1} = 12 \pm 3\ M^{-1}$; these values were used to draw curve E in Fig. 7.2.

Equation 7.14 predicts that at high $[Br^-]$, where $(k_2/k_{-1})[Br^-]$ becomes very much greater than 1, a limiting value of $k_{obsd}/[Br^-]$ (equal to $k_1[H^+]/(K_A + [H^+])$) should be reached. The onset of this effect can be seen in curves D and E of Figs. 7.1 and 7.2 respectively. The aim of the present work was to extend the previous studies of the $[Br^-]$-dependence of the reaction

$$\underline{\text{trans}}\text{-}[Pt(CN)_4BrOH_2]^- + Br^- \longrightarrow \underline{\text{trans}}\text{-}[Pt(CN)_4Br_2]^{2-} + H_2O \qquad (7.15)$$

to much higher $[Br^-]$ and to see whether the function $k_{obsd}/[Br^-]$ does indeed reach a limiting value.

Experimental

Preparation of Complexes

$K_2[Pt(CN)_4]\cdot 3H_2O$

Potassium tetracyanoplatinate(II) was prepared by slowly adding solid $K_2[PtCl_4]$ (ex Johnson Matthey and Mallory; 4.15 g) to a warm solution of KCN (2.60 g in 50 ml). This gave a pale yellow-green solution and a small quantity of brown crystalline precipitate. Addition of further KCN (ca. 0.1 g) did not dissolve the latter, and the solution was cooled and filtered. The filtrate was warmed and its volume reduced to ca. 35 ml. It was cooled and $K_2[Pt(CN)_4]\cdot 3H_2O$ precipitated as pale yellow-green crystals which were removed by filtration. Further evaporation of the filtrate yielded more of

the rather soluble $K_2[Pt(CN)_4]\cdot 3H_2O$. The two crops of crystals were combined and recrystallised from the minimum amount of warm H_2O. The recrystallised product was washed with a little ice-cold H_2O, but since it was required for further synthesis, it was not dried.

trans-$K_2[Pt(CN)_4Br_2]$

$K_2[Pt(CN)_4]\cdot 3H_2O$ (4.3 g) prepared as above was dissolved in the minimum amount of H_2O, and a few ml of ca. 3 M HBr added. Br_2 (1 ml) was added and the solution was warmed (not boiled) on a hot-plate to evaporate the excess Br_2 and reduce the volume to ca. 5 ml. Bright yellow, granular crystals precipitated and were filtered off. They were recrystallised by dissolving in the minimum amount of warm 3 M HBr, then cooling slowly to 4°C. The resulting crystals were filtered off using ice-cold apparatus, washed with a little ice-cold dil. HBr, and dried under vacuum at 35-45°C for 4 hr. The crystals did not change appearance at all on drying, and it is probable that they were originally isolated as the anhydrous salt.[8] The spectroscopic parameters of the product are compared with published values for trans-$K_2[Pt(CN)_4Br_2]$ in Table 7.1.

Kinetics

Preliminary experiments

In initial experiments on the bromide anation of trans-$[Pt(CN)_4BrOH_2]^-$, the bromoaquo-platinum(IV) complex was generated *in situ* by oxidising $K_2[Pt(CN)_4]$ with one equivalent of bromine:

$$Br_2 + [Pt(CN)_4]^{2-} + H_2O \xrightarrow{\text{fast}} Br^- + [BrPt(CN)_4OH_2]^- \qquad (7.16)$$

Although this method was used by the previous[1]-[3] workers, it was found to be rather inconvenient in this study, due to the difficulty of preparing

standard solutions of Br_2 and of preventing the evaporation of Br_2 once they have been standardised. The bromoaquo-substrate was therefore prepared from trans-$[Pt(CN)_4Br_2]^{2-}$ by the reaction

$$\text{trans-}[Pt(CN)_4Br_2]^{2-} + OH^- \longrightarrow \text{trans-}[Pt(CN)_4BrOH]^{2-} + Br^- \qquad (7.17)$$

In order to check the feasibility of preparing the substrate by this method, a known weight of trans-$[Pt(CN)_4Br_2]^{2-}$ was dissolved in 1×10^{-3} M NaOH and its U V spectrum measured. Changes in the U V spectrum of the solution were monitored on the Perkin-Elmer 402 Spectrophotometer for 1 hr, after which time no further change occurred. From Skinner and Jones' results[9] on the kinetics of the alkaline hydrolysis of trans-$[Pt(CN)_4Br_2]^{2-}$, the half-life of reaction 7.17 will be less than 1 min at 25°C, and the ratio $[Pt(CN)_4BrOH^{2-}]/[Pt(CN)_4Br_2^{2-}]$ will be greater than 10^3 at the $[OH^-]$ obtaining. Thus the compound formed after 1 hr was assumed to be trans-$[Pt(CN)_4BrOH]^{2-}$; as shown in Table 7.2 its extinction coefficient at 345 nm is 277 M^{-1} cm^{-1}, in excellent agreement with Skinner and Jones' values[1] of 260 M^{-1} cm^{-1} at 342 nm. An aliquot of the $[Pt(CN)_4BrOH]^{2-}$ solution was added to an equal aliquot of a solution of $HClO_4$ and NaBr to give a final solution that was 8×10^{-5} M in H^+ and 0.02 M in NaBr. The extinction coefficient of this solution at 345 nm is given in Table 7.2, where it is compared with the extinction coefficient (at the same wavelength and under similar conditions of pH and $[Br^-]$) of authentic trans-$[Pt(CN)_4Br_2]^{2-}$. Reaction 7.17 is clearly readily reversible on adding acid and it represents a very convenient method of preparing trans-$[Pt(CN)_4BrOH_2]^-$ *in situ*.

Quantitative Kinetic Experiments

The reaction

$$\underline{\text{trans}}\text{-}[Pt(CN)_4BrOH_2]^- + Br^- \longrightarrow \underline{\text{trans}}\text{-}[Pt(CN)_4Br_2]^{2-} + H_2O \qquad (7.18)$$

was studied using a Durrum-Gibson stopped flow spectrophotometer fitted with a logarithmic converter so that absorbances could be read directly from the oscilloscope screen. The absorbance against time traces were photographed using a Tetronix oscilloscope camera system and Polaroid Land Film type 107. Temperature control in the flow system was achieved by immersing the drive syringes in a water bath through which the water was circulated after passing through a heat exchanger placed in an external thermostat-bath. For all runs temperatures close to the drive syringes were within the range 25.00 ± 0.04°C measured by a precision partial immersion thermometer.

For the kinetic measurements, $\underline{\text{trans}}\text{-}[Pt(CN)_4BrOH_2]^-$ was generated by preparing a solution that was ca. 1×10^{-4} M in $\underline{\text{trans}}\text{-}K_2[Pt(CN)_4Br_2]$, 1.0 M in $NaClO_4$ and 1×10^{-3} M in NaOH. This solution was freshly prepared on each day that kinetic runs were performed, and it was used as the reactant solution in the first of the drive syringes. The second reactant solution was 1.4×10^{-3} M in $HClO_4$, from 8×10^{-3} to 4×10^{-1} M in NaBr, and contained sufficient $NaClO_4$ to maintain the ionic strength at 1.0 M. On mixing equal aliquots of the two solutions in the spectrophotometer, a solution which was 2×10^{-4} M in H^+, 5×10^{-5} M in $\underline{\text{trans}}\text{-}[Pt(CN)_4BrOH_2]^-$, from 4×10^{-3} to 2×10^{-1} M in NaBr and with an ionic strength of 1.0 was generated. Reaction 7.18 was followed by measuring the increasing absorbance at 342 nm.

After the stopped-flow measurements had been completed, 10 ml aliquots of each of the two reactant solutions were mixed and the pH of the combined solution was measured using a Radiometer pH-meter 26. A glass electrode was used as the probe electrode, and a saturated calomel electrode as the

reference electrode. Some difficulty was experienced in making the pH-measurements; although the initial reading was steady for about 1 min, and reasonably constant for all solutions, it then fell extremely rapidly, and did not appear to reach a steady value. Since saturated KCl was used as the salt bridge in the reference electrode, it was felt that precipitation of $KClO_4$ in the pores of the electrode sinter where the KCl solution came into contact with the 1.0 M $NaClO_4$ test solution was the cause of this effect. However, by making rapid measurements of the pH, and soaking the electrodes thoroughly in distilled H_2O between readings, it was found that the pH of all the reactant solutions was 3.554 ±0.002. This value differed somewhat from the value of 3.699 that was calculated from the known concentrations of NaOH and $HClO_4$ in the two solutions. In view of the difficulty of making the pH-measurements, this difference is probably not significant; the one important conclusion for the interpretation of the kinetic measurements, is that whichever value of the pH is correct, the pH is within experimental error the same in all solutions.

Pseudo-first order rate constants, k_{obsd} were obtained by plotting log $(y_\infty - y_t)$ against time where y_t and y_∞ are the ordinates in cm on the stopped flow trace corresponding to the absorbances at 342 nm of the reacting solution at time t, and after completion of the reaction respectively. The assumption of pseudo-first order conditions is an approximation only, since all previous authors have shown that the $[H^+]$-dependence of the reaction rate can be described by the rate law

$$k_{obsd} = \frac{[H^+]}{K_A + [H^+]} f([Br^-]) \qquad (7.19)$$

where $f([Br^-])$ is a function of the concentration of Br^-, and in the present experiments the $[H^+]$ was comparable to that of $[Pt(CN)_4BrOH_2]^-$. Assuming

that the $[H^+]$ was 2.79×10^{-4} M, the experimentally measured value, and that K_A is 3×10^{-2} M (an average of the results of all the previous workers), it can be calculated from equation 7.20

$$K_A = \frac{[H^+][Pt(CN)_4BrOH]}{[Pt(CN)_4BrOH_2]} \qquad (7.20)$$

that in these experiments the initial value of the ratio $[Pt(CN)_4BrOH]/[Pt(CN)_4BrOH_2]$ is greater than 100. Thus the equilibrium

$$[Pt(CN)_4BrOH_2]^- \rightleftharpoons [Pt(CN)_4BrOH]^{2-} + H^+ \qquad (7.2)$$

lies almost entirely to the right hand side, and the initial $[H^+]$ of the solution is 2.79×10^{-4} + [substrate] = 3.29×10^{-4} M. As the $[Pt(CN)_4BrOH_2]^-$ undergoes anation to $[Pt(CN)_4Br_2]^{2-}$, equilibrium 7.2 will be displaced to the left, consuming H^+. The net reaction will therefore be

$$\underline{trans}\text{-}[Pt(CN)_4BrOH]^- + H^+ + Br^- \longrightarrow \underline{trans}\text{-}[Pt(CN)_4Br_2]^{2-} + H_2O \qquad (7.18)$$

and for each mole of $\underline{trans}$-$[Pt(CN)_4Br_2]^{2-}$ produced, 1 mole of H^+ will be consumed. The $[H^+]$ will therefore change continually throughout the reaction from 3.29×10^{-4} M to 2.79×10^{-4} M, and by equation 7.19 the pseudo-first order rate constant will decrease by 15% during the reaction. This effect would give rise to curved first order rate plots, but since the absorbance changes during the reaction were less than 0.1 absorbance unit, uncertainties in the value of y_∞ in some cases more than compensated for the slowing down of the reaction due to consumption of H^+. In view of this, and of the low signal/noise ratio in some of the faster runs, which rendered determination of y_t and y_∞ rather difficult, it was felt that a full second-order analysis of the data according to equation 7.19 was not justified. Thus the rate

constants were obtained from the slope of the graph of $\log(y_\infty - y_t)$ against time, the best straight line being drawn through the points for the first 75% of the reaction; reasonably good rate plots were usually obtained over this period. A typical rate plot is shown in Fig. 7.3.

Results and Discussion

The values obtained for k_{obsd} at the various bromide concentrations used are given in Table 7.3. The average value $\bar{k}$ of k_{obsd} for a given set of runs at a constant concentration of bromide is given in Table 7.5. There are two sets of runs at $[Br^-] = 4 \times 10^{-2}$ M; these were performed on two different days with freshly prepared solutions, and were treated as two different sets of runs rather than one combined set. Within a set of runs the precision is generally fairly good, as can be seen from the standard deviations of $\bar{k}$, which are listed as a percentage, $\sigma_\%$ in column 3 of Table 7.4. A "pooled" standard deviation of $\bar{k}$, $\delta_\%$, defined as the square root of the pooled estimate of the variance of $\bar{k}$ is 2.53%. (The equations for calculating $\delta_\%$ are given in Appendix A.) This value is considerably less than the value of 14.6% which is the mean deviation between the two sets of runs at $[Br^-] = 4 \times 10^{-2}$ M, indicating that although the precision of the measurements within a set of runs is relatively high, the agreement between sets of runs is not as good.

Determination of the rate law

The rate law for the simple redox mechanism (equations 7.12 to 7.13) predicts that for the bromide anation of trans-$[Pt(CN)_4BrOH_2]^-$, the function $k_{obsd}/[Br^-]$ should initially increase linearly with $[Br^-]$, but should eventually reach a limiting value at high $[Br^-]$. A graph of k_{obsd} against $[Br^-]$

was plotted using the average values of k_{obsd} given in Table 7.5. Fig. 7.4 shows the results obtained over the concentration interval 4×10^{-3} M $\leq [Br^-] \leq 6 \times 10^{-2}$ M and Fig. 7.5 those for the concentrations of bromide in the range 6×10^{-2} M $\leq [Br^-] \leq 2 \times 10^{-1}$ M. (The error bars on these and the other graphs will be explained later.) Fig. 7.4 indicates that at low $[Br^-]$ the function $(k_{obsd}/[Br^-])$ begins to reach a limiting value, but at $[Br^-]$ greater than ca. 0.02 M the function begins to increase once more, as shown in Fig. 7.4 and 7.5. This indicates that although at low concentrations of bromide the redox mechanism provides the major pathway for reaction, at higher $[Br^-]$ a pathway giving rise to terms in the rate law that are at least third order in $[Br^-]$ becomes increasingly important. A graph of the function $k_{obsd}/[Br^-]^2$ against $[Br^-]$ was therefore plotted and it is shown in Fig. 7.6. Rearrangement of equation 7.14, the rate law for the redox mechanism, predicts that

$$\frac{k_{obsd}}{[Br^-]^2} = \frac{(k_1 k_2/k_{-1})}{(1 + (k_2/k_{-1})[Br^-])} \times \frac{[H^+]}{(K_A + [H^+])} \qquad (7.21)$$

so that if this mechanism is occurring, the function $k_{obsd}/[Br^-]^2$ should decrease with increasing $[Br^-]$. Fig. 7.6 shows that this does indeed happen, up to a $[Br^-] = 0.03$ M; at concentrations of Br^- greater than this value, the function increases with increasing $[Br^-]$, then appears to reach a limiting value. Fig. 7.4, Fig. 7.5 and Fig. 7.6 suggested that the full rate law for the Br^- anation of trans-$[Pt(CN)_4BrOH_2]^-$ might be of the form

$$k_{obsd} = \frac{a[Br^-]^2}{1 + b[Br^-]} + \frac{c[Br^-]^3}{1 + d[Br^-]} \qquad (7.22)$$

A weighted least squares treatment of the data of Table 7.5 according to equation 7.22 was therefore carried out, assuming that there was a constant percentage error in k_{obsd}. In the analysis it was assumed that in

each set of n_s runs at fixed $[Br^-]$ there were n_s independent determinations of k_{obsd} equal to the average value $\bar{k}$ of k_{obsd} found for that set. The use of average values of k_{obsd} was necessary because the weighting factor, w, associated with an individual point in the least squares procedure is given by

$$w = \frac{1}{(k_{obsd})^2} \tag{7.23}$$

Thus at a constant $[Br^-]$, the weighting factor would always be unduly high for the lowest value of k_{obsd}; the use of average values of k_{obsd} removes this bias. The use of n_s points all with the average value of k_{obsd} ensured that the precision associated with the number of points in the set was not lost. The details of the least squares analysis are given in Appendix D and the computer programme written to perform it in appendix E. The least squares procedure involved an interative refinement of initial estimates a^0, b^0, c^0, d^0 of a, b, c, d. These initial estimates were obtained by assuming that at low concentrations of Br^- equation 7.22 reduces to

$$k_{obsd} = \frac{a[Br^-]^2}{1 + b[Br^-]} \tag{7.24}$$

which gave estimates of a and b. Using these estimates of a and b, values of k_{obsd} at high $[Br^-]$, and the full rate law of equation 7.22, it was then possible to calculate estimates of c and d. These estimates of c and d were used with values of k_{obsd} at low $[Br^-]$ and the full rate law of equation 7.22 to give better estimates of a and b. It was necessary to repeat this procedure several times in order to obtain self-consistent values of a, b, c, d. When the values of these parameters were self-consistent they were used as a^0, b^0, c^0, d^0, the initial estimates of a, b, c, d in the weighted least squares analysis. This lengthy procedure

simply to obtain rough estimates of a, b, c, d was necessary because the percentage error in k_{obsd} is quite high, the function represented by equation 7.22 is mathematically very complicated, and values for a, b, c and d are all interdependent. It has been emphasised by Wentworth[10] that unless the initial estimates of parameters required for a non-linear least squares analysis are reasonably close to the final values obtained, the iterative procedure of the least squares method may not converge, in which case it becomes impossible to solve the least squares equations for the parameters required.

The results finally obtained by the least squares treatment are shown in Table 7.6. The average values of k_{obsd} fit equation 7.22 with a standard deviation of 11.1%. In view of the experimental difficulties involved in stopped flow measurements and the non-pseudo-first order conditions employed in these experiments, a standard deviation of this order of magnitude seems entirely reasonable. Moreover, this figure is comparable to the mean deviation of 14.6% found between the averages of the two sets of runs at $[Br^-]$ = 0.04 M, and it seems likely that much of the imprecision implied by the standard deviation of 11.1% is due to the difficulty of reproducing a given set of data, rather than systematic deviations from the rate law of equation 7.22.

The curves drawn through the experimental points of Figs. 7.4, 7.5 and 7.6 were calculated according to the values of a, b, c, d given in Table 7.6. The error bars of the function $y = k_{obsd}/[Br^-]$ in Figs. 7.4 and 7.5 represent $y \pm \sigma_y$ where σ_y is the standard deviation of y. By the law of propagation of errors, σ_y is given by

$$\sigma_y = \frac{ky}{100} \qquad (7.25)$$

where k is the percentage error (11.1%) of any value of k_{obsd}. Similarly the error bars of the function $z = k_{obsd}/[Br^-]^2$ in Fig. 7.6 represent $z \pm \sigma_z$ where σ_z is the standard deviation of z and is given by

$$\sigma_z = \frac{kz}{100} \tag{7.26}$$

If we define

$$k_A = \frac{a[Br^-]^2}{1 + b[Br^-]} \tag{7.27}$$

and

$$k_B = \frac{c[Br^-]^3}{1 + d[Br^-]} \tag{7.28}$$

then rearrangement of equation 7.22 gives equations 7.29 and 7.30.

$$\frac{[Br^-]}{k_{obsd} - k_B} = \frac{1}{a[Br^-]} + \frac{b}{a} \tag{7.29}$$

$$\frac{[Br^-]^2}{k_{obsd} - k_A} = \frac{1}{c[Br^-]} + \frac{d}{c} \tag{7.30}$$

Hence graphs of $[Br^-]/(k_{obsd}-k_B)$ and $[Br^-]^2/(k_{obsd}-k_A)$ against $1/[Br^-]$ should be linear. These graphs are shown in Figs. 7.7 and 7.8 respectively. Points for $[Br^-]$ greater than 5×10^{-2} M are omitted in Fig. 7.7 since at concentrations of Br^- greater than this figure k_B becomes large compared with k_{obsd} and the corresponding values of $[Br^-]/(k_{obsd}-k_B)$ become very imprecise. The value of 1.564 s^{-1} for k_{obsd} at $[Br^-] = 0.04$ M was also omitted from Fig. 7.7 since this value of k_{obsd} deviates by 29% (nearly three standard deviations) from the value predicted by equation 7.22. At bromide concentrations less than 5×10^{-2} M, k_A is relatively large compared with k_{obsd}; the points for Br^- concentrations less than 5×10^{-2} M are therefore omitted in Fig. 7.8, since at these concentrations the standard deviation of $[Br^-]^2/(k_{obsd}-k_A)$ becomes very large. The error bars in Fig. 7.7

represent $u \pm \sigma_u$ where u is $[Br^-]/(k_{obsd}-k_B)$ and σ_u is the standard deviation of u, calculated from the known standard deviations and covariances of a, b, c, d as indicated in appendix D. The error bars in Fig. 7.8 similarly represent $v \pm \sigma_v$ where v is $[Br^-]^2/(k_{obsd}-k_A)$ and σ_v is the standard deviation of v, calculated as shown in appendix D. Both Fig. 7.7 and Fig. 7.8 are reasonably good straight lines, as predicted by equation 7.22.

Comparison of these results with those of previous workers

As discussed above, trans-$[Pt(CN)_4BrOH_2]^-$ is a moderately strong acid, and the experimental rate law of equation 7.22 would be written more properly as

$$k_{obsd} = \left\{ \frac{a_s[Br^-]^2}{1 + b[Br^-]} + \frac{c_s[Br^-]^3}{1 + d[Br^-]} \right\} f \qquad (7.31)$$

where a_s, c_s are the kinetic parameters for trans-$[Pt(CN)_4BrOH_2]^-$ itself, and f is the fraction of the substrate which is present as $[Pt(CN)_4BrOH_2]^-$ at the experimental pH. From a mass balance on the substrate species the equation

$$[Pt(CN)_4BrOH_2] + [Pt(CN)_4BrOH] = C_t \qquad (7.32)$$

follows, where C_t is the total concentration of substrate species present at any time. From equations 7.31 and 7.32 it follows that

$$f = \frac{[H^+]}{K_A + [H^+]} \qquad (7.33)$$

Substitution of this value for f in equation 7.31 and comparison with equation 7.22 leads to the equalities

$$a = \frac{a_s h}{K_A + h} \qquad (7.34)$$

$$c = \frac{c_s h}{K_A + h} \qquad (7.35)$$

where h represents the $[H^+]$ obtaining during the present studies.

Comparison of the results of this study with those of previous investigations involves the use of equations 7.31 to 7.34. If h_1 represents the $[H^+]$ of a previous study, and k'_{obsd} the pseudo-first order rate constant at a given $[Br^-]$ then

$$k'_{obsd} = \left\{ \frac{a[Br^-]^2}{1 + b[Br^-]} + \frac{c[Br^-]^3}{1 + d[Br^-]} \right\} \times \frac{h}{(K_A+h)} \times \frac{(K_A+h_1)}{h_1} \qquad (7.36)$$

Defining

$$g = \frac{1}{k'_{obsd}} \left\{ \frac{a[Br^-]^2}{1 + b[Br^-]} + \frac{c[Br^-]^3}{1 + d[Br^-]} \right\} \qquad (7.37)$$

it can be seen from equation 7.36 that

$$g = \frac{h_1(K_A+h)}{h(K_A+h_1)} \qquad (7.38)$$

There seemed little point in comparing values of g calculated from equations 7.37 and 7.38, since the value of K_A is not known with any degree of precision. Thus K_A was found to be 2.5×10^{-2} M by Skinner and Jones[1] and 3.16×10^{-2} by Morgan and Jones[3] (both values were obtained from the pH-dependence of the rate constant in the Br^- anation of <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$), whereas Mason[2] found values of 5×10^{-2} M and 1.07×10^{-2} M from the pH-dependences of the anation of this complex by Br^- and by Cl^- respectively. A comparison with the previous work was attempted by using equation 7.37 to calculate values of g for each of the runs performed by Mason[2] at constant pH and varying $[Br^-]$. Since Mason found the rate law

$$k_{obsd} = \frac{[H^+]}{K_A + [H^+]} k[Br^-]^2 + k' \qquad (7.39)$$

the value of k'_{obsd} used in equation 7.37 was taken to be $(k_{obsd}-k')$. The values of g obtained are shown in Table 7.7. The average value, $\bar{g}$, of g appropriate to this set of runs was then calculated, and this value of $\bar{g}$ was used as g in equation 7.38 to calculate K_A. Since the pH of the present study varied during the kinetic run, h in equation 7.38 was assumed to be given by

$$h = h_f + \tfrac{1}{2}C_t \qquad (7.40)$$

where h_f is the $[H^+]$ at the end of the reaction and C_t is the total concentration of Pt(IV) species present. Since h_f was either 2.79×10^{-4} M or 2×10^{-4} M depending on whether the measured or calculated value of the pH was assumed to be correct, calculations for K_A were performed using both values, and the results are shown in Table 7.8. This procedure was followed for Skinner and Jones' two sets of data[1] at pH = 1.00 and 1.90 respectively, and for Morgan and Jones' data[3] at pH = 1.88. In all these three cases, the correction of k'_{obsd} by subtraction of k' was not necessary since k' is negligible compared to k'_{obsd}. The calculation of K_A, or even of g, from Morgan and Jones' results[3] is not strictly justified, since their work was performed at an ionic strength of 0.5 M, and not 1.0 M, but their work has been included for the sake of completeness. The values of g and $\bar{g}$ found for all authors' data are given in Table 7.7, and the values of K_A in Table 7.8. The results in Table 7.8 show that on the whole, regardless of the value assumed for the $[H^+]$ of this study, the values of K_A obtained are reasonably close to those found by other workers. The one exception to this result appears to be the work of Morgan and Jones,[3] and as explained above,

their work is not strictly comparable with the results of this study, or of the other investigations. The variation of the calculated value of K_A with the sets of results that are being compared is most probably due to systematic errors in the $[H^+]$, both in h and in h_1. Thus Mason's values[2] of h_1 were simply calculated from the concentration of $HClO_4$ which was added, Skinner[1] and Morgan[3] measured the pH of their solutions; this work has shown that the two methods are not necessarily equivalent.

An alternative method of comparing the results of the different studies, which eliminates the systematic errors of both h and h_1, can be devised. This method involves "correcting" the results of earlier workers to the pH of this study by use of the equation

$$k_{corr} = k \times \bar{g} \qquad (7.41)$$

where $\bar{g}$ is the correction factor (given in Table 7.8) appropriate to the results in question. Graphs of $[Br^-]/(k_{corr}-k_B)$ against $1/[Br^-]$ were plotted and are shown in Figs. 7.9 and 7.10. (k_B is defined in equation 7.28.) The straight lines in Figs. 7.9 and 7.10 were drawn according to the equation

$$\frac{[Br^-]}{k_{corr} - k_B} = \frac{1}{a[Br^-]} + \frac{b}{a} \qquad (7.42)$$

which is entirely analogous to equation 7.22 except that k_{corr} has replaced k_{obsd}. Using the values of a, b, c, d given in Table 7.6 and of $\bar{g}$ given in Table 7.8, Skinner and Jones' results[1] at pH = 1.00 and 1.90 fit equation 7.42 with standard deviations in k_{corr} of 14.0% and 9.5% respectively. There do seem to be some systematic deviations from equation 7.42 (see Fig. 7.9), but the later, and presumably more accurate, results of Morgan and Jones fit equation 7.42 with a standard deviation of only 5.2%, and the deviations seem to be random. Similarly, Mason's results fit equation 7.42 very well,

the standard deviation being only 2.7%.

Possible mechanisms

There are several mechanisms which can be postulated to explain the rate law found for this reaction. The first to be considered is derived from a mechanism suggested by Mason.[2] From his results at very low $[Br^-]$, where the rate law of equation 7.22 reduces to

$$k_{obsd}/f = a[Br^-]^2 \qquad (7.43)$$

he suggested that the mechanism involved formation of a Br^- ion-paired species, followed by a second order reaction of the ion-pair with another Br^- ion. Although he said that the nature of the second order reaction could not be deduced from the experimental data, he appears to have felt that it must be an A, or more probably, an Ia process. Mechanism A given below represents an adaptation of Mason's mechanism; reactions 7.44 and 7.46 are those originally proposed by Mason, and reactions 7.45 and 7.47 were added in an attempt to explain the third order dependence on $[Br^-]$.

Mechanism A

$$Br^- + [BrPtL_4OH_2]^- \underset{}{\overset{K_{IP}}{\rightleftharpoons}} \underset{A}{\{Br, BrPtL_4OH_2\}^{2-}} \qquad (7.44)$$

$$Br^- + \{Br, BrPtL_4OH_2\}^{2-} \overset{K_{IT}}{\rightleftharpoons} \underset{B}{\{2Br, BrPtL_4OH_2\}^{3-}} \qquad (7.45)$$

$$\underset{A}{\{Br, BrPtL_4OH_2\}^{2-}} + Br^- \xrightarrow{k_1} Br^- + [BrPtL_4Br]^{2-} + H_2O \qquad (7.46)$$

$$\underset{B}{\{2Br, BrPtL_4OH_2\}^{3-}} + Br^- \xrightarrow{k_2} 2Br^- + [BrPtL_4Br]^{2-} + H_2O \qquad (7.47)$$

(In this and all the other mechanisms discussed for this reaction, L

indicates CN.) Species A and B are an ion-pair, and an ion-triplet, respectively, formed between the platinum(IV) substrate and Br^-. As shown in Appendix B, Section (i), this mechanism predicts the rate law

$$\frac{k_{obsd}}{f} = \frac{k_1 K_{IP}[Br^-]^2 + k_2 K_{IP} K_{IT}[Br^-]^3}{1 + K_{IP}[Br^-] + K_{IP}K_{IT}[Br^-]^2} \qquad (7.48)$$

where f is defined in equation 7.33. Since K_{IP} and K_{IT} represent association between two ions of similar charge it is unlikely that they are greater than 0.2 M^{-1}, the association constant calculated by Prue[11] for "association" between two neutral species. Even at 0.2 M Br^-, the highest $[Br^-]$ used in this study, $(K_{IP}[Br^-] + K_{IP}K_{IT}[Br^-]^2)$ therefore would compose only 9% of the denominator in equation 7.48; under these conditions equation 7.48 would approximate to

$$\frac{k_{obsd}}{f} = k_1 K_{IP}[Br^-]^2 + k_2 K_{IP} K_{IT}[Br^-]^3 \qquad (7.49)$$

Equation 7.49 clearly does not resemble the experimental rate law, equation 7.22. If for some reason K_{IP} and K_{IT} were unexpectedly large, so that the full rate law of equation 7.48 would be predicted, the possibility exists that equation 7.48 might represent the variation of k_{obsd} with $[Br^-]$ as well as, or better than, equation 7.22. (Since k_{obsd} obviously depends in a very complex fashion on $[Br^-]$, it is not easy to distinguish by inspection between different polynomial expressions for this dependence.) However, as shown in Appendix C, section (i), equation 7.48 does not predict the minimum found in the graph of $k_{obsd}/[Br^-]^2$ against $[Br^-]$ (Fig. 7.6). Whatever the magnitudes of K_{IP} and K_{IT}, mechanism A can therefore be rejected.

A mechanism where the interchange reactions of steps 7.46 and 7.47 are

not Ia, but Id, can also be considered. In this case, steps 7.46 and 7.47 must now be written as two steps, the first being the formation of an encounter complex (steps 7.50 and 7.52 in mechanism B), and the second being a dissociative interchange within the encounter complex (steps 7.51 and 7.53 in mechanism B). The main reason for considering this mechanism is Skinner and Jones' claim[9] that the bromide-assisted hydrolysis of trans-$[Pt(CN)_4Br_2]^{2-}$ is the Id reaction of a Br^- ion pair. If the reaction

$$\{Br, BrPt(CN)_4Br\}^{3-} + H_2O \longrightarrow \{Br, BrPt(CN)_4OH_2\}^{2-} + Br^- \qquad (7.54)$$

is Id in nature, microreversibility demands that the reverse of this reaction also be Id in nature. Mechanism B shows the reaction sequence for the Id reaction of a bromide ion-pair and triplet with Br^-.

Mechanism B

$$Br^- + [BrPtL_4OH_2]^- \rightleftharpoons^{K_{IP}} \underset{A}{\{Br, BrPtL_4OH_2\}^{2-}} \qquad (7.44)$$

$$Br^- + \underset{A}{\{Br, BrPtL_4OH_2\}^{2-}} \rightleftharpoons^{K_{IT}} \underset{B}{\{2Br, BrPtL_4OH_2\}^{3-}} \qquad (7.45)$$

$$\underset{A}{\{Br, BrPtL_4OH_2\}^{2-}} + Br^- \rightleftharpoons^{K_1} \underset{C}{\{Br, BrPtL_4OH_2, Br\}^{3-}} \qquad (7.50)$$

$$\underset{C}{\{Br, BrPtL_4OH_2, Br\}^{3-}} \xrightarrow{k_1} Br^- + [BrPtL_4Br]^{2-} + H_2O \qquad (7.51)$$

$$\underset{B}{\{2Br, BrPtL_4OH_2\}^{3-}} + Br^- \rightleftharpoons^{K_2} \underset{D}{\{2Br, BrPtL_4OH_2, Br\}^{4-}} \qquad (7.52)$$

$$\{2Br, BrPtL_4OH_2, Br\}^{4-} \xrightarrow{k_2} 2Br^- + [BrPtL_4Br]^{2-} + H_2O \qquad (7.53)$$

In this mechanism, the ion-pairs B and C must be isomeric, the isomerism being caused by the different positions of the associated Br^- ions in the second co-ordination sphere of the complex. This mechanism therefore

requires that in the second co-ordination sphere of the complex there be specific sites for association. The rate law predicted by mechanism B is derived in Appendix C, section (ii), and it is found to be

$$\frac{k_{obsd}}{f} = \frac{k_1K_{IP}K_1[Br^-]^2 + k_2K_{IP}K_{IT}K_2[Br^-]^3}{1 + K_{IP}[Br^-] + (K_{IT}K_{IP} + K_1K_{IP})[Br^-]^2 + K_2K_{IP}K_{IT}[Br^-]^3} \qquad (7.55)$$

In order that the term $K_2K_{IP}K_{IT}[Br^-]^3$ comprise even 10% of the denominator in equation 7.55 at the highest $[Br^-]$ used, it is necessary that the product $K_2K_{IP}K_{IT}$ be at least 12.5 M^{-3}. Since

$$K_2K_{IP}K_{IT} = \beta_3 \qquad (7.56)$$

where β_3 is the overall formation constant of the ion quadruplet $\{2Br, BrPt(CN)_4OH_2, Br\}^{4-}$ from <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$ and $3Br^-$, a value of β_3 of 12.5 M^{-3} is clearly totally unreasonable. Thus equation 7.55 reduces to

$$\frac{k_{obsd}}{f} = \frac{k_1K_{IP}K_1[Br^-]^2 + k_2K_{IP}K_{IT}K_2[Br^-]^3}{1 + K_{IP}[Br^-] + (K_{IT}K_{IP} + K_1K_{IP})[Br^-]^2} \qquad (7.57)$$

which is of the form

$$\frac{k_{obsd}}{f} = \frac{a[Br^-]^2 + b[Br^-]^3}{1 + c[Br^-] + d[Br^-]^2} \qquad (7.58)$$

where

$$a = k_1K_1K_{IP} \qquad (7.59)$$

$$b = k_2K_2K_{IP}K_{IT} \qquad (7.60)$$

$$c = K_{IP} \qquad (7.61)$$

$$d = K_{IP}(K_{IT} + K_1) \qquad (7.62)$$

Equation 7.58 is of the same form as equation 7.48, and it has already been shown (Appendix C, section (i)) that this equation does not predict the variation of k_{obsd} with $[Br^-]$ that is found experimentally. Mechanism B can therefore be eliminated.

The next variation on a classical octahedral substitution mechanism is an adaptation of the mechanism which was proposed for this reaction by Morgan and Jones.[3] Since this mechanism assumes D activation and reaction via an (ion-paired) five-co-ordinate intermediate, it automatically concludes, by the principle of micro-reversibility, that Skinner and Jones' assignment[9] of the hydrolysis of the ion-pair $\{Br, BrPt(CN)_4Br\}^{3-}$ as an Id mechanism is erroneous. This implication of their mechanism was not commented on by Morgan and Jones.[3] Mechanism C shows the adaptation of Morgan and Jones' mechanism; steps 7.44, 7.63 and 7.64 represent these authors' original mechanism, and steps 7.45, 7.65 and 7.66 were added in an attempt to explain the third order dependence on $[Br^-]$ in equation 7.22.

Mechanism C

$$Br^- + [BrPtL_4OH_2]^- \overset{K_{IP}}{\rightleftharpoons} \underset{A}{\{Br, BrPtL_4OH_2\}}^{2-} \qquad (7.44)$$

$$Br^- + \underset{A}{\{Br, BrPtL_4OH_2\}}^{2-} \overset{K_{IT}}{\rightleftharpoons} \underset{B}{\{2Br, BrPtL_4OH_2\}}^{3-} \qquad (7.45)$$

$$\underset{A}{\{Br, BrPtL_4OH_2\}}^{2-} \overset{K_1}{\rightleftharpoons} \underset{C}{\{Br, BrPtL_4\}}^{2-} + H_2O \qquad (7.63)$$

$$\underset{C}{\{Br, BrPtL_4\}}^{2-} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (7.64)$$

$$\underset{B}{\{2Br, BrPtL_4OH_2\}}^{3-} \overset{K_3}{\rightleftharpoons} \underset{D}{\{2Br, BrPtL_4\}}^{3-} + H_2O \qquad (7.65)$$

$$\{2Br, BrPtL_4\}^{3-} + Br^- \xrightarrow{k_4} 2Br^- + [BrPtL_4Br]^{2-} \qquad (7.66)$$

As in mechanisms A and B, species A is an ion-pair and species B an ion-triplet formed between Br^- and the hexa-co-ordinate platinum(IV) substrate; species C and D are the corresponding species derived from the five-co-ordinate species $\{BrPtL_4\}^-$. Following Skinner and Jones[1] and Morgan and Jones,[3] equations 7.44, 7.45, 7.63, 7.65 are assumed to be rapid pre-equilibria, and equations 7.64 and 7.66 to be rate-determining. Consistent with their nature as association constants between ions of the same charge, K_{IP} and K_{IT} are assumed to be very small; since penta-co-ordinate Pt(IV) species have not been detected in solution, K_1 and K_2 are also assumed to be very small. With these assumptions, Mechanism C predicts that the rate law will be

$$\frac{k_{obsd}}{f} = k_2K_1K_{IP}[Br^-]^2 + k_4K_3K_{IP}K_{IT}[Br^-]^3 \qquad (7.67)$$

Equation 7.67 is derived in Appendix C, section (iii). Equation 7.67 is not of the same form as the experimental rate law, equation 7.22, so Morgan and Jones' mechanism[3] as such does not predict the correct form of the rate law and can accordingly be eliminated.

However, mechanism C in fact assumes that the rates of reactions 7.64 and 7.66 are negligible compared with those of the reverse of reactions 7.63 and 7.65 respectively. If this restriction is lifted, the more general mechanism D is obtained, where $k_2[Br^-]$ and $k_4[Br^-]$ are no longer negligible compared to k_{-1} and k_{-3} respectively.

Mechanism D

$$Br^- + [\underset{S}{BrPtL_4OH_2}]^- \overset{K_{IP}}{\rightleftharpoons} \{Br, \underset{A}{BrPtL_4OH_2}\}^{2-} \qquad (7.44)$$

$$Br^- + \{Br, \underset{A}{BrPtL_4OH_2}\}^{2-} \overset{K_{IT}}{\rightleftharpoons} \{2Br, \underset{B}{BrPtL_4OH_2}\}^{3-} \qquad (7.45)$$

$$\underset{A}{\{Br, BrPtL_4OH_2\}}^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{C}{\{Br, BrPtL_4\}}^{2-} + H_2O \qquad (7.63)$$

$$\underset{C}{\{Br, BrPtL_4\}}^{2-} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (7.64)$$

$$\underset{B}{\{2Br, BrPtL_4OH_2\}}^{3-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{D}{\{2Br, BrPtL_4\}}^{3-} + H_2O \qquad (7.65)$$

$$\{2Br, BrPtL_4\}^{3-} + Br^- \xrightarrow{k_4} 2Br + [BrPtL_4Br]^{2-} \qquad (7.66)$$

This mechanism predicts the rate law

$$\frac{k_{obsd}}{f} = \frac{k_1k_2K_{IP}[Br^-]^2}{k_{-1} + k_2[Br^-]} + \frac{k_3k_4K_{IT}K_{IP}(Br^-]^3}{k_{-3} + k_4[Br^-]} \qquad (7.68)$$

which is of the same form as the experimental rate law (equation 7.22), so that mechanism D cannot be eliminated immediately. However, this mechanism predicts that the Br^- ion pair, A, is very much more reactive than the substrate, since there is no term in the rate law corresponding to reaction of the substrate itself. (Skinner and Jones' original claim[1] that there was such a term was disproved by Mason[2] and by Morgan and Jones.[3]) This situation is very unusual; as shown in Table 3.1 on page 135, ion pairs are generally only 1 to 5 times more reactive than their parent complex towards dissociative activation. Moreover, comparison of the predicted rate law (equation 7.68) with that found experimentally (equation 7.22) gives

$$\frac{c}{d} = k_3K_{IP}K_{IT}f \qquad (7.69)$$

$$\frac{a}{b} = k_1K_{IP}f \qquad (7.70)$$

so that

$$\frac{cb}{ad} = \frac{k_3K_{IT}}{k_1} \qquad (7.71)$$

Using the experimental values of a, b, c, d given in Table 7.6, k_3K_{IT}/k_1 is calculated to be 125 M^{-1}. Since it was assumed implicitly in the derivation of equation 7.68 that even at the highest concentrations of Br^- (0.2 M), $K_{IP}[Br^-]$ and $K_{IT}[Br^-]$ were very much less than 1, K_{IP} must be very much smaller than 5; and because of the more unfavourable electrostatic contribution to the free energy of formation of the ion triplet, K_{IT} would be expected to be very much smaller than K_{IP}. Also, Poë and Vaughan[5] using a spectroscopic method found that the ion-pair formation constant for the equilibrium

$$Br^- + [BrPt(CN)_4Br]^{2-} \rightleftharpoons \{Br, BrPt(CN)_4Br\}^{3-} \qquad (7.72)$$

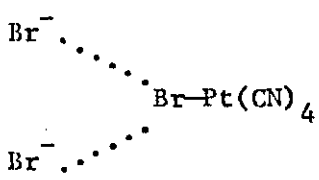
was less than 0.1 M^{-1}. If it is assumed that the ion-pair $\{Br, BrPt(CN)_4OH_2\}^{2-}$ is roughly equivalent to <u>trans</u>-$[BrPt(CN)_4Br]^{2-}$, K_{IT} also becomes less than 0.1 M^{-1}. This means that k_3/k_1 is greater than $125/0.1 = 1.25 \times 10^3$. It seems wholly unreasonable to assume that the ion-triplet $\{2Br, BrPt(CN)_4OH_2\}^{3-}$ will be over a thousand times more reactive than the ion-pair $\{Br, BrPt(CN)_4OH_2\}^{2-}$ towards dissociative activation. In addition, it is necessary to propose some kind of specific association between Br^- ions and $\{BrPt(CN)_4\}^-$ in D, in order to explain why these species require the presence of a second and a third Br^- ion in their second co-ordination sphere before they can collapse to the $[BrPt(CN)_4Br]^{2-}$ product. In order to account for the fact that Br^- accelerated, rather than retarded, the supposedly dissociative hydrolysis of <u>trans</u>-$[Pt(CN)_4Br_2]^{2-}$, Skinner and Jones[9] proposed a mechanism involving the $\{Br, BrPt(CN)_4Br\}^{3-}$ ion-pair, and proposed that this species had the structure I

$$\{Br^-.....Br\text{–}Pt(CN)_4\text{–}Br\}^{3-} \qquad (I)$$

where the Br^- ligand trans- to the associated free Br^- ion is the leaving group. An attractive interaction, indicated in I by dotted lines, between the associated Br^- ion and the co-ordinated Br^- ligand, was suggested to be the binding force within the aggregate. The high positive charge of the central Pt atom polarises electrons in the Pt–Br bond, making the co-ordinated Br^- relatively positive, and hence susceptible to electron donation by free Br^-. Following this example, the structure of the ion-paired intermediate C would be II

$$\{Br^-.....Br\text{–}Pt(CN)_4\}^{2-} \qquad (II)$$

and that of the ion-triplet species D would be III



(III)

In each case the associated Br^- ions are located across the molecule, trans to the vacant co-ordination site, and collapse of C or D to give the dibromo-product cannot be accomplished without considerable rearrangement of the molecular geometry. However, in structure III it is difficult to see why the two Br^- ions prefer to occupy adjacent positions in the second co-ordination shell, when electrostatic considerations suggest they would be located at antipodes of the complex. An alternative structure for D would be IV

$$\{Br^-.....Br^-.....Br\text{–}Pt(CN)_4\}^{3-} \qquad (IV)$$

which is derived from II by considering that there is extensive polarisation in the Br...Br–Pt bond, so that the Br^-...Br becomes analogous to Br_2, and can accept electron donation by a further Br^- ion to give the structure IV

which corresponds to Br_3^-. Since Skinner and Jones[9] state quite definitely that the Pt and Br^- ions retain their oxidation states of +IV and -I respectively, the extent of polarisation in the Br...Br–Pt bond of II must be rather small, and it seems unlikely that the associated Br^- ion would become sufficiently positive that the attractive interaction discussed above would be greater than the electrostatic repulsion between II and another Br^- ion. Thus it is hard to accept the physical reality of an ion-triplet species formed by the supposed geometrically specific association between three negative ions.

One final piece of evidence against this mechanism is the fact that at an ionic strength of 0.5 M, and at low concentrations of Br^- where the rate law of equation 7.68 reduces to

$$\frac{k_{obsd}}{f} = k_{Br}[Br^-]^2 \qquad (7.73)$$

where

$$k_{Br} = \frac{k_1 k_2 K_{IP}}{k_{-1}} \qquad (7.74)$$

Mason[2] found that the activation parameters associated with k_{Br} were $\Delta H^{\ddagger}_{Br} = 9.3 \pm 1.5$ kcal mol^{-1} and $\Delta S^{\ddagger}_{Br} = -2 \pm 4$ e.u. (The values found by Morgan and Jones[3] at an ionic strength of 1.0 M, at Br^- concentrations where equation 7.73 is just becoming inappropriate are not significantly different from Mason's.) These values can be contrasted with the activation parameters found by Domingos et al.[12] for the Cl^- anation of $[IrCl_5OH_2]^{2-}$; this reaction is postulated to occur by a D mechanism, and the activation parameters in 1.0 M Cl^- solution are $\Delta H^{\ddagger} = 27.6 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = 7.3 \pm 3.5$ e.u. Corresponding to equation 7.74 we can write

$$\Delta H^{\ddagger}_{Br} = \Delta H^{\ddagger}_1 + \Delta H^{0}_{IP} \qquad (7.75)$$

where $\Delta H_1^{\ddagger}$ is the apparent enthalpy of activation associated with the product k_1k_2/k_{-1} and ΔH_{IP}^0 is the enthalpy of formation of the ion-pair, species A. In order that $\Delta H_1^{\ddagger}$ be comparable to Domingos' value for $\Delta H^{\ddagger}$, ΔH_{IP}^0 must be within 1 or 2 kcal mol^{-1} of the difference between $\Delta H_{Br}^{\ddagger}$ and $\Delta H^{\ddagger}$, i.e., ΔH_{IP}^0 is ca. (9.3 - 27.6) or -16.3 kcal mol^{-1}. This value is totally unreasonable; although the enthalpies of formation of aggregates of similarly charged ions are not known, enthalpies of formation of ion pairs between oppositely charged ions generally lie between the limits -3 to +5 kcal mol^{-1}.(13)

Mechanisms A to D exhaust the possible classical substitution mechanisms that can be postulated for this reaction, and all have been found to be inadequate. As Poë and his co-workers have emphasised,(7) the substitution reactions of anionic Pt(IV) complexes are all consistent with a redox mechanism where the incoming nucleophile reduces the substrate to the corresponding Pt(II) species in a rate determining step which is followed by the fast re-oxidation of the Pt(II) intermediate to give the Pt(IV) product. As indicated on page 274, the simple redox mechanism predicts the rate law

$$\frac{k_{obsd}}{f} = \frac{a[Br^-]^2}{1 + b[Br^-]} \qquad (7.76)$$

where

$$a = \frac{k_1k_2}{k_{-1}} \qquad (7.77)$$

$$b = \frac{k_2}{k_{-1}} \qquad (7.78)$$

k_1 being the rate constant for the reduction of trans-$[Pt(CN)_4BrOH_2]^-$ to $[Pt(CN)_4]^{2-}$ and k_{-1} and k_2 being the rate constants for the re-oxidation of the Pt(II) complex in the presence of H_2O or Br^- respectively. Obviously, the simple mechanism of Poë et al. will not completely explain the observed dependence of k_{obsd} on $[Br^-]$. However, it does predict one part of the

two-part rate law, and qualitatively it seemed likely that the mechanism for reaction 7.15 involved two parallel pathways, one being the usual redox reaction of the substrate with Br^-, and the other involving the presence of more than two Br^- ions in the rate-determining transition state. The first redox mechanism to be considered arises from a comment by Skinner and Jones[9] on the mechanism for the bromide-assisted hydrolysis of trans-$[Pt(CN)_4Br_2]^{2-}$. They claimed that if Br_2 were produced by reduction of trans-$[Pt(CN)_4Br_2]^{2-}$ by Br^-, under the alkaline conditions obtaining it would be hydrolysed to HOBr. Thus mechanism E considers the possibility that in the Br^- anation of trans-$[Pt(CN)_4BrOH_2]^-$, Br_2 produced by reduction of the substrate by Br^- can react with another Br^- ion to give Br_3^-; this can then re-oxidise the Pt(II) complex to the dibromo-product or the bromoaquo-substrate.

Mechanism E

$$Br^- + [BrPtL_4OH_2]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br_2 + [PtL_4]^{2-} + OH_2 \qquad (7.79)$$

$$Br_2 + Br^- \overset{K_{Br}}{\rightleftharpoons} Br_3^- \qquad (7.80)$$

$$Br_2 + [PtL_4]^{2-} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (7.81)$$

$$Br_3^- + [PtL_4]^{2-} + OH_2 \xrightarrow{k_3} 2Br^- + [BrPtL_4OH_2]^- \qquad (7.82)$$

$$Br_3^- + [PtL_4]^{2-} + Br^- \xrightarrow{k_4} 2Br^- + [BrPtL_4Br]^{2-} \qquad (7.83)$$

As shown in Appendix C, section (v), this mechanism predicts the rate law

$$\frac{k_{obsd}}{f} = \frac{k_1k_2[Br^-]^2 + k_1k_4K_{Br}[Br^-]^3}{k_{-1} + (k_2 + k_3K_{Br})[Br^-] + k_4K_{Br}[Br^-]^2} \qquad (7.84)$$

Equation 7.84 is of the form

$$\frac{k_{obsd}}{f} = \frac{a[Br^-]^2 + b[Br^-]^3}{1 + c[Br^-] + d[Br^-]^2} \qquad (7.85)$$

and it has already been shown (Appendix C, section (i)), that regardless of the values of a, b, c and d, this expression does not predict the minimum in the graph of $k_{obsd}/[Br^-]^2$ against $[Br^-]$ that is found experimentally (Fig. 7.6). Mechanism E can therefore be rejected.

The failure of mechanism E to explain the experimental results indicated that the reaction pathway which was higher order in $[Br^-]$ involved the direct interaction of two Br^- ions with the substrate, rather than with the reactive intermediate generated by reduction of the substrate by Br^-. Reaction 7.15 was therefore considered to proceed by the Br^- reduction of a bromide-substrate ion pair, as well as by the more usual redox mechanism. The ion pair was assumed to have a definite geometry, and the binding forces within the ion-pair were assumed to be very localised, as shown in mechanism F.

Mechanism F

$$Br^- + [BrPtL_4OH_2]^- \overset{K}{\rightleftharpoons} \{Br....BrPtL_4OH_2\}^{2-} \qquad (7.86)$$

$$\{Br....BrPtL_4OH_2\}^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br_2 + [PtL_4]^{2-} + OH_2 \qquad (7.87)$$

$$Br^- + \{Br....BrPtL_4OH_2\}^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Br_3^- + [PtL_4]^{2-} + OH_2 \qquad (7.88)$$

$$Br^- + Br_2 \underset{k_{-Br}}{\overset{k_{Br}}{\rightleftharpoons}} Br_3^- \qquad (7.80)$$

$$Br_2 + [PtL_4]^{2-} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (7.81)$$

$$Br_3^- + [PtL_4]^{2-} + Br^- \xrightarrow{k_4} 2Br^- + [BrPtL_4Br]^{2-} \qquad (7.83)$$

Steps 7.86, 7.87, 7.81 represent the normal redox pathway, and equation 7.80 is assumed, as before, to be a very rapid equilibrium. As shown in Appendix C, section (vi), this mechanism predicts the rate law

$$\frac{k_{obsd}}{f} = \frac{k_2k_1k_{-3}K[Br^-]^2 + k_4k_3k_{-1}K[Br^-]^3}{k_{-1}k_{-3}(1 + \frac{k_2}{k_{-1}}[Br^-])} \qquad (7.89)$$

which is of the form

$$\frac{k_{obsd}}{f} = \frac{a[Br^-]^2 + b[Br^-]^3}{1 + c[Br^-]} \qquad (7.90)$$

As shown in Appendix C, section (vi), this rate law will not predict the minimum found in the graph of $k_{obsd}/[Br^-]^2$ against $[Br^-]$, and mechanism F can therefore be completely discounted.

The next mechanism to be considered is a variation of mechanism F in that the Br_2 and Br_3^- generated in steps 7.87 and 7.88 respectively do not diffuse away from the $[Pt(CN)_4]^{2-}$ into the body of the solution, but remain co-ordinated to the platinum(II) species. Thus in mechanism G outlined below, species B and C are five-co-ordinate platinum(II) complexes, there being a Br_2 molecule and a Br_3^- ion respectively co-ordinated along the z-axis of the complex, perpendicular to the plane of the four CN^- ligands.

Mechanism G

$$Br^- + [BrPtL_4]^- \rightleftharpoons \underset{A}{\{Br....BrPtL_4OH_2\}^{2-}} \qquad (7.86)$$

$$\{Br....BrPtL_4OH_2\}^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{B}{\{Br_2....PtL_4\}^{2-}} + OH_2 \qquad (7.91)$$

$$Br^- + \{Br....BrPtL_4OH_2\}^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \{Br_3^-....PtL_4\}^{3-} + OH_2 \qquad (7.92)$$

$$Br^- + \{Br_2....PtL_4\}^{2-} \underset{k'_{-Br}}{\overset{k'_{Br}}{\rightleftharpoons}} \{Br_3^-....PtL_4\}^{3-} \qquad (7.93)$$

$$\{Br_2....PtL_4\}^{2-} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (7.94)$$

$$\{Br_3^-....PtL_4\}^{3-} + Br^- \xrightarrow{k_4} 2Br^- + [BrPtL_4Br]^{2-} \qquad (7.95)$$

Equilibrium 7.93 is analogous to the equilibrium of equation 7.80, and like the latter, it was assumed to be established very rapidly. As shown in Appendix C, section (vii), the rate law predicted by this mechanism is

$$\frac{k_{obsd}}{f} = \frac{k_1K(k_2 + k_4K'_{Br}[Br^-])[Br^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} \qquad (7.96)$$

which is of the form

$$\frac{k_{obsd}}{f} = \frac{a[Br^-]^2 + b[Br^-]^3}{1 + c[Br^-]} \qquad (7.97)$$

As shown in Appendix C, section (vi), regardless of the values of a, b, and c, equation 7.97 will not predict the minimum found in the graph of $k_{obsd}/[Br^-]^2$ against $[Br^-]$. Mechanism G is therefore unacceptable.

The final mechanism to be considered is identical to that of mechanism G except that the equilibrium of equation 7.93 is considered to be established so slowly relative to the rates of reactions 7.94 and 7.95 and the reverse of reactions 7.91 and 7.92, that it does not act as a perturbation on the system, and its existence can be ignored. The reaction sequence of mechanism H therefore represents this modification of the redox mechanism.

Mechanism H

$$Br^- + [BrPtL_4OH_2]^- \overset{K}{\rightleftharpoons} \underset{A}{\{Br....BrPtL_4OH_2\}^{2-}} \qquad (7.86)$$

$$\{Br....BrPtL_4OH_2\}^{2-} \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} \underset{B}{\{Br_2....PtL_4\}^{2-}} + OH_2 \qquad (7.91)$$

$$Br^- + \{Br..BrPtL_4OH_2\}^{2-} \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} \underset{C}{\{Br_3^-....PtL_4\}^{3-}} + OH_2 \qquad (7.92)$$

$$\{Br_2....PtL_4\}^{2-} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (7.94)$$

$$\{Br_3^-....PtL_4\}^{3-} + Br^- \xrightarrow{k_4} 2Br^- + [BrPtL_4Br]^{2-} \qquad (7.95)$$

As shown in Appendix C, section (viii), the rate law predicted by this mechanism is

$$\frac{k_{obsd}}{f} = \frac{k_1k_2K[Br^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} + \frac{k_3k_4K[Br^-]^3}{k_{-3}(1 + \frac{k_4}{k_{-3}}[Br^-])} \qquad (7.98)$$

which is of the same form as the experimental rate law (equation 7.22).

In addition to predicting the correct form of the rate law, mechanism H agrees well with the known chemistry of platinum(IV) and platinum(II) complexes. Thus although association between two negatively charged species is unlikely in terms of simple electrostatic interactions, the specific geometry and interaction proposed for the species $\{Br....BrPt(CN)_4OH_2\}^{2-}$ suggest this species should be designated as a charge-transfer complex, rather than an ion-pair. The existence of such complexes between platinum(IV) compounds and halide ions has already been proposed to explain the spectroscopic interactions which occur between trans-$[Pt(CN)_4X_2]^{2-}$ and X^- (X = Cl, Br)[7] and between $[PtBr_6]^{2-}$ and Br^-.[14]

For the tetracyano-complexes the spectrum is unaffected by the addition of relatively large amounts of $[Pt(CN)_4]^{2-}$ so the redox reaction

$$X^- + [XPt(CN)_4X]^{2-} \rightleftharpoons X_3^- + [Pt(CN)_4]^{2-} \qquad (7.99)$$

is not responsible for the spectroscopic changes. At a fixed wavelength the increase in absorbance is linear up to 2.0 M bromide or 4.0 M chloride, suggesting that K for these complexes is less than 0.1 M^{-1}. In agreement with the assumptions of mechanism H, charge transfer complexes of halide ions and anionic platinum(IV) complexes do exist, and the equilibrium constants governing their formation are small.

Evidence for the specific nature of the interactions within these complexes comes from studies of the association of halide ions with cationic platinum(IV) complexes. When free X^- is added to trans-$[Pten_2X_2]^{2+}$ (X = Cl , Br) new peaks grow in the UV spectrum at 240 nm (X = Cl) and 260 nm (X = Br).[15][16] The positions of these peaks are close to the absorption maxima of Cl_2 in Cl^- solution and Br_2 in Br^- solution respectively,[17] but the addition of $[Pten_2]^{2+}$ does not affect the absorbance, so the redox equilibrium

$$X^- + [Pten_2X_2]^{2+} \rightleftharpoons X_3^- + [Pten_2]^{2+} \qquad (7.100)$$

cannot be causing the spectroscopic interaction. However, the similarity of the spectrum of the ion-pairs to that of the corresponding trihalide ion led Poë[15] to propose that the associated species had the specific geometry $\{X....XPten_2X\}^+$, and to suggest that X^- to Pt charge transfer had occurred to some extent. This view is reinforced by Fleischauer and Adamson's study[18] of the photoaquation of trans-$[Pt(NH_3)_4Br_2]^{2+}$. Flash photolysis

of this complex in the presence of sodium bromide generates a transient species, identified as Br_2^-, which is not produced by flashing solutions of <u>trans</u>-$[Pt(NH_3)_4Br_2](ClO_4)_2$ or sodium bromide alone. Thus the structure assigned to the charge-transfer complex of bromide and $[Pt(CN)_4BrOH_2]^-$ seems very reasonable.

Having settled the structure of the charge-transfer complex (A), the question as to the nature of the complexes $\{Br_2....Pt(CN)_4\}^{2-}$ and $\{Br_3^-....Pt(CN)_4\}^{3-}$ (species (B) and (C) in mechanism H) then arises. The formation of five-co-ordinate adducts by square planar complexes of platinum(II) has been postulated many times,[19] and Harris and Livingstone[20] have emphasised that the presence of π-acceptor ligands in the complex enhances the tendency to form such species. Consistent with this hypothesis, $[Ni(CN)_5]^{3-}$ is readily formed from $[Ni(CN)_4]^{2-}$ and CN^-[21] and $[Ptdiars_2]^{2+}$ readily forms five-co-ordinate adducts with Cl^-, Br^-, I^-, N_3^-, SCN^-, $SeCN^-$ or thiourea.[22][23] The formation of adducts of square planar Pt(II) complexes and molecular halogens has also been suggested. Jones and Morgan[24] studied the oxidative addition of Cl_2 to $[PtCl_4]^{2-}$ in water, at 25°C, in which the first reaction is

$$Cl_2 + [PtCl_4]^{2-} + H_2O \longrightarrow [PtCl_5OH_2]^- + Cl^- \qquad (7.101)$$

followed by the slower anation of the chloroaquo-intermediate

$$[PtCl_5OH_2]^- + Cl^- \longrightarrow [PtCl_6]^{2-} + OH_2 \qquad (7.102)$$

Unlike the corresponding oxidative addition of Br_2 to $[Pt(CN)_4]^{2-}$,[1]-[3] reaction 7.101 was slow enough to be studied with a stopped flow spectrophotometer, and the rate of the oxidation was found to be independent of the concentration of Cl_2.[24] Good first-order rate plots were obtained,

even when the concentration of Cl_2 was equal to that of $[PtCl_4]^{2-}$. This implies that even at reactant concentrations as low as 5×10^{-5} M, the equilibrium

$$Cl_2 + [PtCl_4]^{2-} \overset{K_{ass}}{\rightleftharpoons} \{Cl_2....PtCl_4\}^{2-} \qquad (7.103)$$

is saturated. Even if it assumed that departure from linear rate plots could only be detected if 50% of the $[PtCl_4]^{2-}$ were uncomplexed, since

$$K_{ass} = \frac{[Cl_2....PtCl_4]}{[PtCl_4][Cl^-]} \qquad (7.104)$$

and

$$[PtCl_4] = [Cl^-] = [Cl_2....PtCl_4] = 2.5 \times 10^{-5} \qquad (7.105)$$

it follows that K_{ass} is greater than 4×10^4 M^{-1}. Similarly, Hopgood and Jenkins[25] found an equilibrium constant of $(2.7 \pm 0.7) \times 10^4$ M^{-1} for the reaction

$$I_2 + [Pt(acac)_2] \rightleftharpoons \{I_2....Pt(acac)_2\} \qquad (7.106)$$

in CCl_4 at 31.3°C.

Kinetic evidence is also available to support the suggestion that the equilibrium constant for the reaction

$$Br_2 + [Pt(CN)_4]^{2-} \rightleftharpoons \{Br_2....Pt(CN)_4\}^{2-} \qquad (7.107)$$

is large. However, since this relies on the premise that the Br^--assisted hydrolysis of trans-$[Pt(CN)_4Br_2]^{2-}$ occurs by a redox mechanism it is first necessary to digress somewhat and consider the mechanism of the hydrolysis of trans-$[Pt(CN)_4Br_2]^{2-}$. Skinner and Jones[9] studied the reaction

$$[Pt(CN)_4Br_2]^{2-} + H_2O \longrightarrow [Pt(CN)_4BrOH_2]^- + Br^- \qquad (7.108)$$

in the presence of OH^- and Br^- and found the rate law

$$k_{obsd} = k[Br^-] + k'[OH^-] \qquad (7.109)$$

As indicated in Chapter 6, the mechanism proposed to explain the second term of this rate law involved an Id substitution of OH^- in the substrate, the dependence of the rate on the $[OH^-]$ representing an "accidental bimolecularity" which arises from the necessity that before reaction can occur, OH^- must be present in the second co-ordination sphere of the complex. It is hard to envisage the occurrence of this "accidental bimolecularity", since the second co-ordination sphere of the complex presumably contains only H_2O molecules and (maybe) an OH^- ion. The presence of the OH^- ion seems superfluous when a H_2O molecule is ideally situated to "capture" the vacant co-ordination site, and a Grotthus chain mechanism[26] can convert the aquo-complex to its hydroxy-analogue at a rate which is limited only by the mobility of a proton.

It seems most reasonable, therefore, to ascribe the term in the rate law that is dependent on $[OH^-]$ to the occurrence of the redox mechanism shown in equations 7.110 and 7.111.

$$HO^- + [BrPt(CN)_4Br]^{2-} \rightleftharpoons \{HOBr....Pt(CN)_4\}^{2-} + Br^- \qquad (7.110)$$

$$\{HOBr....Pt(CN)_4\}^{2-} + OH_2 \longrightarrow HO^- + [BrPt(CN)_4OH_2]^- \qquad (7.111)$$

Skinner and Jones[9] ascribed the dependence of the rate on $[Br^-]$ to a mechanism involving Id loss of Br^- from a $\{Pt(CN)_4Br_2, Br\}^{2-}$ ion-pair. It has already been shown (page 292) that the anation of trans-$[Pt(CN)_4BrOH_2]^-$ by Br^- does not occur by the Id substitution reaction of the $[Pt(CN)_4BrOH_2, Br]^{2-}$ ion-pair with a further Br^- ion. Therefore, by the

principle of micro-reversibility, Skinner and Jones' mechanism cannot apply to the reverse reaction. The mechanism giving rise to the $[Br^-]$-dependence in equation 7.109 must therefore involve the reactions

$$Br^- + [BrPt(CN)_4Br]^{2-} \overset{K'}{\rightleftharpoons} \{Br....BrPt(CN)_4Br\}^{3-} \qquad (7.112)$$

$$\{Br....BrPt(CN)_4Br\}^{3-} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \{Br_2....Pt(CN)_4\}^{2-} + Br^- \qquad (7.113)$$

$$Br^- + \{Br....BrPt(CN)_4Br\}^{3-} \underset{k_4}{\overset{k_{-4}}{\rightleftharpoons}} \{Br_3^-....Pt(CN)_4\}^{3-} + Br^- \qquad (7.114)$$

$$\{Br_2....Pt(CN)_4\}^{2-} + OH_2 \xrightarrow{k_{-1}} Br^- + [BrPt(CN)_4OH_2]^- \qquad (7.115)$$

$$\{Br_3^-....Pt(CN)_4\}^{3-} + OH_2 \xrightarrow{k_{-3}} 2Br^- + [BrPt(CN)_4OH_2]^- \qquad (7.116)$$

The rate law predicted by this mechanism, and its implications, will be discussed later. However, it appears that the mechanism of the hydrolysis of trans-$[Pt(CN)_4Br_2]^{2-}$ in the presence of Br^- or OH^- does involve the formation of Br_2, HOBr or Br_3^- and $[Pt(CN)_4]^{2-}$. Skinner and Jones[9] showed that the "decomposition" (presumably by reduction to $[Pt(CN)_4]^{2-}$, although the exact nature of the product was not specified by these authors) of trans-$[Pt(CN)_4Br_2]^{2-}$ was accelerated by both aniline and phenol. However, at the same concentration of additive, the rates of decomposition were different, depending on whether aniline or phenol was added as the bromine scavenger. As indicated in Chapter 6 (page 264), if free Br_2 is produced, the rates of decomposition of $[Pt(CN)_4Br_2]^{2-}$ should be the same at the same concentrations of scavenger. That the rates are in fact different constitutes extra evidence that the intermediates in equations 7.91, 7.92, and 7.110 are $\{Br_2....Pt(CN)_4\}^{2-}$, $\{Br_3^-....Pt(CN)_4\}^{3-}$, and $\{HOBr....Pt(CN)_4\}^{2-}$ respectively.

There is also some evidence which supports the feasibility of producing the species $\{Br_3^-....Pt(CN)_4\}^{3-}$ by the reactions

$$Br^- + \{Br....BrPt(CN)_4OH_2\}^{2-} \longrightarrow \{Br_3^-....Pt(CN)_4\}^{3-} + OH_2 \qquad (7.92)$$

and

$$Br^- + \{Br....BrPt(CN)_4Br\}^{3-} \longrightarrow \{Br_3^-....Pt(CN)_4\}^{3-} + Br^- \qquad (7.114)$$

Woodruff and Margerum[27] observed that the ring closure reaction of $[Co(EDTA)Br]^{2-}$ was accelerated by Br_2, and proposed the bimolecular reaction

$$[Co(EDTA)Br]^{2-} + Br_2 \longrightarrow [Co(EDTA)]^- + Br_3^- \qquad (7.117)$$

in which Br_2 acts as an electrophile. The transition state for reaction 7.117 presumably has the structure $\{(EDTA)Co....Br....Br{-}Br\}^{2-}$ which is somewhat similar to the structure $\{Br(CN)_4Pt....Br{-}Br{-}Br\}^{3-}$.

One final aspect of mechanism H which deserves comment is the postulate that the equilibrium interconverting B and C is slow compared with the internal re-oxidation reactions of these species. At first sight this is rather surprising, since it might be expected that the reaction

$$Br^- + \{Br_2....PtL_4\}^{2-} \rightleftharpoons \{Br_3^-....Pt(CN)_4\}^{3-} \qquad (7.93)$$

would be analogous to the reaction

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (7.118)$$

which is known to occur at rates approaching diffusion control.[28] A possible explanation for this difference may lie in the nature of the $Pt....Br_2$ and $Pt....Br_3^-$ bonding of B and C respectively. Square planar Pt(II) complexes can be considered to act as biphilic agents; the presence

of two vacant co-ordination sites renders them good electrophiles, whereas the presence of non-bonding electron density suggests that in different circumstances they could also behave as fairly good nucleophiles. Both types of behaviour are known to occur. Thus much has been written about the tendency of square planar d^8 complexes to expand their co-ordination shells, accepting electron density from Lewis bases to give five-co-ordinate complexes, and specific examples were mentioned earlier. Examples of Pt(II) square planar complexes acting as nucleophiles are somewhat rarer. However, CF_3CO_2H, CH_3CO_2H and H_3BO_3 all accelerate the rate of $^*Cl^-$ exchange of trans-$[Ptpy_2Cl_2]$,[29] HNO_2 catalyses the reaction of several Pt(II) complexes,[30] and the catalysis of the reaction

$$\text{trans-}[Ptpip_2Cl_2] + Y^- \longrightarrow \text{trans-}[Ptpip_2ClY] + Cl^- \qquad (7.119)$$

($Y = NO_2^-$, $^*Cl^-$) by HNO_2 and H_3BO_3 has been studied in detail.[31] The rate law for reaction 7.119 is

$$k_{obsd} = k_1 + k_2[Y^-] + k_3[Y^-][HA] \qquad (7.120)$$

where HA = HNO_2, H_3BO_3, and k_1, k_2 are the rate constants for the normal substitution pathways where the substrate undergoes nucleophilic attack by the solvent, S, and Y^- respectively. The reaction pathway proposed for the [HA]-dependent term in equation 7.120 was the nucleophilic attack of Y^- on the six-co-ordinate species $[HA....Ptpip_2Cl_2....S]$ where HA and S are co-ordinated along the z-axis of the complex, perpendicular to the plane of the other ligands. Because the less electrophilic NO_2^- ion does not give rise to a term in the rate law corresponding to $k_3[Y^-][HA]$, HA was considered to act as an electrophile in the six-co-ordinate complex. The catalysis is easily explained if the Pt—HA bond involves electron donation

from filled Pt d-orbitals to π* orbitals of HA; since this reduces the electron density on the Pt centre, the complex is rendered more susceptible to nucleophilic attack. Additional evidence for the formation of an [HA....$Ptpip_2Cl_2$....S] adduct comes from the observation that the absorption spectrum of trans-[$Ptpip_2Cl_2$] is enhanced in the presence of HNO_2, but not in the presence of NO_2^-.[31]

The reactive intermediate $\{Br_2....Pt(CN)_4\}^{2-}$ may well be similar to [HA....$Ptpip_2Cl_2$....S], in that the Pt(II) ion acts as an electron donor in both cases. The tendency for Br_2 to act as an electrophile is best exemplified by the formation of the polyhalide ions Br_2Cl^- and Br_3^-,[32] but charge transfer complexes where Br_2 accepts electron-density from organic molecules such as dioxane or benzene are also well known.[33] In all cases, the linear Br–Br....D arrangement (where D is the donor molecule or ion) is observed.[32][33] It thus seems very likely that in the complex $Br_2....Pt(CN)_4$, the electron donation is in the sense Pt → Br_2. Moreover, Morgan and Jones[3] suggested that in the adduct $\{Cl_2....PtCl_4\}^{2-}$ the Pt–Cl_2 bond was formed by overlap of the filled Pt(II) d_{z^2} orbital with an empty σ_u^* antibonding orbital of the Cl_2. Thus they proposed that Pt(II) was acting as the electron donor.

On the other hand, the electron donation in the complex $\{Br_3^-....Pt(CN)_4\}^{3-}$ should be similar to that in $[X....Pt(diars)_2]^+$ where X^- acts as an electron donor.[22][23] (X^- = Cl^-, Br^-, I^-, N_3^-, NCS^-.) This is because Br_3^- is itself already a charge transfer complex, and the ion possesses a high electron density, so it is unlikely to be susceptible to further nucleophilic donation. Moreover, electron acceptance by the Pt(II) centre provides a means of very efficient electron delocalisation over the entire molecule since the presence of "soft" CN^- ligands renders

the complex very polarisable.

The hypothesis that the bonding in $\{Y....Pt(CN)_4\}$ depends on whether Y is Br_2 or Br_3^- seems to be compatible with the chemistry of these two species, and with what is known of the interactions of Pt(II) complexes with similar species. It is now easy to see why the equilibrium

$$Br^- + \{Br_2....PtL_4\}^{2-} \rightleftharpoons \{Br_3^-....PtL_4\}^{2-} \qquad (7.93)$$

should not be established rapidly; interconversion of $\{Br_2....PtL_4\}^{2-}$ and $\{Br_3^-....PtL_4\}^{3-}$ not only requires the formation of the encounter complex $\{Br^-, Br_2....Pt(CN)_4\}^{3-}$, but also necessitates an electronic redistribution within the complex. This might well increase the free energy of activation for reaction 7.93 and decreases the rate of equilibration of the two intermediates.

Implications of Mechanism H

From the above discussion there is a good deal of kinetic and non-kinetic evidence to suggest that mechanism H is the mechanism of the Br^- anation of trans-$[Pt(CN)_4BrOH_2]^-$. Having established the reasonableness of this mechanism, it is now possible to consider some of its implications.

From a comparison of equation 7.121, the rate law predicted by mechanism H under conditions where less than 100% of the substrate is in the bromoaquo-form

$$k_{obsd} = \frac{[H^+]}{K_A + [H^+]} \left\{ \frac{k_1 k_2 K[Br^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} + \frac{k_3 k_4 K[Br^-]^3}{k_{-3}(1 + \frac{k_4}{k_{-3}}[Br^-])} \right\} \qquad (7.121)$$

and the rate law found experimentally (equation 7.22)

$$k_{obsd} = \frac{a[Br^-]^2}{1 + b[Br^-]} + \frac{c[Br^-]^3}{1 + d[Br^-]} \qquad (7.22)$$

it can be seen that

$$a = \frac{[H^+]}{(K_A + [H^+])} \times \frac{k_1 k_2 K}{k_{-1}} \qquad (7.122)$$

$$b = \frac{k_2}{k_{-1}} \qquad (7.123)$$

$$c = \frac{[H^+]}{(K_A + [H^+])} \times \frac{k_3 k_4 K}{k_{-3}} \qquad (7.124)$$

$$d = \frac{k_4}{k_{-3}} \qquad (7.125)$$

From equations 7.122 to 7.125

$$\frac{a}{b} = \frac{[H^+]}{(K_A + [H^+])} \times k_1 K \qquad (7.126)$$

$$\frac{c}{d} = \frac{[H^+]}{(K_A + [H^+])} \times k_3 K \qquad (7.127)$$

and

$$\frac{bc}{ad} = \frac{k_3}{k_1} \qquad (7.128)$$

Substituting the experimental values of a, b, c and d into equation 7.128, the ratio k_3/k_1 is found to be 125 ±10 M^{-1}. (The error limits are calculated as shown in appendix D, section 2c .) If we define $\Delta G_1^{\ddagger}$ and $\Delta G_3^{\ddagger}$ as the free energies of activation of reactions 7.91 and 7.92 respectively,

$$\{Br....BrPtL_4OH_2\}^{2-} \longrightarrow \{Br_2....PtL_4\}^{2-} \qquad (7.91)$$

$$Br^- + \{Br....BrPtL_4OH_2\}^{2-} \longrightarrow \{Br_3^-....PtL_4\}^{3-} \qquad (7.92)$$

then from the transition state theory[34]

$$\ln k_1 = \ln\left(\frac{kT}{h}\right) - \frac{\Delta G_1^{\ddagger}}{RT} \qquad (7.129)$$

$$\ln k_3 = \ln\left(\frac{kT}{h}\right) - \frac{\Delta G_3^{\ddagger}}{RT} \qquad (7.130)$$

From 7.129 and 7.130

$$\Delta G_3^{\ddagger} - \Delta G_1^{\ddagger} = RT \ln(k_1/k_3) \qquad (7.131)$$

If the transition states for reactions 7.91 and 7.92 are denoted as $\{Br....Br....PtL_4....OH_2\}^{\ddagger}$ and $\{Br....Br....Br....PtL_4....OH_2\}^{\ddagger}$ respectively, then a <u>formal</u> equilibrium constant $K_{Br}^{\ddagger}$ can be written for the equilibrium

$$\underset{}{Br^-} + \underset{B^{\ddagger}}{\{Br...Br...PtL_4...OH_2\}^{\ddagger}} \overset{K_{Br}^{\ddagger}}{\rightleftharpoons} \underset{C^{\ddagger}}{\{Br...Br...Br...PtL_4...OH_2\}^{\ddagger}} \qquad (7.132)$$

and the standard free energy $\Delta G_{Br}^{\ddagger}$ of equilibrium 7.132 will be given by

$$\Delta G_{Br}^{\ddagger} = G(C^{\ddagger}) - G(B^{\ddagger}) - G(Br^-) \qquad (7.133)$$

where G(X) represents the free energy of the species X. Using the same notation

$$\Delta G_1^{\ddagger} = G(B^{\ddagger}) - G(A) + G(H_2O) \qquad (7.134)$$

$$\Delta G_3^{\ddagger} = G(C^{\ddagger}) - G(A) - G(Br^-) + G(H_2O) \qquad (7.135)$$

where G(A) is the free energy of the charge transfer complex, $\{Br^-....BrPtL_4OH_2\}^{2-}$. From 7.134 and 7.135

$$\Delta G_3^{\ddagger} - \Delta G_1^{\ddagger} = G(C^{\ddagger}) - G(B^{\ddagger}) - G(Br^-) \qquad (7.136)$$

From 7.136 and 7.133

$$\Delta G_{Br}^{\ddagger} = \Delta G_3^{\ddagger} - \Delta G_1^{\ddagger} \qquad (7.137)$$

But

$$\Delta G^{\ddagger}_{Br} = -RT \ln K^{\ddagger}_{Br} \qquad (7.138)$$

From 7.138 and 7.131

$$-RT \ln K^{\ddagger}_{Br} = RT \ln(k_1/k_3) \qquad (7.139)$$

Hence

$$K^{\ddagger}_{Br} = \frac{k_3}{k_1} \qquad (7.140)$$

Thus the formal equilibrium constant for reaction 7.132 is 125 ±10 M^{-1}. This can be compared with the equilibrium constant for the reaction

$$Br^- + Br_2 \rightleftharpoons Br_3^- \qquad (7.80)$$

which at 25°C and in 1.0 M $NaClO_4$ has the value[35] 13.5 M^{-1}. It can be seen that co-ordination to Pt(II) in the transition state enhances the affinity of the incipient Br_2 for Br^-. This is not surprising, since delocalisation of electron density via the Pt(II) ion and the π-bonded CN^- ligands has already been postulated to occur in the ground state complex $\{Br_3^-....Pt(CN)_4\}^{3-}$. This delocalisation should be possible even in the transition state, where the Br_3^- is only in the process of formation.

There is another way to explain the value of the ratio k_3/k_1, without using a pseudo-thermodynamic argument. The alternative explanation considers the effect of Br^- in reaction 7.92 as a pseudo-alpha effect.[36] Thus reaction 7.92 can be separated into two further elementary processes: formation of an encounter complex (reaction 7.141) and electron transfer within the encounter complex (reaction 7.142).

$$Br^- + \underset{A}{\{Br...BrPtL_4OH_2\}^{2-}} \overset{K_{ec}}{\rightleftharpoons} \underset{C'}{\{Br,Br...BrPtL_4OH_2\}^{3-}} \qquad (7.141)$$

$$\underset{C'}{\{Br,Br...BrPtL_4OH_2\}^{3-}} \xrightarrow{k'_3} \underset{C}{\{Br_3^-...PtL_4\}^{3-}} + OH_2 \qquad (7.142)$$

In C' the additional Br^- ion is located in the third co-ordination sphere of the complex, co-linear with the $Br^-...Br$-Pt bond (or interaction) system. The fourth-order rate constant, k_3, is now given by

$$k_3 = K_{ec}k'_3 \qquad (7.143)$$

so that

$$\frac{k_3}{k_1} = \frac{k'_3K_{ec}}{k_1} \qquad (7.144)$$

Since K_{ec} must be very much less than unity, k'_3/k_1 must be very much greater than 125. If we consider the composition of the charge-transfer complex $\{Br...BrPtL_4OH_2\}^{2-}$, we can rewrite equation 7.91 as

$$\{HOH,Br...BrPtL_4OH_2\} \longrightarrow \{HOH...Br_2...PtL_4\}^{2-} + OH_2 \qquad (7.145)$$

where the interaction between the H_2O molecule and Br^- or Br_2 is predominantly hydrogen-bonding. It can now be seen that k'_3 is much greater than k_1 because of a pseudo-alpha effect. In reaction 7.142 the process of electron transfer from the Br^- in the second co-ordination sphere of the complex to the Pt(IV) will be greatly facilitated by donation of electron density from the Br^- ion in the third co-ordination sphere. The closer the nature of the transition state is to that of the products, the more greatly developed this electron donation will be. In reaction 7.145, on the other hand, the only way electron density can be transferred from the hydrogen-bonded H_2O molecule is by breaking the H...Br hydrogen bond. Breaking this hydrogen bond will contribute a relatively small amount of electron density to the bromide ion and the alpha effect of the water molecule will be very small. The very large alpha effect of bromide relative to that of water

will make k'_3 very large compared to k_1. Even though K_{ec} is very much less than unity, k'_3 is sufficiently large that k_3, which is the product of K_{ec} and k'_3 is 125 times greater than k_1.

From equation 7.123 the competition ratio for reoxidation of $\{Br_2...Pt(CN)_4\}^{2-}$ in the presence of Br^- and H_2O can be calculated to be $87 \pm 16\ M^{-1}$. Similarly, equation 7.125 gives the competition ratio for reoxidation of $\{Br_3^-...Pt(CN)_4\}^{3-}$ in the presence of Br^- and H_2O as $6.0 \pm 1.2\ M^{-1}$. The relative values of the ratios are entirely consistent with electrostatic considerations. Thus the triple negative charge on $\{Br_3^-...Pt(CN)_4\}^{3-}$ makes it relatively harder for the Br^- ion to approach the intermediate, compared with the neutral H_2O molecule. With the doubly charged intermediate $\{Br_2...Pt(CN)_4\}^{2-}$, approach of the Br^- ion is not so unfavourable compared with H_2O so the competition ratio is higher.

The values obtained for the competition ratios do raise some questions about Skinner and Jones' data[9] for the hydrolysis of $[Pt(CN)_4Br_2]^{2-}$ in the presence of OH^- and Br^-. The reaction is essentially the reverse of the Br^- anation of <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$, and as discussed earlier the mechanism demanded by microreversibility is as shown in equations 7.110 to 7.116.

$$HO^- + [BrPtL_4Br]^{2-} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \{HOBr...PtL_4\}^{2-} + Br^- \qquad (7.110)$$

$$\{HOBr...PtL_4\}^{2-} + OH_2 \xrightarrow{k_6} OH^- + [BrPtL_4OH_2]^- \qquad (7.111)$$

$$Br^- + [BrPtL_4Br]^{2-} \overset{K'}{\rightleftharpoons} \{Br...BrPtL_4Br\}^{3-} \qquad (7.112)$$

$$\{Br...BrPtL_4Br\}^{3-} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \{Br_2...PtL_4\}^{2-} + Br^- \qquad (7.113)$$

$$Br^- + \{Br...BrPtL_4Br\}^{3-} \underset{k_4}{\overset{k_{-4}}{\rightleftharpoons}} \{Br_3^-...PtL_4\}^{3-} + Br^- \qquad (7.114)$$

$$\{Br_2...PtL_4\}^{2-} + OH_2 \xrightarrow{k_{-1}} Br^- + [BrPtL_4OH_2]^- \qquad (7.115)$$

$$\{Br_3^-...PtL_4\}^{3-} + OH_2 \xrightarrow{k_{-3}} 2Br^- + [BrPtL_4OH_2]^- \qquad (7.116)$$

The rate law for this mechanism is derived in appendix C, section ix, where it is found to be

$$k_{obsd} = \frac{k_5k_6[OH^-]}{k_6 + k_{-5}[Br^-]} + \frac{k_{-1}k_{-2}K'[Br^-]}{k_{-1} + k_2[Br^-]} + \frac{k_{-3}k_{-4}K'[Br^-]^2}{k_{-3} + k_4[Br^-]} \qquad (7.146)$$

Equation 7.146 can be compared with the experimental rate law

$$k_{obsd} = k[OH^-] + k'[Br^-] \qquad (7.109)$$

It can be seen that equation 7.146 correctly predicts the variation of k_{obsd} with the $[OH^-]$ at a fixed $[Br^-]$, under which conditions equation 7.146 reduces to

$$k_{obsd} = A[OH^-] + B \qquad (7.147)$$

where

$$A = \frac{k_5}{(1 + \frac{k_{-5}}{k_6}[Br^-])} \qquad (7.148)$$

$$B = \frac{k_{-2}K'[Br^-]}{(1 + \frac{k_2}{k_{-1}}[Br^-])} + \frac{k_{-4}K'[Br^-]^2}{(1 + \frac{k_4}{k_{-3}}[Br^-])} \qquad (7.149)$$

Comparison of equations 7.147 and 1.109 gives

$$k = \frac{k_5}{(1 + \frac{k_{-5}}{k_6}[Br^-])} \qquad (7.150)$$

Equation 7.150 predicts that although at a fixed $[Br^-]$ k_{obsd} should be proportional to $[OH^-]$, the constant of proportionality, k, should be a function of the $[Br^-]$. Unfortunately, Skinner and Jones[9] only obtained the $[OH^-]$-dependence of k_{obsd} at one $[Br^-]$, so this prediction cannot be checked.

At a fixed $[OH^-]$ and varying $[Br^-]$, equation 7.146 reduces to

$$k_{obsd} = \frac{C}{(1 + \frac{k_{-5}}{k_6}[Br^-])} + \frac{k_{-2}K'[Br^-]}{(1 + \frac{k_2}{k_{-1}}[Br^-])} + \frac{k_{-4}K'[Br^-]^2}{(1 + \frac{k_4}{k_{-3}}[Br^-])} \quad (7.151)$$

where

$$C = k_5[OH^-] \quad (7.152)$$

Equation 7.151 will reduce to equation 7.109 under three sets of conditions:

Set (1)

For all $[Br^-]$ studied:--

(a) $$\frac{k_{-5}}{k_6}[Br^-] << 1 \quad (7.153)$$

(b) $$\frac{k_{-2}K'[Br^-]}{(1 + \frac{k_2}{k_{-1}}[Br^-])} >> \frac{k_{-4}K'[Br^-]^2}{(1 + \frac{k_4}{k_{-3}}[Br^-])} \quad (7.154)$$

(c) $$\frac{k_2}{k_{-1}}[Br^-] << 1 \quad (7.155)$$

Set (2)

For all $[Br^-]$ studied:--

(a) As for I(a)

(b) $$\frac{k_{-2}K'[Br^-]}{(1 + \frac{k_2}{k_{-1}}[Br^-])} << \frac{k_{-4}K'[Br^-]^2}{(1 + \frac{k_4}{k_{-3}}[Br^-])} \quad (7.156)$$

(c) $$\frac{k_4}{k_{-3}}[Br^-] >> 1 \quad (7.157$$

Set (3)

For all $[Br^-]$ studied:--

(a) As for I(a)

(b) $$\frac{k_{-2}K'[Br^-]}{(1 + \frac{k_2}{k_{-1}}[Br^-])} \text{ is comparable to } \frac{k_{-4}K'[Br^-]^2}{(1 + \frac{k_4}{k_{-3}}[Br^-])} \qquad (7.158)$$

(c) As for I(c) and 2(c)

Nothing is known about the value of the competition ratio k_{-5}/k_6, nor are the relative magnitudes of the terms

$k_{-2}K'[Br^-]/(1 + (k_2/k_{-1})[Br^-])$ and $k_{-4}K'[Br^-]^2/(1 + (k_4/k_{-3})[Br^-])$

known. However, from this work k_2/k_{-1} is known to be 87 ± 16 and k_4/k_{-3} to be 6.0 ± 1.2. The maximum range of Skinner and Jones' results is for pH = 9.0 and $0 \leq [Br^-] \leq 0.5$ M, with values of k_{obsd} at $[Br^-]$ = 0.0, 0.2, 0.3 and 0.5 M. Condition 1(c) is certainly not met under these conditions, since even at 0.2 M Br^- $k_2[Br^-]/k_{-1}$ is 17.4 ± 3.2. Hence the sets of conditions outlined above in (1) and (3) are not obeyed at all $[Br^-]$ and these conditions cannot explain the observed rate law. On the other hand, equation 7.109 is obeyed at pH = 8.5 by the values of k_{obsd} at $[Br^-]$ = 0.0, 0.05 and 0.1 M. At these $[Br^-]$, condition 2(c) is not met, since even at 0.1 M Br^-, k_4/k_{-3} is only 0.6 ± 0.12. Hence the set of conditions outlined in (2) cannot explain the observed rate law. The most reasonable explanation for the observation of equation 7.109 as the experimental rate law is that equation 7.109 is in fact an oversimplified interpretation of the data. Skinner and Jones'[9] points are rather sparse, and the linear dependence of k_{obsd} on $[Br^-]$ may well represent a balance between the decrease in the first two terms of equation 7.146 as the $[Br^-]$ increases, and the corresponding increase of the third term under the same conditions. The $[Br^-]$-dependence is, in any case, rather small, k_{obsd} at pH = 9.0 increasing by less than a factor of 3 over the $[Br^-]$ range $0 \leq [Br^-] \leq 0.5$ M. Further investigation of this reaction, paying particular attention to the variation of k_{obsd} with the $[Br^-]$

at low $[Br^-]$, seems indicated. In addition, an investigation of the variation of k_{obsd} with the $[OH^-]$ at different fixed $[Br^-]$ should be carried out to check the predictions of equation 7.150.

Extension of mechanism H to other anation reactions of Pt(IV) complexes

If mechanism H is considered to apply to the general reaction

$$\underline{trans}\text{-}[PtL_4YOH_2]^{n-} + X^- \longrightarrow \underline{trans}\text{-}[PtL_4YX]^{(n+1)-} + OH_2 \qquad (7.159)$$

the reaction sequence shown in equations 7.160 to 7.165 is obtained.

$$[YPtL_4OH_2]^{n-} \overset{K_A}{\rightleftharpoons} [YPtL_4OH]^{(n+1)-} + H^+ \qquad (7.160)$$

$$X^- + [YPtL_4OH_2]^{n-} \overset{K}{\rightleftharpoons} \{X...YPtL_4OH_2\}^{(n+1)-} \qquad (7.161)$$

$$\{X...YPtL_4OH_2\}^{(n+1)-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{XY...PtL_4\}^{(n+1)-} + OH_2 \qquad (7.162)$$

$$X^- + \{X...YPtL_4OH_2\}^{(n+1)-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \{X_2Y...PtL_4\}^{(n+2)-} + OH_2 \qquad (7.163)$$

$$\{XY...PtL_4\}^{(n+1)-} + X^- \xrightarrow{k_2} X^- + [YPtL_4X]^{(n+1)-} \qquad (7.164)$$

$$\{X_2Y...PtL_4\}^{(n+2)-} + X^- \xrightarrow{k_4} 2X^- + [YPtL_4X]^{(n+1)-} \qquad (7.165)$$

This reaction sequence gives the rate law

$$\frac{k_{obsd}}{f} = \frac{k_1k_2K[X^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[X^-])} + \frac{k_3k_4K[X^-]^3}{k_{-3}(1 + \frac{k_4}{k_{-3}}[X^-])} \qquad (7.166)$$

where

$$f = \frac{[H^+]}{K_A + [H^+]} \qquad (7.33)$$

Mason[2] studied the Cl^- anation of $\underline{trans}\text{-}[Pt(CN)_4BrOH_2]^-$ and found

that over the concentration range 4.0×10^{-3} M $\leq [Cl^-] \leq 1.6 \times 10^{-2}$ M, the rate law was

$$\frac{k_{obsd}}{f} = k[Cl^-] \tag{7.167}$$

This rate law can be derived from equation 7.166 if for all $[Cl^-]$ used in the study

$$\frac{k_2[Cl^-]}{k_{-1}} >> 1 \tag{7.168}$$

and

$$\frac{k_3k_4K[Cl^-]^3}{k_{-3}(1 + \frac{k_4}{k_{-3}}[Cl^-])} << \frac{k_1k_2K[Cl^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Cl^-])} \tag{7.169}$$

Combining equations 7.169 and 7.168 gives the rather simpler condition

$$\frac{k_3k_4[Cl^-]^2}{k_{-3}(1 + \frac{k_4}{k_{-3}}[Cl^-])} << k_1 \tag{7.170}$$

Since equation 7.168 must hold even at the lowest $[Cl^-]$ of Mason's study, it follows that $\frac{k_2}{k_{-1}}$, the competition ratio of Cl^- and H_2O for the intermediate $\{ClBr...Pt(CN)_4\}^{2-}$, is greater than 250.

By using results obtained for the Br^- anation of <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$, and assuming that trends established for this reaction are also applicable to the Cl^- anation of this complex, it is possible to make a rough estimate of the relative magnitudes of the left and right hand sides of equation 7.170. It was shown earlier that the ratio k_3/k_1 equals the equilibrium constant $K_x^{\ddagger}$ for the hypothetical reaction

$$X^- + \{X...Y...PtL_4...OH_2\}^{\ddagger} \rightleftharpoons \{X...X...Y...PtL_4...OH_2\}^{\ddagger} \tag{7.171}$$

and $K_x^{\ddagger}$ can be compared with the equilibrium constant, K_x for the equilibrium

$$X^- + XY \rightleftharpoons X_2Y^- \tag{7.172}$$

For the Br^- anation of <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$ it was found that

$$\frac{K_{Br}^{\ddagger}}{K_{Br}} = 9.26 \tag{7.173}$$

If we assume that for the Cl^- anation of the same complex

$$\frac{K_{Cl}^{\ddagger}}{K_{Cl}} = \frac{K_{Br}^{\ddagger}}{K_{Br}} \tag{7.174}$$

then

$$K_{Cl}^{\ddagger} = 9.26\ K_{Cl} \tag{7.175}$$

Unfortunately, K_{Cl} is not known, but the equilibrium constant K'_{Cl} for the formation of the trichloride ion

$$Cl^- + Cl_2 \rightleftharpoons Cl_3^- \tag{7.176}$$

is only 0.2 M^{-1};[32] K_{Cl} would be expected to be much less than K'_{Cl}, because the reaction

$$Cl^- + ClBr \rightleftharpoons [Cl\text{-}Cl\text{-}Br]^- \tag{7.177}$$

requires that Cl^- be bonded to the negative end of the Br-Cl dipole. From equation 7.177 it follows that

$$K_{Cl}^{\ddagger} << 1.85\ M^{-1} \tag{7.178}$$

i.e., for the Cl^- anation of <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$

$$\frac{k_3}{k_1} << 1.85\ M^{-1} \tag{7.179}$$

We can rewrite the left hand side of equation 7.170 as

$$\frac{k_3 k_4 [Cl^-]^2}{k_{-3}(1 + \frac{k_4}{k_{-3}} [Cl^-])} = k_3 \times \frac{D}{1 + D} [Cl^-] \qquad (7.180)$$

where

$$D = \frac{k_4 [Cl^-]}{k_{-3}} \qquad (7.1\ 1)$$

Since

$$\frac{D}{1 + D} < 1 \qquad (7.182)$$

it follows that

$$\frac{k_3 k_4 [Cl^-]^2}{k_{-3}(1 + \frac{k_4}{k_{-3}} [Cl^-])} < k_3 [Cl^-] \qquad (7.183)$$

From equations 7.183 and 7.179

$$\frac{k_3 k_4 [Cl^-]^2}{k_{-3}(1 + \frac{k_4}{k_{-3}} [Cl^-])} << 1.85\ k_1 [Cl^-] \qquad (7.184)$$

At the highest $[Cl^-]$ used by Mason (1.6×10^{-2} M), equation 7.184 becomes

$$\frac{k_3 k_4 [Cl^-]^2}{k_{-3}(1 + \frac{k_4}{k_{-3}} [Cl^-])} << 2.96 \times 10^{-2} k_1 \qquad (7.185)$$

Thus even at the highest concentrations of Cl^- used by Mason, the condition of equation 7.170 is obeyed, and it is not surprising that a term in the rate law corresponding to the production of the intermediate $\{Cl_2Br...Pt(CN)_4\}^{3-}$ is not observed. It can thus be seen that the kinetic parameters obtained for the Br^- anation of <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$ are quite consistent with the

experimental data for the Cl^- anation of the same complex. Furthermore, the non-existence of a term involving $[Cl^-]^3$ in the rate law for the anation by Cl^- can be ascribed to the low affinity of Cl^- for the Cl atom in BrCl, or even in the transition state $\{Cl...Cl...Br...Pt(CN)_4...OH_2\}^{\ddagger}$.

Mechanism H is not only consistent with the reactions of different anions with <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$, but it can also explain the results of Br^- anation studies of a variety of Pt(IV) substrates. Elding and Gustafson (14) studied the Br^- anation of $[PtB_5OH_2]^-$ and <u>cis</u>-$[PtBr_4(OH_2)_2]$ and found that in each case the rate law

$$k_{obsd} = k[Br^-] + k'(Br^-)^2 \qquad (7.186)$$

was obeyed. This rate law is entirely consistent with the rate law (equation 7.22) found for the Br^- anation of <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$, being the limiting form of equation 7.22 obtained when both $b[Br^-]$ and $d[Br^-]$ are very much larger than unity. For the anation of $[PtBr_5OH_2]^-$, equation 7.186 is obeyed over the concentration range 2.5×10^{-2} M $\leq [Br^-] \leq$ 4×10^{-1} M, so in this system the competition ratios k_2/k_{-1} and k_4/k_{-3} must both be much greater than 40 M^{-1}. Similarly, for the anation of <u>cis</u>-$[PtBr_4(OH_2)_2]$, equation 7.186 is obeyed over the concentration range 1×10^{-2} M $\leq [Br^-] \leq 3 \times 10^{-1}$ M so k_2/k_{-1} and k_4/k_{-3} must both be much greater than 100 M^{-1}.

Under Elding and Gustafson's conditions,[14] 100% of the substrates in the reactions

$$[BrPtBr_4OH_2]^- + Br^- \longrightarrow [PtBr_6]^{2-} + H_2O \qquad (7.187)$$

$$[BrPtBr_3(H_2O)_2] + Br^- \longrightarrow [PtBr_5OH_2]^- + H_2O \qquad (7.188)$$

were in the bromoaquo-form, so that f in equation 7.166 becomes equal to

unity and the rate law predicted by mechanism H becomes

$$k_{obsd} = \frac{k_1 k_2 K[Br^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} + \frac{k_3 k_4 K[Br^-]^3}{k_{-3}(1 + \frac{k_4}{k_{-3}}[Br^-])} \qquad (7.189)$$

Comparison of equations 7.189 and 7.186, assuming that $k_2[Br^-]/k_{-1}$ and $k_4[Br^-]/k_{-3}$ are both much greater than unity gives

$$k = k_1 K \qquad (7.190)$$

$$k' = k_3 K \qquad (7.191)$$

Hence

$$\frac{k'}{k} = \frac{k_3}{k_1} \qquad (7.192)$$

From equation 7.140 the ratio k_3/k_1 gives the equilibrium constant for the hypothetical reaction

$$Br^- + \{Br...Br...PtL_4...OH_2\}^{\ddagger} \rightleftharpoons \{Br...Br...Br...PtL_4...OH_2\}^{\ddagger} \qquad (7.193)$$

where $L_4 = Br_4$ or Br_3OH_2. From Elding and Gustafson's values for k' and k, $K^{\ddagger}_{Br}$ can be calculated to be 25 M^{-1} for $[PtBr_5OH_2]^-$ and 12.5 M^{-1} for <u>cis</u>-$[Pt\ Br_4(OH_2)_2]$. These values can be compared with the corresponding value of $K^{\ddagger}_{Br} = 125 \pm 10\ M^{-1}$ found in this work for Br^- anation of <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$. The high value of $K^{\ddagger}_{Br}$ found when L in equation 7.193 is CN^- has already been explained by assuming that the polarisable CN^- ligand, aided by Pt-CN <u>π</u>-bonding, can delocalise electron density over the whole of the activated complex $\{Br...Br...Br...PtL_4...OH_2\}^{\ddagger}$. When the four <u>cis</u>-ligands are Br^-, the relatively high polarisability of Br^- will again aid electron delocalisation in the incipient Br_3^- complex of platinum(II), but the delocalisation will be less efficient than when the <u>cis</u>-ligands are CN^-. With

cis-$[PtBr_4(OH)_2]$ one of the soft cis-Br^- ligands has been replaced by a hard, non-polarisable[37] H_2O molecule. The electron delocalisation in the transition state $\{Br...Br...Br...PtL_4...OH_2\}^{\ddagger}$ therefore decreases and $K^{\ddagger}_{Br}$ becomes smaller.

One final system to which mechanism H can be applied is the Br^- anation of the cationic complex trans-$[Pt(NH_3)_4BrOH_2]^{3+}$. For this reaction Mason[2] found the rate law

$$\frac{k_{obsd}}{f} = k[Br^-]^2 \qquad (7.194)$$

which was obeyed over the concentration range $0.01\ M \leq [Br^-] \leq 0.03\ M$. This rate law is consistent with equation 7.166, the rate law predicted by mechanism H if it is assumed that

$$\frac{k_2}{k_{-1}}[Br^-] << 1 \qquad (7.195)$$

and

$$\frac{k_3k_4K[Br^-]^3}{k_{-3}(1 + \frac{k_4}{k_{-3}}[Br^-])} << \frac{k_1k_2K[Br^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} \qquad (7.196)$$

for all the $[Br^-]$ studied. Since equation 7.195 must be obeyed even at 0.03 M Br^-, it follows that for this system k_2/k_{-1} must be much less than 33 M^{-1}. Moreover, by combining equations 7.195 and 7.196 we obtain

$$\frac{k_3k_4K[Br^-]^3}{k_{-3}(1 + \frac{k_4}{k_{-3}}[Br^-])} << \frac{k_1k_2}{k_{-1}}K[Br^-]^2 \qquad (7.197)$$

which can be rewritten as

$$\frac{k_3k_4[Br^-]}{k_{-3}(1 + \frac{k_4}{k_{-3}}[Br^-])} << \frac{k_1k_2}{k_{-1}} \qquad (7.198)$$

If we now assume that the relative values of the competition ratios of Br^- and H_2O for the intermediates $\{Br_2...PtL_4\}^{(n+1)-}$ and $\{Br_3^-...PtL_4\}^{(n+2)-}$ are unaffected by whether L is CN^- or NH_3 then the ratio R defined in equation 7.199 will be the same for the Br^- anation of <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$ and <u>trans</u>-$[Pt(NH_3)_4Br_2]^{2+}$.

$$R = \frac{k_4}{k_{-3}} \times \frac{k_{-1}}{k_2} \qquad (7.199)$$

From the Br^- anation of the tetracyano-complex

$$R = \frac{6}{87} = 6.90 \times 10^{-2} \qquad (7.200)$$

From equations 7.199 and 7.200

$$\frac{k_4}{k_{-3}} = \frac{6}{87}\frac{k_2}{k_{-1}} \qquad (7.201)$$

From equations 7.201 and 7.198 and knowing that k_2/k_{-1} is much less than 33 M^{-1}, we obtain

$$k_3[Br^-] \ll 14.5\ k_1 \qquad (7.202)$$

This must be true even at 0.03 M Br^-, the highest $[Br^-]$ used by Mason, so

$$k_3 \ll 483\ k_1 \qquad (7.203)$$

This means that $K_{Br}^{\ddagger}$, the formal equilibrium constant for the reaction

$$Br^- + \{Br...Br...Pt(NH_3)_4...OH_2\}^{\ddagger} \rightleftharpoons \{Br...Br...Br...Pt(NH_3)_4...OH_2\}^{\ddagger} \qquad (7.204)$$

is very much less than 483 M^{-1}. A rather more useful limit to the value of $K_{Br}^{\ddagger}$ for reaction 7.204 can be obtained if it is assumed that a contribution to k_{obsd} from the term $k_3k_4[Br^-]^3/k_{-3}(1 + (k_4/k_{-3})[Br^-])$ could be detected

if it was even 10% of the value of the term $k_1k_2[Br^-]^2/k_{-1}(1 + k_2/k_{-1}[Br^-])$. This changes the inequality of equation 7.198 to

$$\frac{k_3k_4[Br^-]}{k_{-3}(1 + \frac{k_4}{k_{-3}}[Br^-])} < (0.1)\frac{k_1k_2}{k_{-1}} \qquad (7.205)$$

and gives the value of $K_{Br}^{\ddagger}$ for equation 7.204 as less than 48.3 M^{-1}. This value is very much less than the value of $K_{Br}^{\ddagger}$ found when the four cis-ligands are CN^-, in agreement with the hypothesis that a soft, π-bonding ligand such as CN^- would stabilise the incipient Pt(II)-Br_3^- complex by electron delocalisation more readily than would a hard, σ-bonding ligand like NH_3. On the other hand, the extra 4 and 3 units of positive charge on $[Pt(NH_3)_4BrOH_2]^{3+}$ compared with $[PtBr_5OH_2]^-$ and cis-$[PtBr_4(OH_2)_2]$ respectively would give a higher positive charge to the incipient Pt(II) complex, and make it more ready to accept electron donation from the incipient Br_3^- ion. The effect of the overall charge of the complex is relatively small, since $K_{Br}^{\ddagger}$ for the uninegative complex $[PtBr_5OH_2]^-$ is greater than $K_{Br}^{\ddagger}$ for the neutral cis-$[PtBr_4(OH_2)_2]$. However, the very large difference in charge of 4 units between trans-$[Pt(NH_3)_4Br_2]^{3+}$ and $[PtBr_5OH_2]^-$ could well make $K_{Br}^{\ddagger}$ for the former complex larger than that for the latter, in spite of the lower polarisability of NH_3 compared to Br^-. In order to obtain an estimate of the relative magnitudes of the effects of the charge on the complex and the polarisability of the cis-ligands on $K_{Br}^{\ddagger}$ it would be necessary to extend Mason's study of the anation of trans-$[Pt(NH_3)_4BrOH_2]^{3+}$ to much higher $[Br^-]$, so that the value of $K_{Br}^{\ddagger}$ for this system can be defined more closely.

Summary

The bromide anation of trans-$[Pt(CN)_4BrOH_2]^-$ has been studied and found to obey the rate law

$$k_{obsd} = \frac{a[Br^-]^2}{1 + b[Br^-]} + \frac{c[Br^-]^3}{1 + d[Br^-]}$$

The mechanism proposed for this reaction involves the formation of a charge-transfer complex between the substrate and Br^-. This complex reacts by two pathways, either undergoing an auto-redox reaction to give a Br_2 adduct of $[Pt(CN)_4]^{2-}$, or reacting with Br^- in a redox reaction which forms a Br_3^- adduct of $[Pt(CN)_4]^{2-}$. The adducts then undergo the reverse redox reactions to regenerate the substrate in the presence of H_2O, or to form the dibromo-product in the presence of Br^-. The natures of the Br_2-Pt and Br_3^--Pt bonding in the two adducts are different, so equilibration between the two species is slow compared to their rates of reoxidation. A good deal of kinetic and non-kinetic evidence is adduced for this mechanism and it is shown that it explains the results obtained in other anation reactions of Pt(IV) complexes.

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Table 7.1

Spectroscopic parameters for trans-$K_2[Pt(CN)_4Br_2]$

λ_{max} [e]	ϵ_{max} [f]	reference
346	1230	(a)
	1160	(b)
342	1140	(c)
342	1200	(d)

(a) This work in H_2O

(b) This work in 0.02 M NaBr and 1.16×10^{-3} M $HClO_4$

(c) Skinner and Jones, J. Amer. Chem. Soc., 1969, 91, 1984

(d) D. H. Vaughan, Ph.D. Thesis, University of London, 1968

(e) nm

(f) $M^{-1}\ cm^{-1}$

Table 7.2

Spectroscopic data for the reaction

$$\underline{\text{trans}}\text{-}[Pt(CN)_4BrOH]^- + H^+ + Br^- \longrightarrow \underline{\text{trans}}\text{-}[Pt(CN)_4Br_2]^{2-} + H_2O$$

Compound	Means of Preparation	Conditions	ϵ at 345 nm*
$[Pt(CN)_4Br_2]^{2-}$	from solid, pure $K_2[Pt(CN)_4Br_2]$	$[Br^-] = 0.02$ M $[H^+] = 1.16 \times 10^{-3}$ M	1160
$[Pt(CN)_4BrOH]^-$	$[Pt(CN)_4Br_2]^{2-} + OH^-$	$[OH^-] = 1.0 \times 10^{-3}$ M	277
$[Pt(CN)_4Br_2]^{2-}$	Regenerated from $[Pt(CN)_4BrOH]^- + H^+ + Br^-$	$[H^+] = 8 \times 10^{-4}$ M $[Br^-] = 0.02$ M	1150

*in M^{-1} cm^{-1}

Table 7.3

trans-$[Pt(CN)_4BrOH_2]^-$ + Br^-

Observed pseudo-first order rate constants

10^3 [Br^-] (M)	10^2 k_{obsd} (s^{-1})
4.00	2.878, 2.878, 2.964, 2.964, 3.161, 3.161
5.00	5.188, 5.188, 5.608, 5.608, 5.493, 5.493
6.00	5.733, 5.733, 5.417, 5.417, 5.610, 5.282, 5.066, 5.066
7.00	7.949, 7.949, 8.586, 8.586, 8.046, 8.046, 8.091, 8.091
8.00	10.95, 10.95, 11.15, 11.15, 11.10, 11.10
9.00	12.62, 12.62, 14.13, 14.13, 16.76, 16.76, 17.63, 17.63, 17.32
10.0	14.31, 14.31, 14.08, 14.04, 13.02, 12.78, 12.78
12.0	22.06, 22.06, 25.71, 25.71, 25.94, 25.94, 26.53
16.0	40.46, 40.46, 44.69, 44.69, 43.83, 43.83, 45.29, 45.29
20.0	52.89, 52.89, 52.23, 51.77, 48.93, 47.18, 47.18
30.0	122.6, 122.6, 110.4, 115.0, 115.0, 108.1, 103.5, 103.5
40.0*	165.4, 165.4, 145.7, 180.6, 141.6, 147.9, 147.9
40.0*	203.7, 203.7, 197.0, 204.8, 249.7, 207.6, 207.6
50.0	373.5, 373.5, 307.7, 350.2, 350.2, 338.2, 313.0, 313.0
60.0	490.7, 490.7, 407.0, 412.1, 448.4, 434.1, 434.1, 364.3
70.0	803.7, 803.7, 731.3, 765.0, 765.0, 723.3, 682.2, 682.2
80.0	1023, 1023, 973.4, 1040, 884.9, 936.3, 936.3
90.0	1356, 1356, 1132, 1141, 1299, 1299, 1261, 1261
100	1874, 1874, 1824, 1598, 1840, 1844, 1902, 1902
110	2461, 2461, 2226, 2127, 2353, 2408, 2408
120	2936, 2936, 2974, 2161, 2795, 2795, 2869

Table 7.3, continued

10^3 [Br^-] (M)	10^2 k_{obsd} (s^{-1})
130	3627, 3627, 3432, 3408, 3137, 3036, 3036
140	3523, 3523, 3375, 3694, 3940
150	4469, 4469, 4406, 4228, 4074, 4083, 4083
160	4393, 4393, 4917, 5139, 5139, 4721, 4575, 4575
170	6201, 6201, 6497, 6497, 5429, 5264, 5445, 5445
180	6674, 6674, 6533, 6679, 6102, 6102, 6369
190	6784, 6784, 6892, 6557, 6557, 7563, 7563
200	7997, 7997, 6950, 7711, 7185, 7812, 7812

*Different sets of runs

Table 7.4

trans-$[Pt(CN)_4BrOH_2]^-$ + Br^-

Reproducibility of pseudo-first order rate constants

10^3 $[Br^-]$	No. of points	$\sigma_{\%}$ †	10^3 $[Br^-]$	No. of points	$\sigma_{\%}$ †
4.00	6	1.77	70.0	8	2.29
5.00	6	1.46	80.0	7	2.24
6.00	8	1.75	90.0	8	2.41
7.00	8	1.14	100	8	1.91
8.00	6	0.34	110	7	2.04
9.00	9	4.55	120	7	3.84
10.0	7	2.00	130	7	2.94
12.0	7	2.93	140	5	2.67
16.0	8	1.62	150	7	1.65
20.0	7	1.95	160	8	2.27
30.0	8	2.38	170	8	3.16
40.0*	7	3.45	180	7	1.53
40.0*	7	3.16	190	7	2.35
50.0	8	2.77	200	7	2.02
60.0	8	3.46			

Using a pooled estimate of variance, the percentage error in the average rate constant for a set of runs = 2.53%.

---

† $\sigma_{\%}$ = standard deviation of the average value of k_{obsd} for a set of runs, expressed as a percentage.

* different sets of runs

Table 7.5

trans-$[Pt(CN)_4BrOH_2]^-$ + Br^-

Average rate constants and their variation with $[Br^-]$

10^3 $[Br^-]$ (M)	10^2 k_{obsd} (s^{-1})	no. of points	10^3 $[Br^-]$ (M)	10^2 k_{obsd} (s^{-1})	no. of points
4.00	3.001	6	70.0	744.5	8
5.00	5.430	6	80.0	973.8	7
6.00	5.415	8	90.0	1263	8
7.00	8.168	8	100	1832	8
8.00	11.07	6	110	2349	7
9.00	15.51	9	120	2781	7
10.0	13.62	7	130	3329	7
12.0	24.85	7	140	3611	5
16.0	43.57	8	150	4259	7
20.0	50.44	7	160	4731	8
30.0	112.6	8	170	5872	8
40.0*	156.4	7	180	6448	7
40.0*	210.6	7	190	6957	7
50.0	339.9	8	200	7638	7
60.0	435.2	8			

* different sets of runs

Table 7.6

trans-$[Pt(CN)_4BrOH_2]^- + Br^-$

Variation of k_{obsd} with $[Br^-]$ assuming the rate law

$$k_{obsd} = \frac{a[Br^-]^2}{1 + b[Br^-]} + \frac{c[Br^-]^3}{1 + d[Br^-]}$$

$a = (2.50 \pm 0.17) \times 10^3\ M^{-2}\ s^{-1}$

$b = 87 \pm 16\ M^{-1}$

$c = (2.17 \pm 0.22) \times 10^4\ M^{-3}\ s^{-1}$

$d = 6.0 \pm 1.2\ M^{-1}$.

covariance of a and b = $2.590 \times 10^3\ M^{-3}\ s^{-1}$

covariance of a and c = $2.732 \times 10^5\ M^{-5}\ s^{-2}$

covariance of a and d = $1.368 \times 10^2\ M^{-3}\ s^{-1}$

covariance of b and c = $2.955 \times 10^4\ M^{-4}\ s^{-1}$

covariance of b and d = $1.497 \times 10^1\ M^{-2}$

covariance of c and d = $2.511 \times 10^3\ M^{-4}\ s^{-1}$

Standard deviation in k_{obsd} = 11.1%

Table 7.7

Comparison of the results found in this study with those of previous workers

Mason Inorg. Chem., 1971, 10, 1914

$$[H^+] = h_1 = 8.0 \times 10^{-3} \text{ M}$$

10^3 [Br^-]	10^3 g
0.7685	42.7
0.6935	43.0
0.6185	43.5
0.5370	41.3
0.5185	42.9
0.4185	41.3
0.3185	42.4
0.2685	40.9
0.1685	44.3

Average value of g = $\bar{g} = 42.5 \times 10^{-3}$

Skinner & Jones J. Amer. Chem. Soc., 1969, 91, 4405

$$[H^+] = h_1 = 1 \times 10^{-1} \text{ M}$$

10^3 [Br^-]	10^3 g
32.0	9.79
25.6	8.40
22.4	7.45
19.2	7.43
16.0	7.26
12.8	6.94
11.2	6.69
9.6	7.56
8.0	6.17

Average value of g = $\bar{g} = 7.52 \times 10^{-3}$

continued...

Table 7.7, continued

Skinner & Jones J. Amer. Chem. Soc., 1969, 91, 4405

$$[H^+] = h_1 = 1.26 \times 10^{-2}\ M$$

$10^3\ [Br^-]$	$10^3\ g$	
40.0	24.0	
32.0	21.6	
24.0	21.4	
16.0	18.4	Average value of g =
12.8	21.5	$\bar{g} = 20.5 \times 10^{-3}$
9.6	19.7	
8.0	18.7	
6.4	18.8	

Morgan & Jones J. Inorg. Nucl. Chem., 1972, 34, 275

$$[H^+] = h_1 = 1.318 \times 10^{-2}\ M$$

$10^3\ [Br^-]$	$10^3\ g$	
25.0	38.8	
20.0	40.0	
17.5	41.0	Average value of g =
15.0	40.6	$\bar{g} = 41.1 \times 10^{-3}$
12.5	42.2	
10.0	39.9	
7.5	45.3	

Table 7.8

Calculation of K_A

Reference	$10^3 h_1$ (M)	$10^3 \bar{g}$	$10^2 K_A$ (M)	
			d	e
a	100	7.523	6.7	4.2
a	12.6	20.5	-8.2	8.4
b	13.18	41.12	6.5	1.5
c	8.0	42.5	1.6	0.9

a Skinner and Jones

b Morgan and Jones

c Mason

d h taken as 3.04×10^{-4} M

e h taken as 2.25×10^{-4} M

Published values of K_A

2.5×10^{-2} M reference 1

5.0×10^{-2}, 1.07×10^{-2} M reference 2

3.16×10^{-2} M reference 3

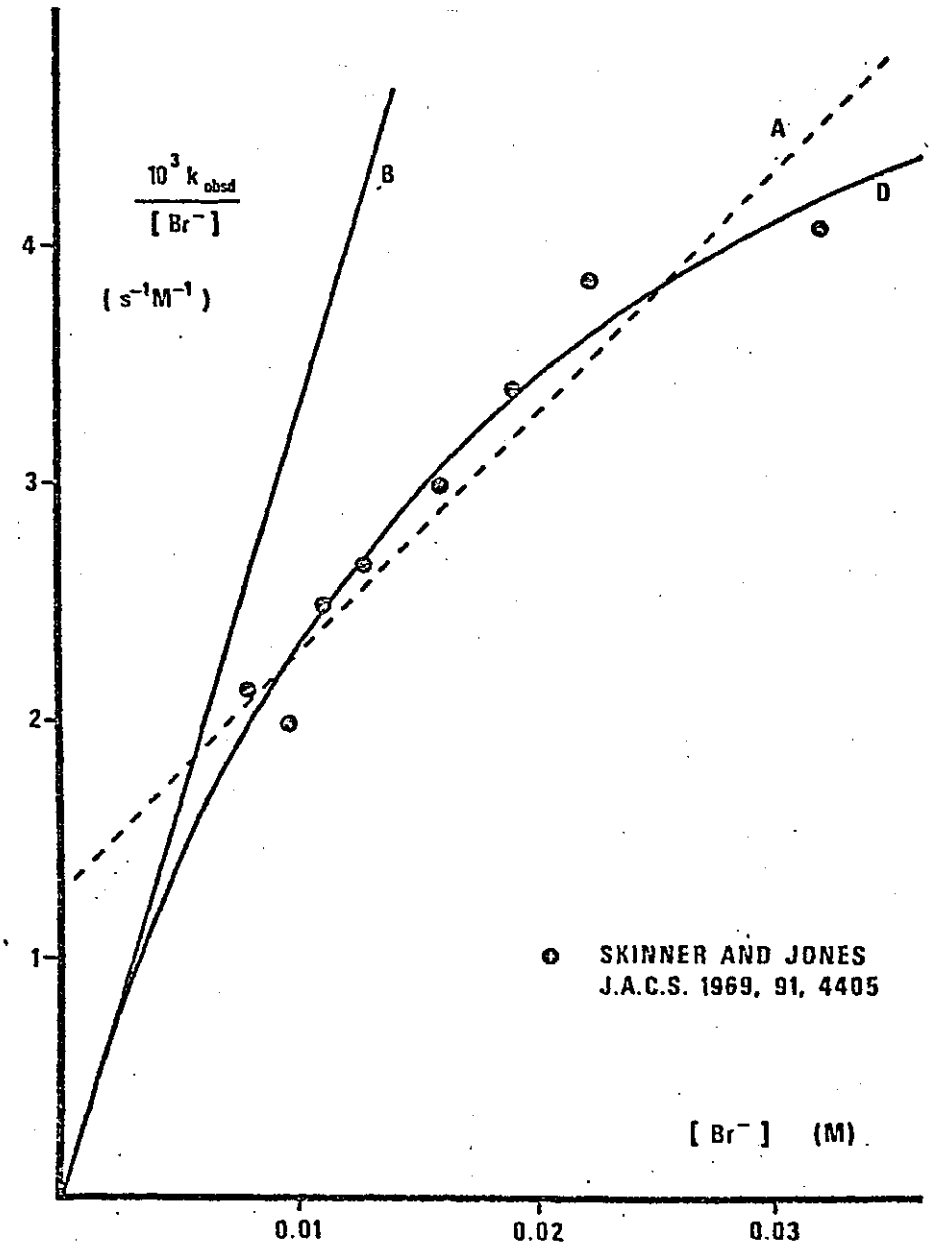


Fig. 7.1 Data of Skinner and Jones at pH = 1.00 re-interpreted according to the redox mechanism

A line drawn by Skinner and Jones according to the rate law of equation 7.6

B line drawn according to Mason's rate law of equation 7.8

D curve drawn according to the rate law predicted by the redox mechanism (equation 7.14)

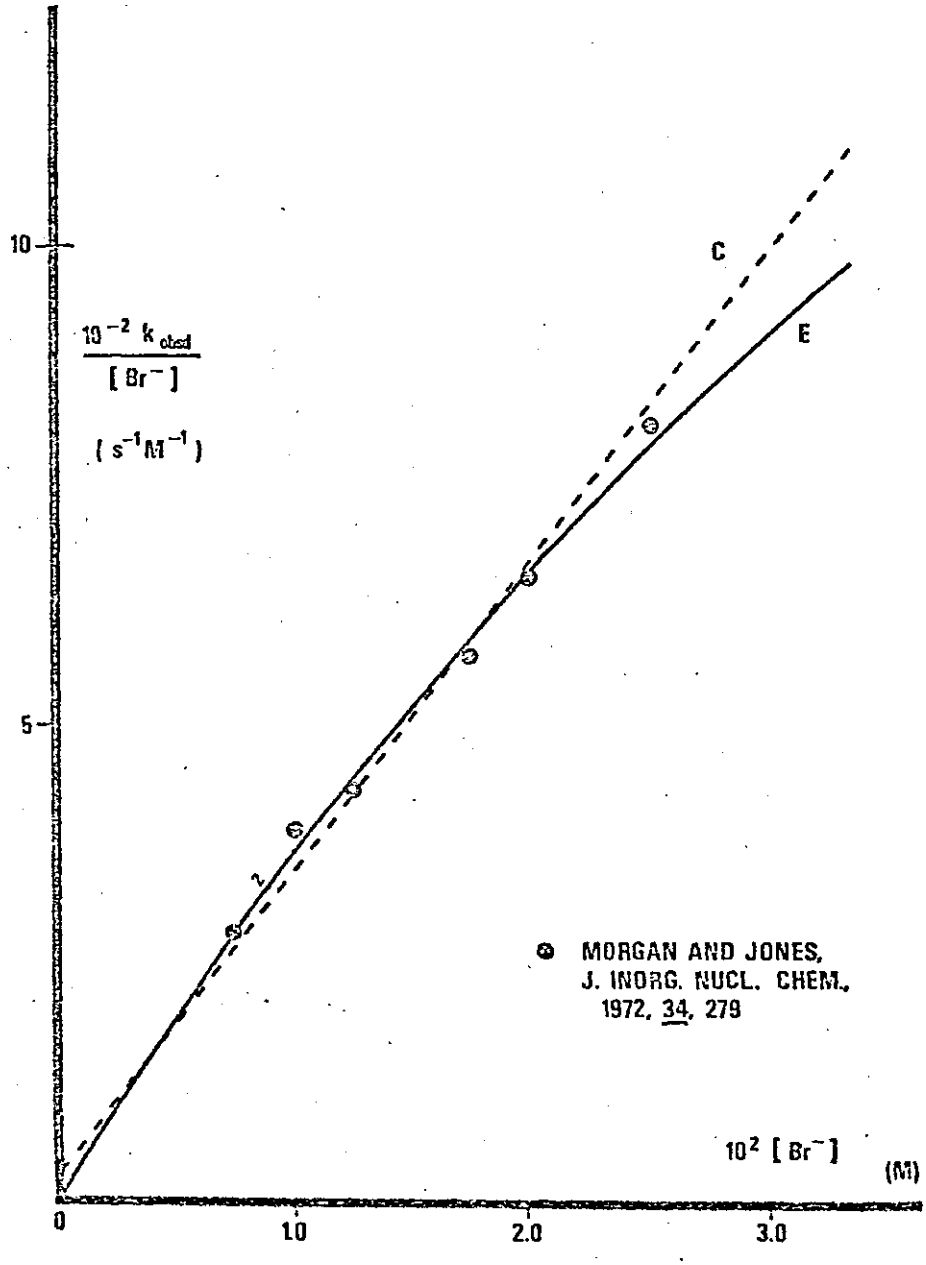


Fig. 7.2 Data of Morgan and Jones re-interpreted according to the redox mechanism

C line drawn by Morgan and Jones according to the rate law of equation 7.11

E curve drawn according to the rate law predicted by the redox mechanism (equation 7.14)

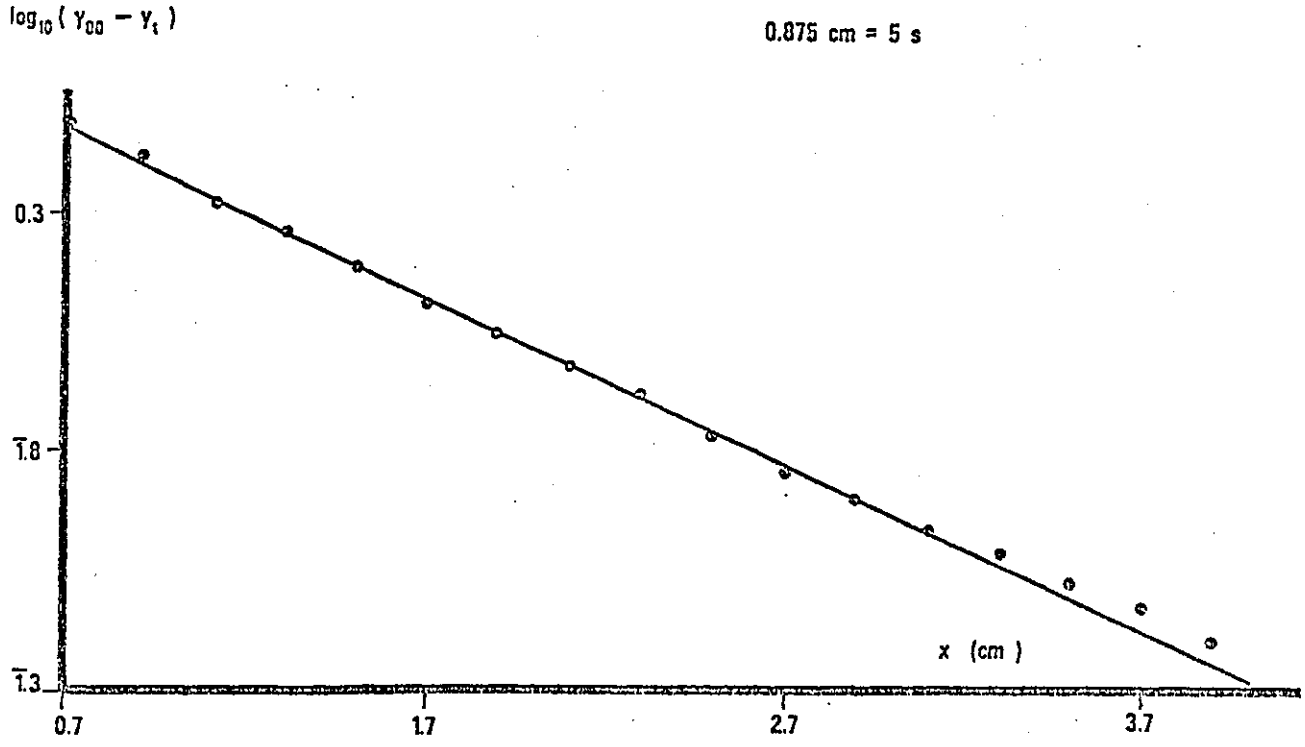


Fig. 7.3 Typical pseudo-first-order rate plot obtained for the bromide anation of <u>trans</u>-$[Pt(CN)_4BrOH_2]^-$

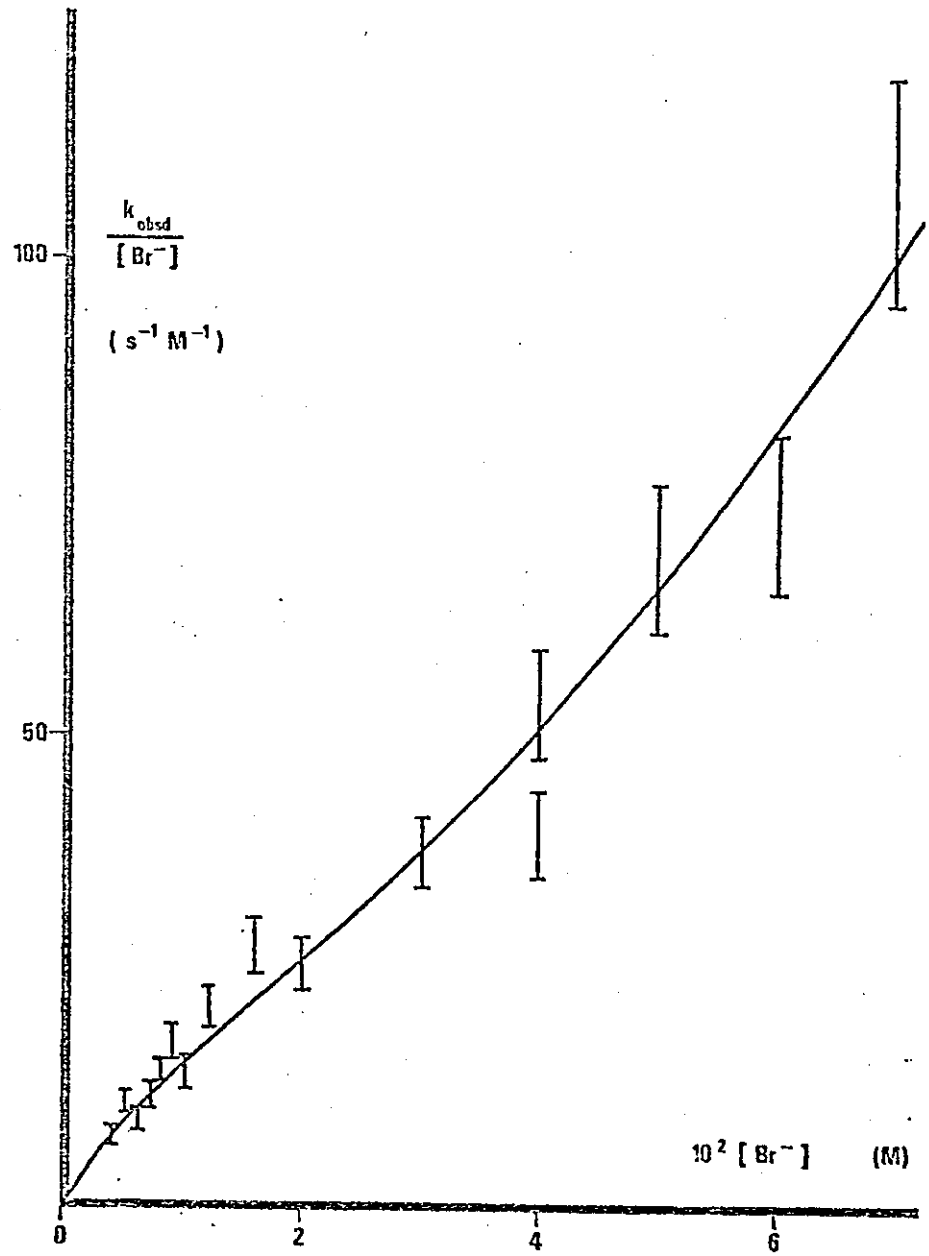


Fig. 7.4 $k_{obsd}/[Br^-]$ as a function of $[Br^-]$ at low bromide ion concentrations

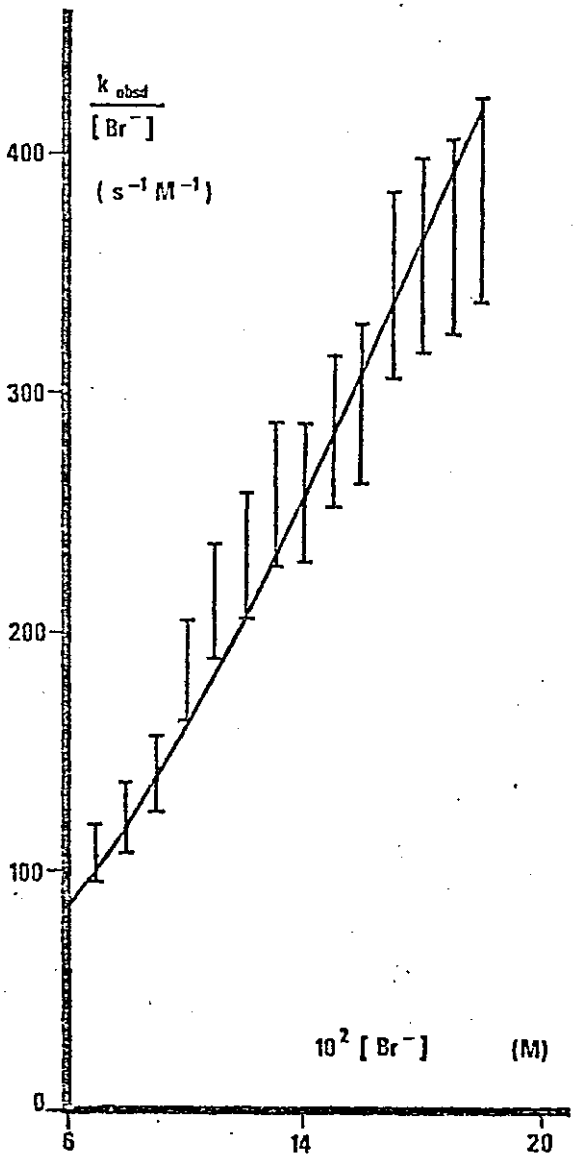


Fig. 7.5 $k_{obsd}/[Br^-]$ as a function of $[Br^-]$ at high bromide ion concentrations

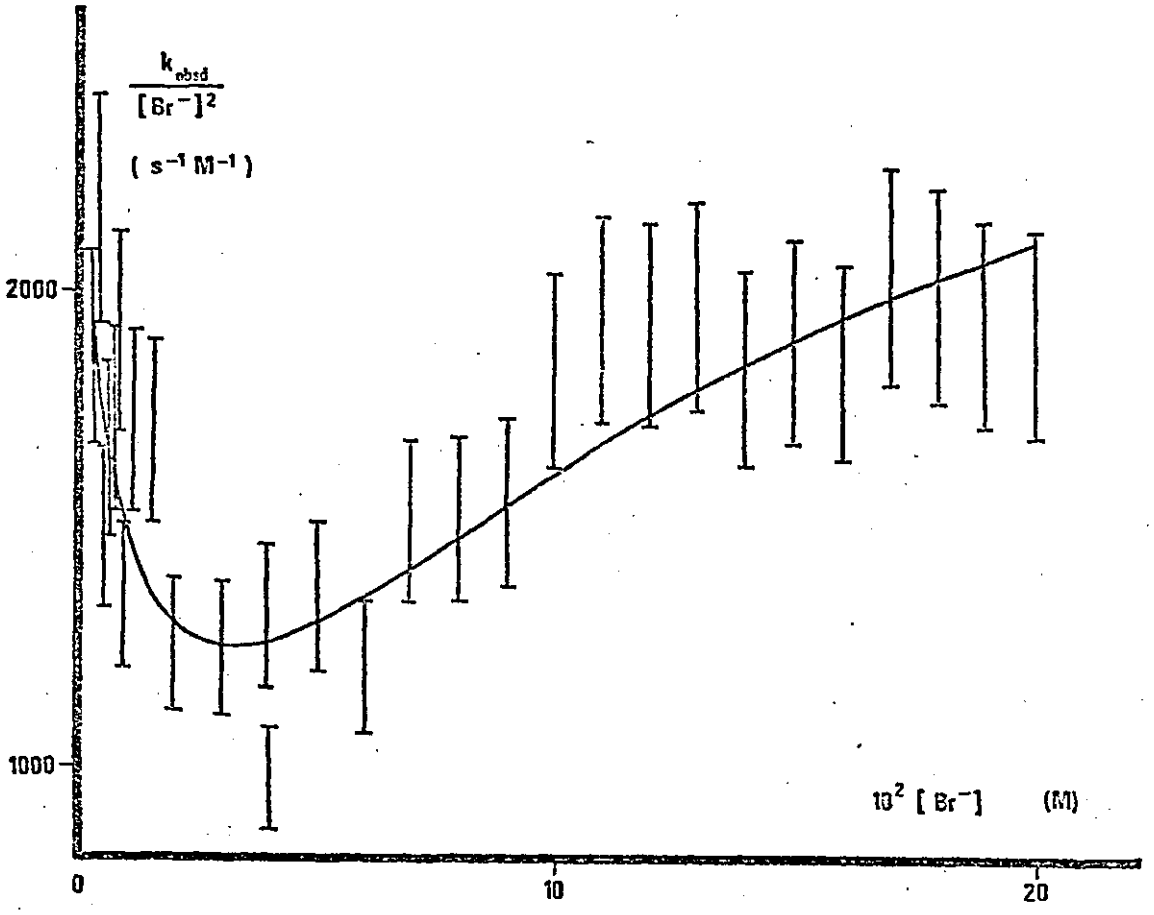


Fig. 7.6 $k_{obsd}/[Br^-]^2$ as a function of the bromide ion concentration

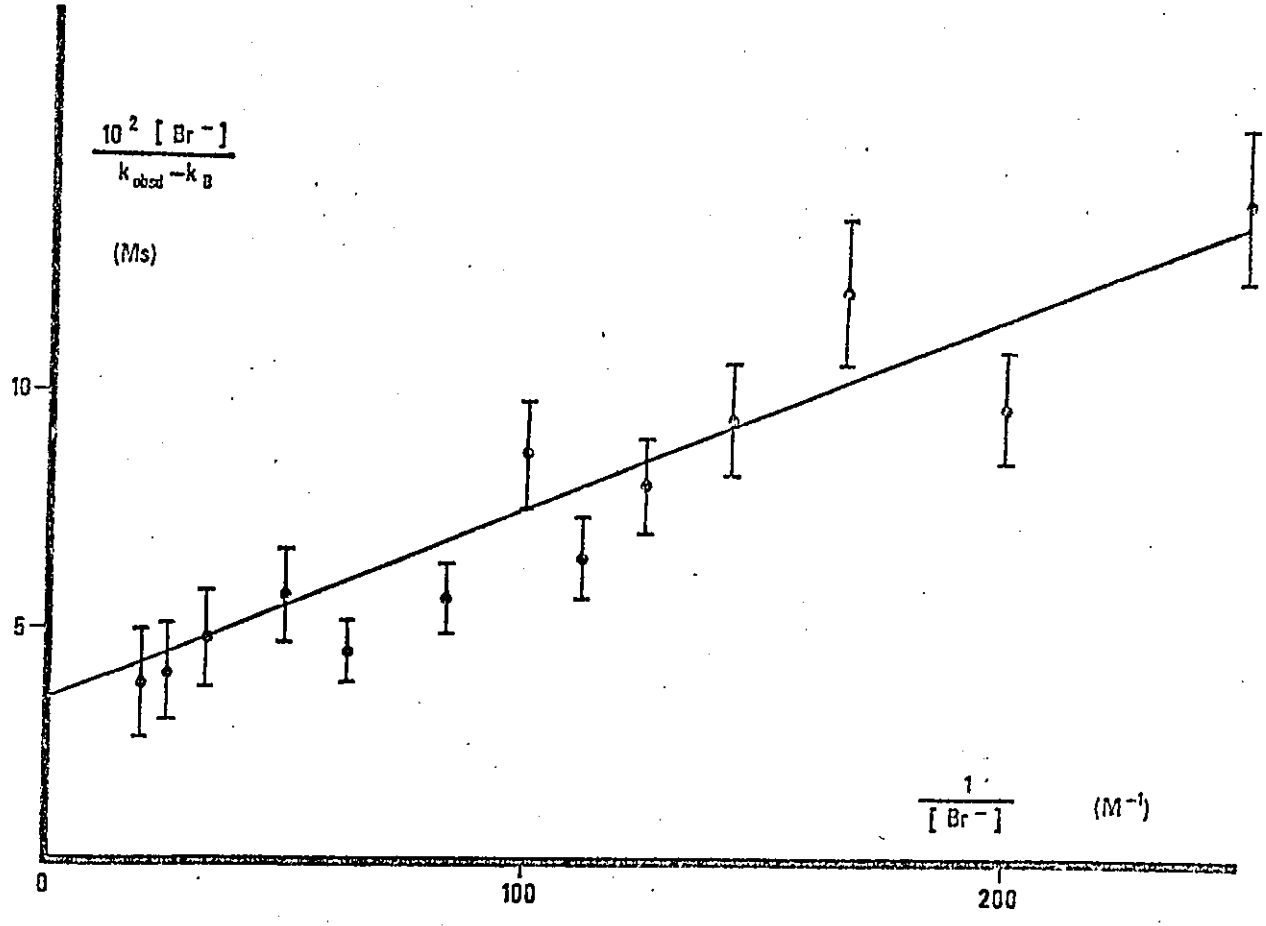


Fig. 7.7 $[Br^-]/(k_{obsd}-k_B)$ as a function of the reciprocal of the bromide ion concentration

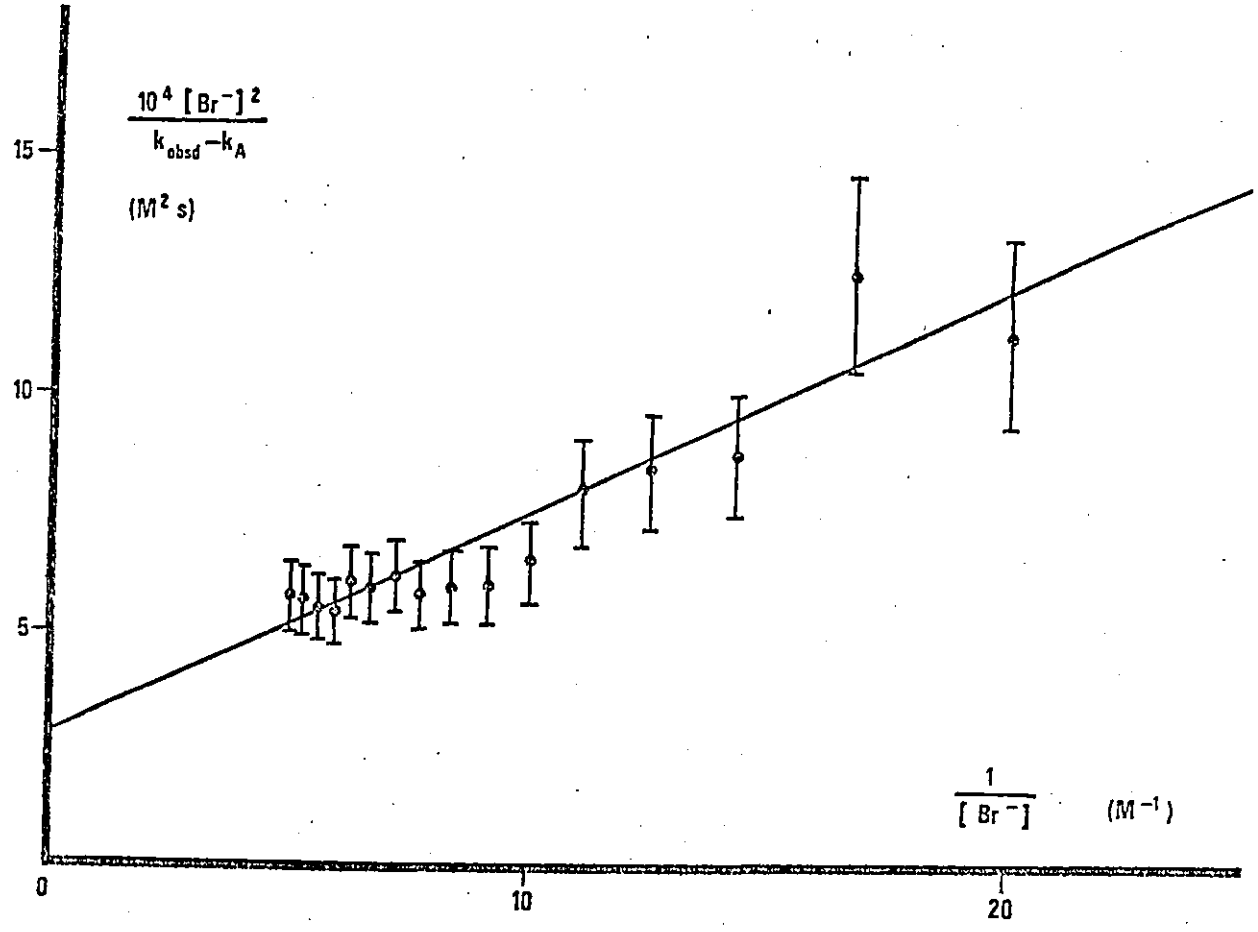


Fig. 7.8 $[Br^-]^2/(k_{obsd}-k_A)$ as a function of the reciprocal of the bromide ion concentration

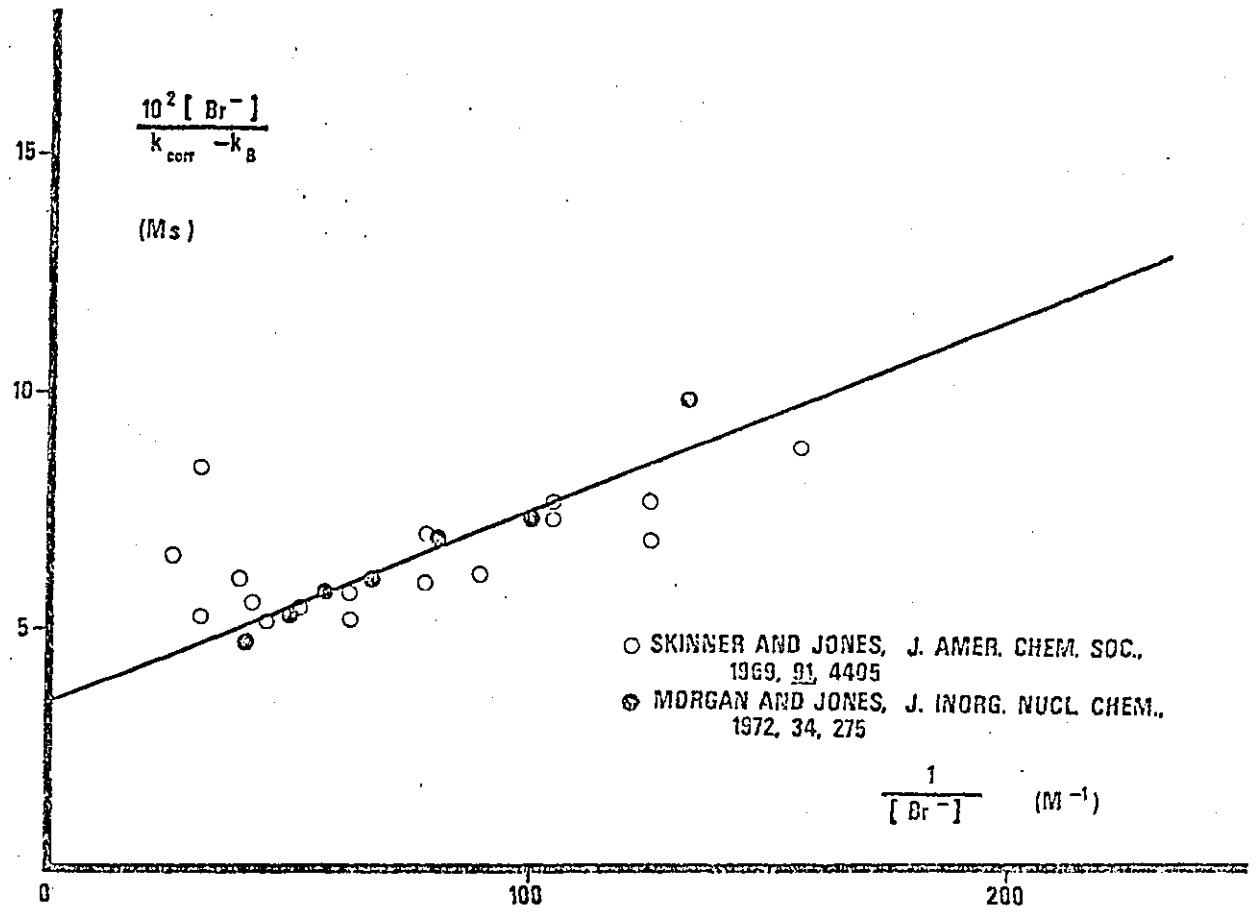


Fig. 7.9 The results of Skinner and Jones and of Morgan and Jones re-interpreted according to the rate law of equation 7.22

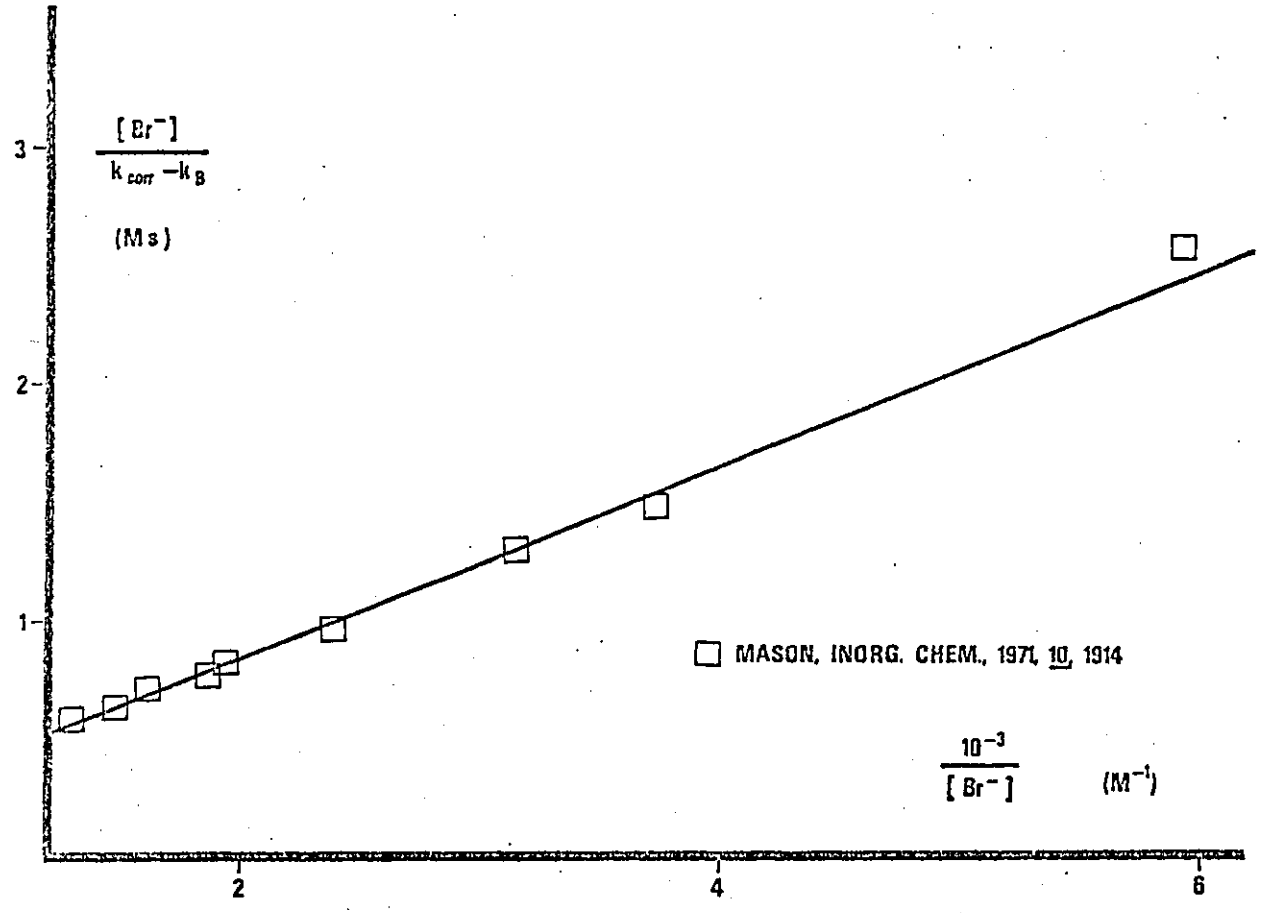


Fig. 7.10 Mason's results re-interpreted according to the rate law of equation 7.22

APPENDIX A

Statistical Analysis of Experimental Data in Part I

Case 1 ; Calculation of the unweighted mean of a series of observations

The unweighted mean, $\bar{y}$, of a series of N observations y_i is given by

$$\bar{y} = \frac{\sum_i y_i}{N} \qquad (A.1)$$

where $\sum_i$ denotes summation over all values of i from i = 1 to i = N.

The standard deviation, σ_i , of an individual value of y_i is given by

$$\sigma_i = \sqrt{\frac{\sum_i (\bar{y} - y_i)^2}{N - 1}} \qquad (A.2)$$

By applying the law of propagation of errors to equation A.1, the standard deviation, $\sigma_{\bar{y}}$ of $\bar{y}$ is given by

$$\sigma_{\bar{y}} = \sqrt{\frac{N \sigma_i^2}{N^2}} \qquad (A.3)$$

which simplifies to

$$\sigma_{\bar{y}} = \frac{\sigma_i}{\sqrt{N}} \qquad (A.4)$$

Case 2 ; Calculation of the weighted mean of a series of observations

The weighted mean, $\bar{y}$, of a series of observations y_i , each with a different standard deviation, σ_i , is given

by

$$\bar{y} = \frac{\sum_i w_i y_i}{\sum_i w_i} \qquad (A.5)$$

where w_i is a weighting factor defined as

$$w_i = \frac{1}{\sigma_i^2} \qquad (A.6)$$

By applying the law of propagation of errors to equation A.5, the standard deviation, $\sigma_{\bar{y}}$, of $\bar{y}$ is given as

$$\sigma_{\bar{y}} = \frac{\sqrt{\sum_i w_i^2 \sigma_i^2}}{\sum_i w_i} \qquad (A.7)$$

From equations A.6 and A.7 it follows that

$$\sigma_{\bar{y}} = \frac{1}{\sqrt{\sum_i w_i}} \qquad (A.8)$$

Case 3 : The unweighted least squares analysis of the linear dependence of a series of observations, y, on the "fixed" parameter, x

The experimental values, x_i , of x are "fixed" in the Berkson sense, so that there is considered to be no error in the value of x_i , all the error of the observation being associated with the corresponding value, y_i , of y. The mathematical relationship between y and x is assumed to conform to the ideal law

$$y = \alpha + \beta x \qquad (A.9)$$

The "best" value, $\hat{\alpha}$, of α according to the least squares

treatment is given by

$$\hat{\alpha} = \frac{\sum_i x_i^2 \sum_i y_i - \sum_i x_i y_i \sum_i x_i}{N\sum_i x_i^2 - (\sum_i x_i)^2} \qquad (A.10)$$

where N is the number of observations.

The "best" value, $\hat{\beta}$, of β is given by

$$\hat{\beta} = \frac{N \sum_i x_i y_i - \sum_i x_i \sum_i y_i}{N\sum_i x_i^2 - (\sum_i x_i)^2} \qquad (A.11)$$

and the standard deviation, $\hat{\sigma}_y$, of an individual value of y_i is given by

$$\hat{\sigma}_y = \sqrt{\frac{\sum_i (y_i - \hat{\beta}x_i - \hat{\alpha})^2}{N - 2}} \qquad (A.12)$$

By the law of propagation of errors applied to equation A.10, the standard deviation, $\hat{\sigma}_{\hat{\alpha}}$, of the intercept $\hat{\alpha}$ is given by

$$\sigma_{\hat{\alpha}} = \hat{\sigma}_y \frac{\sqrt{\sum_j (\sum_i x_i^2 - x_j \sum_i x_i)^2}}{N\sum_i x_i^2 - (\sum_i x_i)^2} \qquad (A.13)$$

where $\sum_j$ denotes summation over all values of j from j = 1 to j = N. Equation A.13 simplifies to

$$\sigma_{\hat{\alpha}} = \hat{\sigma}_y \sqrt{\frac{\sum_i x_i^2}{N \sum_i x_i^2 - (\sum_i x_i)^2}} \qquad (A.14)$$

Similarly, the standard deviation, $\sigma_{\hat{\beta}}$, of the slope $\hat{\beta}$ is given by

$$\sigma_{\hat{\beta}} = \hat{\sigma}_y \frac{\sqrt{\sum_j (Nx_j - \sum_i x_i)^2}}{N\sum_i x_i^2 - (\sum_i x_i)^2} \qquad (A.15)$$

which simplifies to

$$\sigma_{\hat{\beta}} = \hat{\sigma}_y \sqrt{\frac{N}{N \sum_i x_i^2 - (\sum_i x_i)^2}} \qquad (A.16)$$

The covarience, $\sigma_{\hat{\alpha}\hat{\beta}}$, between $\hat{\alpha}$ and $\hat{\beta}$ is given by

$$\sigma_{\hat{\alpha}\hat{\beta}} = \frac{-\sum_i x_i}{N \sum_i x_i^2 - (\sum_i x_i)^2} \qquad (A.17)$$

Case 3a ; The application of this treatment to the temperature-dependence of a first-order rate constant, k_r, which has been measured under conditions where the observed rate constant, k_{obsd}, equals k_r

This case corresponds to pseudo-first-order rate constants found at very low concentrations of entering ligand, where the reaction proceeds by a single, first-order pathway and the rate law is

$$k_{obsd} = k_r \qquad (A.18)$$

The temperature-dependence of k_r can be described by the Eyring equation

$$\log_{10}(k_r/T) = \log_{10}(k/h) - \frac{\Delta H^{\ddagger}}{2.303RT} + \frac{\Delta S^{\ddagger}}{2.303R} \qquad (A.19)$$

where T is the absolute temperature, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ the enthalpy and entropy of activation, and k, h, R are Boltzmann's constant, Planck's constant, and the universal gas constant, respectively. Equation A.19 corresponds to equation A.9 if

$$y = \log_{10}(k_r/T) \qquad (A.20)$$

$$x = \frac{1}{T} \qquad (A.21)$$

so that

$$\hat{\alpha} = \log_{10}(k/h) + \frac{\Delta S^{\ddagger}}{2.303R} \qquad (A.22)$$

$$\hat{\beta} = \frac{-\Delta H^{\ddagger}}{2.303R} \qquad (A.23)$$

Once $\hat{\alpha}$ and $\hat{\beta}$ have been calculated, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be calculated from equations A.22 and A.23. The standard deviations, σ_H and σ_S, of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are given by equations A.24 and A.25 respectively.

$$\sigma_H = 2.303R(\sigma_{\hat{\beta}}) \qquad (A.24)$$

$$\sigma_S = 2.303R(\sigma_{\hat{\alpha}}) \qquad (A.25)$$

where $\sigma_{\hat{\alpha}}$ and $\sigma_{\hat{\beta}}$ are defined in equations A.14 and A.16.

This treatment of the data assumes that there is a constant percentage standard deviation, P, which is temperature-independent, associated with an individual determination of k_{obsd}. Thus the standard deviation, σ_{ki}, of any value, k_i of k_{obsd} is given by

$$\sigma_{ki} = \frac{Pk_i}{100} \qquad (A.26)$$

The standard deviation, σ_i, of the corresponding value of y_i is given by

$$y_i + \sigma_i = \log_{10}(k_i + \sigma_{ki}) \qquad (A.27)$$

From equations A.26 and A.20

$$\sigma_i = \log_{10}(1 + \sigma_{ki}/k_i) \qquad (A.28)$$

and from equations A.28 and A.26

$$\sigma_i = \log_{10}(1 + P/100) \qquad (A.29)$$

Since P is a constant, σ_i is also a constant, and the unweighted least squares treatment is clearly appropriate. An estimate of the value of P can be obtained from equation A.29 if the standard deviation σ_y defined in equation A.12 is substituted for σ_i. Thus

$$P = 100(\text{antilog}(\hat{\sigma}_y) - 1) \qquad (A.30)$$

Case 4 ; The weighted least squares analysis of the linear dependence of a series of observations, y , on the "fixed" parameter, x

As for case 3, the experimental values, x_i , of x are "fixed" in the Berkson sense, and the ideal relationship between y and x is assumed to be that of equation A.9. If the standard deviation of any value, y_i , of y is assumed to be σ_i, then the weighting factor, w_i, associated with y_i is given by

$$w_i = \frac{1}{\sigma_i^2} \qquad (A.31)$$

The "best" estimate, $\hat{\alpha}$, of α is given by

$$\hat{\alpha} = \frac{\sum_i w_i y_i \sum_i w_i x_i^2 - \sum_i w_i x_i y_i \sum_i w_i x_i}{\sum_i w_i \sum_i w_i x_i^2 - (\sum_i w_i x_i)^2} \qquad (A.32)$$

whilst the "best" estimate, $\hat{\beta}$, of β is given by

$$\hat{\beta} = \frac{\sum_i w_i \sum_i w_i x_i y_i - \sum_i w_i x_i \sum_i w_i y_i}{\sum_i w_i \sum_i w_i x_i^2 - (\sum_i w_i x_i)^2} \qquad (A.33)$$

Application of the law of propagation of errors to equation

A.32 gives the standard deviation, $\sigma_{\hat{\alpha}}$, of $\hat{\alpha}$ as

$$\sigma_{\hat{\alpha}} = \frac{\sqrt{\sum_j w_j \left(\sum_i w_i x_i^2 - x_j \sum_i w_i x_i \right)^2}}{\sum_i w_i \sum_i w_i x_i^2 - \left(\sum_i w_i x_i \right)^2} \qquad (A.34)$$

Equation A.34 simplifies to

$$\sigma_{\hat{\alpha}} = \sqrt{\frac{\sum_i w_i x_i^2}{\sum_i w_i \sum_i w_i x_i^2 - \left(\sum_i w_i x_i \right)^2}} \qquad (A.35)$$

Similarly, the law of propagation of errors applied to equation A.33 gives the standard deviation, $\sigma_{\hat{\beta}}$, of $\hat{\beta}$ as

$$\sigma_{\hat{\beta}} = \frac{\sqrt{\sum_j w_j \left(x_j \sum_i w_i - \sum_i w_i x_i \right)^2}}{\sum_i w_i \sum_i w_i x_i^2 - \left(\sum_i w_i x_i \right)^2} \qquad (A.36)$$

which simplifies to

$$\sigma_{\hat{\beta}} = \sqrt{\frac{\sum_i w_i}{\sum_i w_i \sum_i w_i x_i^2 - \left(\sum_i w_i x_i \right)^2}} \qquad (A.37)$$

The covariance, $\sigma_{\hat{\alpha}\hat{\beta}}$, of $\hat{\alpha}$ and $\hat{\beta}$ is given by

$$\sigma_{\hat{\alpha}\hat{\beta}} = \frac{- \sum_i w_i x_i}{\sum_i w_i \sum_i w_i x_i^2 - \left(\sum_i w_i x_i \right)^2} \qquad (A.38)$$

<u>Case 4a</u> ; <u>The application of this treatment to the linear dependence of pseudo-first-order rate constants, k_{obsd} , on the concentration of added ligand Y</u>

The rate law

$$k_{obsd} = k_1 + k_2[Y] \qquad (A.39)$$

corresponds to equation A.9 if

$$y = k_{obsd} \tag{A.40}$$

$$x = [Y] \tag{A.41}$$

$$\alpha = k_1 \tag{A.42}$$

$$\beta = k_2 \tag{A.43}$$

If it is assumed that there is a constant percentage error, P , in k_{obsd} , then the standard deviation, σ_i , of y_i is given by

$$\sigma_i = \frac{Py_i}{100} \tag{A.44}$$

Since P/100 is a constant, the weighting factor, w_i , for y_i can be taken as

$$w_i = \frac{1}{y_i^2} \tag{A.45}$$

The value of P can be estimated from the experimental data using the equation

$$P = 100 \sqrt{\frac{\sum_i w_i (y_i - \hat{\alpha} - \hat{\beta} x_i)^2}{N - 2}} \tag{A.46}$$

where N is the number of observations and $\hat{\alpha}$ and $\hat{\beta}$ are given by equations A.32 and A.33 respectively. However, the standard deviations, $\sigma_{\hat{\alpha}}$ and $\sigma_{\hat{\beta}}$, of $\hat{\alpha}$ and $\hat{\beta}$ are now given by equations A.47 and A.48 respectively.

$$\sigma_{\hat{\alpha}} = \frac{P}{100} \sqrt{\frac{\sum_i w_i x_i^2}{\sum_i w_i \sum_i w_i x_i^2 - \left(\sum_i w_i x_i \right)^2}} \tag{A.47}$$

$$\sigma_{\hat{\beta}} = \frac{P}{100} \sqrt{\frac{\sum_i w_i}{\sum_i w_i \sum_i w_i x_i^2 - \left(\sum_i w_i x_i \right)^2}} \tag{A.48}$$

The covariance, $\sigma_{\hat{\alpha}\hat{\beta}}$, of $\hat{\alpha}$ and $\hat{\beta}$ is given by

$$\sigma_{\hat{\alpha}\hat{\beta}} = \frac{-P^2}{10^4}\left\{\frac{\sum_i w_i x_i}{\sum_i w_i \sum_i w_i x_i^2 - (\sum_i w_i x_i)^2}\right\} \qquad (A.49)$$

Case 4b ; The application of this treatment to the temperature-dependence of simple rate constants when the absolute values of the standard deviations of these rate constants are known, and are not identical for all points

The temperature-dependence of the rate constant, k_r , can be represented by the Eyring equation (equation A.19), which conforms to equation A.9 if

$$y = \log_{10}(k_r/T) \qquad (A.20)$$

$$x = \frac{1}{T} \qquad (A.21)$$

Since the standard deviation, σ_{ki} , of a given value, k_i , of k_r is known, the standard deviation, σ_i , of the corresponding value of y_i is given by

$$\sigma_i = \log_{10}(1 + \sigma_{ki}/k_i) \qquad (A.28)$$

and the weighting factor, w_i , for y_i by

$$w_i = \frac{1}{\sigma_i^2} \qquad (A.31)$$

The values of $\hat{\alpha}$, $\hat{\beta}$, $\sigma_{\hat{\alpha}}$, $\sigma_{\hat{\beta}}$ and $\sigma_{\hat{\alpha}\hat{\beta}}$ are given by equations A.32, A.33, A.35, A.37 and A.38 respectively. The "best" values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, σ_H and σ_S are given by

$$\Delta H^{\ddagger} = -2.303R\hat{\beta} \qquad (A.50)$$

$$\Delta S^{\ddagger} = 2.303R\hat{\alpha} - \log_{10}(k/h) \qquad (A.51)$$

$$\sigma_H = 2.303R(\sigma_{\hat{\beta}}) \qquad (A.24)$$

$$\sigma_S = 2.303R(\sigma_{\hat{\alpha}}) \qquad (A.25)$$

The correction of a standard deviation for the finite number of degrees of freedom associated with its determination

In all the above cases, the standard deviation, σ, calculated from a set of experimental data is in itself uncertain because it is based on a sample of the population to which it belongs, rather than the whole population. For the mathematical functions

$$y = \alpha + \beta x \qquad (A.52)$$

$$y = \gamma \qquad (A.53)$$

where α, β, γ are constants, the whole population corresponds to an infinite number of observations. It is possible to allow for the induced uncertainty by using the equation

$$\sigma_{corr} = \left(\frac{t_n}{t_\infty}\right)\sigma \qquad (A.54)$$

where σ_{corr} is the "corrected" standard deviation, t_n is the value of Student's t parameter at the 95% confidence level for the n degrees of freedom associated with the determination of σ, and t_∞ is the corresponding parameter for an infinite number of degrees of freedom. The value of n is given by the equation

$$n = N - m \qquad (A.55)$$

where N is the number of observations and m the number of constants connecting the "fixed" and observed variables. For example, for the standard deviation of an unweighted or a weighted mean (cases 1 and 2), m is 1. For two variables,

y and x connected by the equation

$$y = \alpha + \beta x \qquad (A.9)$$

the value of m is 2.

Case 5 ; The use of pooled variances

If the standard deviation, σ_y , of a quantity, y , is estimated by M different experiments, then provided that the statistical samples on which these estimates are based belong to a common population, the "best" value, $\bar{\sigma}_y$, of σ_y is given by

$$\bar{\sigma}_y = \sqrt{\frac{\sum_k n_k \sigma_k^2}{\sum_k n_k}} \qquad (A.56)$$

where σ_k is the "k" th estimate of σ_y , n_k is the number of degrees of freedom associated with the "k" th experiment, and $\sum_k$ denotes summation over all values of k from k = 1 to k = M. σ_k is the experimental value of σ_y, and is not corrected for the finite number of degrees of freedom associated with it. Instead, the pooled standard deviation, $\bar{\sigma}_y$, is corrected for the number of degrees of freedom using equation A.54, and taking

$$n = \sum_k n_k \qquad (A.57)$$

Case 5a ; The application of pooled variances to the ligand-dependences of pseudo-first-order rate constants at several

different temperatures, and the effect of this treatment on the activation parameters derived from this data

For a given reaction, it is possible to postulate that the percentage deviation, P , of the pseudo-first-order rate constants, k_{obsd} , is a constant which is temperature-independent. This is in fact the assumption which was made in calculating activation parameters from values of k_{obsd} at low ligand concentrations (case 3a). With this assumption, the values, P_k , of P found by the application of case 4a to the ligand-dependences of k_{obsd} at a variety of temperatures belong to a common population, and the pooled percentage deviation, $\overline{P}$, of k_{obsd} is given by

$$\overline{P} = \sqrt{\frac{\sum_k n_k P_k^2}{\sum_k n_k}} \qquad (A.58)$$

The total number of degrees of freedom associated with $\overline{P}$ is $\sum_k n_k$.

The effect of pooling the percentage deviations of k_{obsd} on the derived values of the activation parameters for the first- and second-order pathways for the base hydrolyses of trans-$[Rhen_2ClOH]^+$ and trans-$[Rhen_2Cl_2]^+$ is shown in Table A.1. For each reaction, the activation parameters, $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$, $\Delta H_2^{\ddagger}$, $\Delta S_2^{\ddagger}$, were determined in the following two ways :-

Method A

At each temperature, values of k_1 , k_2 , their standard deviations, σ_1 and σ_2 , and the percentage deviation, P, of k_{obsd} were calculated using the treatment of case 4a. After correction of σ_1 and σ_2 for the number of degrees of freedom associated with their estimation (equation A.54), k_1 and σ_1 and k_2 and σ_2 were separately used in the treatment of case 4b to give values of $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$, $\Delta S_2^{\ddagger}$, and the corresponding standard deviations.

Method B

Values of k_1 , k_2 and P were calculated at each temperature as in method A. For each reaction, the values of P found at the different temperatures were pooled according to the treatment of case 5a to give a value for $\bar{P}$. The values, $\bar{\sigma}_\alpha$ and $\bar{\sigma}_\beta$, of the standard deviations of k_1 and k_2 at each temperature were then calculated using equations A.59 and A.60, and the data points for the temperature in question.

$$\bar{\sigma}_\alpha = \frac{\bar{P}}{100}\sqrt{\frac{\sum_i w_i x_i^2}{\sum_i w_i \sum_i w_i x_i^2 - (\sum_i w_i x_i)^2}} \qquad \text{(A.59)}$$

$$\bar{\sigma}_\beta = \frac{\bar{P}}{100}\sqrt{\frac{\sum_i w_i}{\sum_i w_i \sum_i w_i x_i^2 - (\sum_i w_i x_i)^2}} \qquad \text{(A.60)}$$

Equations A.59 and A.60 correspond to equations A.47 and A.48, with the temperature-dependent parameter, P , replaced by the temperature-independent parameter, $\bar{P}$. The standard

deviations, $\bar{\sigma}_\alpha$ and $\bar{\sigma}_\beta$, were then corrected for the number of degrees of freedom using equation A.54 and taking

$$n = \sum_k n_k \qquad (A.57)$$

The values of k_1 and k_2 and their corrected standard deviations were then used separately in the treatment of case 4b to give estimates of $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$, $\Delta H_2^{\ddagger}$, $\Delta S_2^{\ddagger}$, and their respective standard deviations.

The results of both methods, given in Table A.1, show that although the two methods often give very similar values for the activation parameters, this is not always true. For the second-order reaction of <u>trans</u>-$[Rhen_2ClOH]^+$ with hydroxide, method A puts a good deal of weight on one point, whereas method B puts more nearly equal weighting on all points. Method B thus appears to be experimentally, as well as theoretically, more justifiable than method A. Method B was therefore used to determine all the activation parameters calculated in this thesis.

<u>General reference</u>

J. Mandel, "Statistical Analysis of Experimental Data", Wiley, New York, 1964

Table A.1

The effect of pooling variances on the activation parameters calculated for concurrent first- and second- order reactions

(a) trans-$[Rhen_2ClOH]^+ + OH^-$; first-order pathway (k_1)

Temperature (°C)	$10^5 k_1$ (s^{-1})	$10^{-3} w_i$ Method A	$10^{-3} w_i$ Method B
75.75	91.40	7.571	14.81
71.80	60.49	1.293	14.47
64.80	28.59	1.192	14.51
58.02	13.30	21.58	15.25
53.77	7.667	1.304	15.12
49.89	4.669	594.8	14.39
45.50	2.685	9.004	14.67
$\Delta H_1^{\ddagger}$ (kcal mol^{-1}) =		25.45 ± 0.19	25.14 ± 0.15
$\Delta S_1^{\ddagger}$ (e.u.) =		0.27 ± 0.58	-0.67 ± 0.46

(b) trans-$[Rhen_2ClOH]^+ + OH^-$; second-order pathway (k_2)

Temperature (°C)	$10^5 k_1$ ($M^{-1}s^{-1}$)	$10^{-1} w_i$ Method A	$10^{-1} w_i$ Method B
75.75	33.70	34.31	65.27
71.80	25.68	8.433	82.66
64.80	11.98	7.665	81.07
58.02	4.031	65.66	47.00
53.77	2.692	6.181	61.14
49.89	1.865	2870	73.42
45.50	0.9807	39.79	63.57
$\Delta H_1^{\ddagger}$ (kcal mol^{-1}) =		24.16 ± 0.89	25.84 ± 0.70
$\Delta S_1^{\ddagger}$ (e.u.) =		-5.56 ± 2.74	-0.49 ± 2.10

Continued.....

Table A.1 (continued)

(c) $trans\text{-}[Rhen_2Cl_2]^+ + OH^-$; first-order pathway (k_1)

Temperature (°C)	$10^6 k_1$ (s^{-1})	$10^{-3} w_1$ Method A	$10^{-3} w_1$ Method B
77.70	32.12	1.931	3.461
74.62	23.38	4.997	4.797
71.74	16.04	0.8260	3.209
67.95	11.43	1.165	3.345
64.86	7.047	1.532	3.399
64.33	7.696	1.162	3.455
62.21	5.330	2.201	3.462
$\Delta H_1^{\ddagger}$ (kcal mol^{-1}) =		26.37 ± 0.81	26.06 ± 0.63
$\Delta S_1^{\ddagger}$ (e.u.) =		-4.24 ± 2.37	-5.14 ± 1.84

(d) $trans\text{-}[Rhen_2Cl_2]^+ + OH^-$; second-order pathway (k_2)

Temperature (°C)	$10^6 k_1$ ($M^{-1}s^{-1}$)	$10^{-2} w_1$ Method A	$10^{-2} w_1$ Method B
77.70	40.31	6.156	10.90
74.62	25.70	13.18	8.828
71.74	16.83	2.110	7.896
67.95	9.843	2.198	6.089
64.86	5.595	2.531	5.638
64.33	5.165	1.501	4.246
62.21	3.853	3.103	4.805
$\Delta H_2^{\ddagger}$ (kcal mol^{-1}) =		35.01 ± 1.86	35.07 ± 1.42
$\Delta S_2^{\ddagger}$ (e.u.) =		20.81 ± 5.38	21.00 ± 4.14

APPENDIX B

Computer programmes used in Part I

PROGRAMME B1

Calculation of an unweighted mean

This programme corresponds to case 1 of appendix A.

```
*************************************************
*     WATFIV
*
*                                   C.P.J.VUIK
*
*     74/003
*************************************************

$JOBW    C.P.J.VUIK       30 310YNYNYYY
C PROGRAMME TO CALCULATE AN UNWEIGHTED MEAN VALUE
      DIMENSION X(700),D(700),D2(700),BR(700)
      CHARACTER*80 TITLE
      WRITE (6,3006)
 3006 FORMAT (1H1,2X,18HUNWEIGHTED AVERAGE //)
      READ(5,2100) M
 2100 FORMAT (I4)
      DO 21 J = 1,M
      READ (5,3004) TITLE
 3004 FORMAT (A80)
      WRITE (6,1025)
 1025 FORMAT (1H0,1X,120(1H*) //)
      WRITE (6,4001) TITLE
 4001 FORMAT (1H0,5X,A80 //)
      WRITE (6,1025)
      READ (5,2100) N
      SUMX = 0.0
      SUMD2 = 0.0
      DO 1 I = 1,N
      READ (5,1000) X(I)
 1000 FORMAT (E12.5)
      SUMX = SUMX + X(I)
    1 CONTINUE
      WRITE (6,1001)
 1001 FORMAT (1H0,2X,4HX(I))
      P = N
      XMEAN = SUMX/P
      DO 2 I = 1,N
      D(I) = X(I) - XMEAN
      D2(I) = D(I)*D(I)
      SUMD2 = SUMD2 + D2(I)
      WRITE (6,1002) X(I)
 1002 FORMAT (1H0,2X,G12.5)
    2 CONTINUE
      VXI = SUMD2/(P-1.0)
      EXI = SQRT(VXI)
      VXMEAN = VXI/P
      EXMEAN = SQRT(VXMEAN)
      PCENT = 100.0*EXMEAN/XMEAN
      PERK = 100.0*EXI/XMEAN
      WRITE (6,1003)XMEAN, EXMEAN, EXI
 1003 FORMAT (1H0,2X, 8HXMEAN = , E16.8/ 3X, 30HSTANDARD DEVIATION OF XM
     *EAN = , E16.8/ 3X, 29HSTANDARD DEVIATION OF X(I) = , E16.8)
      WRITE (6,1007) PCENT
 1007 FORMAT (1H0,2X,29HSIGMAXMEAN AS A PERCENTAGE = , G12.5)
      WRITE (6,1009) PERK
 1009 FORMAT (1H0,2X,7HPERK = , G12.5)
      WRITE (6,1008)
 1008 FORMAT (1H0,1H  //1X,120(1H*) //)
   21 CONTINUE
```

```
      STOP
      END
$DATA
```

PROGRAMME B2

Calculation of a weighted mean

This programme corresponds to case 2 of appendix A.

```
*****************************************************
*     WATFIV
*
*                                        C.P.J.VUIK
*
*     74/003
*****************************************************

$JOBW   C.P.J.VUIK       30 310YNYNYYY
C PROGRAMME TO CALCULATE WEIGHTED AVERAGES
      DIMENSION X(700),W(700),WX(700),SIG(700),SIG2(700)
      CHARACTER*80 TITLE
      READ (5,2100) M
 2100 FORMAT (I4)
      WRITE (6,1000)
 1000 FORMAT (1H1,2X,17HWEIGHTED AVERAGES //)
      DO 21 J = 1,M
      READ (5,1010) TITLE
 1010 FORMAT (A80)
      WRITE (6,1011) TITLE
 1011 FORMAT (1H0,2X,A80)
      READ (5,2100) N
      SUMW = 0.0
      SUMWX = 0.0
      WRITE (6,1004)
 1004 FORMAT (1H0,2X,4HX(I),18X,6HSIG(I),16X,4HW(I))
      DO 1 I = 1,N
      READ (5,1002) X(I), SIG(I)
 1002 FORMAT (2(E12.5))
      SIG2(I) = SIG(I)*SIG(I)
      W(I) = 1.0/SIG2(I)
      WX(I) = W(I)*X(I)
      SUMWX = SUMWX + WX(I)
      SUMW = SUMW + W(I)
    1 CONTINUE
      XMEAN = SUMWX/SUMW
      SIG2XM = 1.0/SUMW
      SIGXM = SQRT(SIG2XM)
      DO 2 I = 1,N
      WRITE (6,1003) X(I),SIG(I),W(I)
 1003 FORMAT (1H0,1X,3(G12.5,10X))
    2 CONTINUE
      WRITE (6,1005) XMEAN
 1005 FORMAT (1H0,2X,8HXMEAN = ,E16.8)
      WRITE (6,1012) SIGXM
 1012 FORMAT (1H0,2X,30HSTANDARD DEVIATION IN XMEAN = , G12.5)
      WRITE (6,1013)
 1013 FORMAT (1H0,1X,1H  //1X,120(1H*) ///)
   21 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B3

Calculation of pooled variances

This programme corresponds to case 5 of appendix A.

```
*************************************************************
*     WATFIV
*
*                                          C.P.J.VUIK
*
*     74/003
*************************************************************

$JOBW   C.P.J.VUIK       30 310YNYNYYY
C PROGRAMME FOR POOLED VARIANCES
      DIMENSION SIG(500),NDF(500),VARN(500),P(500)
      CHARACTER*80 TITLE
      READ (5,2100) M
 2100 FORMAT (I4)
      WRITE (6,3000)
 3000 FORMAT (1H1,2X,16HPOOLED VARIENCES //)
      DO 21 J = 1,M
      SUMNDF = 0.0
      SUMVAR = 0.0
      READ (5,5000) TITLE
 5000 FORMAT (A80)
      WRITE (6,6002)
 6002 FORMAT (1H0,1X,120(1H*) //)
      WRITE (6,6001) TITLE
 6001 FORMAT (1H0,5X,A80 //)
      WRITE (6,6002)
      WRITE (6,1003)
 1003 FORMAT (1H0,2X,6HSIG(I),20X,5HDF(I))
      READ (5,2100) N
      DO 1 I = 1,N
      READ (5,1000) SIG(I), NDF(I)
 1000 FORMAT (E12.5, I4)
      P(I) = NDF(I)
      VARN(I) = SIG(I)*SIG(I)*P(I)
      SUMNDF = SUMNDF + P(I)
      SUMVAR = SUMVAR + VARN(I)
      WRITE (6,1004) SIG(I), NDF(I)
 1004 FORMAT (1H0,1X,G16.8,10X,I4)
    1 CONTINUE
      POOLVA = SUMVAR/SUMNDF
      POLSIG = SQRT(POOLVA)
      WRITE (6,1001) POLSIG
 1001 FORMAT (1H0,2X,28HPOOLED STANDARD DEVIATION = , G16.8)
      WRITE (6,1002) SUMNDF
 1002 FORMAT (1H0,2X,37HTOTAL NUMBER OF DEGREES OF FREEDOM = , G16.8)
      WRITE (6,6000)
 6000 FORMAT (1H0,1X,1H //1X,120(1H*) ///)
   21 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B4

Unweighted least squares analysis for the equation

$$y = \alpha + \beta x$$

This programme corresponds to case 3 of appendix A.

```
*************************************************
*     WATFIV
*
*                                        C.P.J.VUIK
*
*     74/003
*************************************************

$JOBW   C.P.J.VUIK       30 310YNYNYYY
C UNWEIGHTED LEAST SQUARES FOR Y = ALPHA + BETA*X
      DIMENSION OBSDK(100), TEMP(100), ABSTEM(100),C(100),Y(100),X(100),
     6X2(100),XY(100), D(100),D2(100), F(100), G(100), F2(100), G2(100),
     6YCALC(100)
      CHARACTER*80 TITLE
      READ (5,2100) M
 2100 FORMAT (I4)
      DO 21 J = 1,M
      READ (5,4000) TITLE
 4000 FORMAT (A80)
      WRITE (6,1024)
 1024 FORMAT (1H1,1X,120(1H*) //)
      WRITE (6,4001) TITLE
 4001 FORMAT (1H0,5X,A80 //)
      WRITE (6,1025)
 1025 FORMAT (1H0,1X,120(1H*) //)
      READ (5,1000) N
 1000 FORMAT (I4)
      I = 0
      SUMX = 0.0
      SUMY = 0.0
      SUMX2 = 0.0
      SUMXY = 0.0
      SUMD2 = 0.0
      SUMF2 = 0.0
      SUMG2  = 0.0
      DO 1 I = 1,N
      READ (5,1002) Y(I),X(I)
 1002 FORMAT (2(E12.5))
      X2(I) = X(I)*X(I)
      XY(I) = X(I)*Y(I)
      SUMX = SUMX + X(I)
      SUMY = SUMY + Y(I)
      SUMX2 = SUMX2 + X2(I)
      SUMXY = SUMXY + XY(I)
    1 CONTINUE
      P = N
      Q = P*SUMX2 - SUMX*SUMX
      ALPHA = (SUMX2*SUMY - SUMXY*SUMX)/Q
      BETA = (P*SUMXY - SUMY*SUMX)/Q
      DO 2 I = 1,N
      YCALC(I) = ALPHA + BETA*X(I)
      D(I) = Y(I)- YCALC(I)
      D2(I) = D(I)*D(I)
      F(I) = SUMX2 -X(I)*SUMX
      G(I) = P*X(I) - SUMX
      F2(I) = F(I)*F(I)
      G2(I) = G(I)*G(I)
      SUMD2 = SUMD2 + D2(I)
      SUMF2 = SUMF2 + F2(I)
```

```
      SUMG2 = SUMG2 + G2(I)
    2 CONTINUE
      DK2 = SUMD2/(P-2.0)
      DK = SQRT(DK2)
      DKPCT = 100.0*DK
      VALPHA = SUMF2*DK2/(D*D)
      EALPHA = SQRT(VALPHA)
      VBETA = SUMG2*DK2/(D*D)
      EBETA = SQRT(VBETA)
      WRITE (6,1003)
 1003 FORMAT (1H0,5X,4HX(I),16X,4HY(I),16X,8HYCALC(I))
      DO 3 I = 1,N
      WRITE (6,1006) X(I),Y(I),YCALC(I)
 1006 FORMAT (1H0,5X,3(G12.5,8X))
    3 CONTINUE
      WRITE (6,1004) ALPHA
 1004 FORMAT (1H0,5X,12HINTERCEPT = ,G12.5)
      WRITE (6,1009) EALPHA
 1009 FORMAT (1H0,5X,34HSTANDARD DEVIATION IN INTERCEPT = ,G12.5)
      WRITE (6,1005) BETA
 1005 FORMAT (1H0,5X,8HSLOPE = ,G12.5)
      WRITE (6,1011) EBETA
 1011 FORMAT (1H0,5X,30HSTANDARD DEVIATION IN SLOPE = ,G12.5)
      WRITE (6,1019) DKPCT
 1019 FORMAT (1H0,5X,26HSTANDARD DEVIATION IN Y = ,G12.5,2H %)
      WRITE (6,1012) N
 1012 FORMAT (1H0,5X,19HNUMBER OF POINTS = ,I4)
   21 CONTINUE
      WRITE (6,1023)
 1023 FORMAT (1H0,1X,1H  //1X,120(1H*) /////)
      STOP
      END

$DATA
```

PROGRAMME B5

Weighted least squares analysis for the equation

$$y = \alpha + \beta x$$

This programme corresponds to case 4a of appendix A.

```
*************************************************************
*     WATFIV
*
*                                          C.P.J.VUIK
*
*     74/003
*************************************************************

$JOBW    C.P.J.VUIK       30 310YNYNYYY
C WEIGHTED LEAST SQUARES PROGRAMME FOR Y = ALPHA + BETA (X)
      DIMENSION X(100),Y(100),W(100),WX(100),WX2(100),F(100),A(100),
     6G(100),B(100),AY(100),BY(100),D(100),DY2(100),DEVY(100),FY2(100),
     6GY2(100),YCALC(100)
      CHARACTER*80 TITLE
      READ (5, 2100) M
 2100 FORMAT(I4)
      WRITE (6,3001)
 3001 FORMAT (1H1,2X,45HWEIGHTED LEAST SQUARES FOR Y = ALPHA + BETA*X)
      DO 21 J = 1,M
      READ (5,4000) TITLE
 4000 FORMAT (A80)
      WRITE (6,4001) TITLE
 4001 FORMAT (1H0,2X,A80)
      READ (5,1000) N, TEMP
 1000 FORMAT (I4, F6.2)
      I = 0
      SUMW = 0.0
      SUMWX = 0.0
      SUMWX2 = 0.0
      SUMAY = 0.0
      SUMBY = 0.0
      SUMDY2 = 0.0
      SUMFY2 = 0.0
      SUMGY2 = 0.0
      DO 1 I = 1,N
      READ (5,1001) X(I), Y(I)
 1001 FORMAT (2(G12.5))
      W(I) = 1.0/(Y(I)*Y(I))
      WX(I) = W(I)*X(I)
      WX2(I) = W(I)*X(I)*X(I)
      SUMW = SUMW + W(I)
      SUMWX = SUMWX + WX(I)
      SUMWX2 = SUMWX2 + WX2(I)
    1 CONTINUE
      D = SUMW*SUMWX2 - SUMWX*SUMWX
      DO 2 I = 1,N
      F(I) = SUMWX2 - X(I)*SUMWX
      A(I) = F(I)*W(I)
      G(I) = X(I)*SUMW - SUMWX
      B(I) = G(I)*W(I)
      AY(I) = A(I)*Y(I)
      BY(I) = B(I)*Y(I)
      SUMAY = SUMAY + AY(I)
      SUMBY = SUMBY + BY(I)
    2 CONTINUE
      ALPHA = SUMAY/D
      BETA = SUMBY/D
      DO 3 I = 1,N
      YCALC(I) = ALPHA + BETA*X(I)
```

```
      D(I) = Y(I) - YCALC(I)
      DEVY(I) = D(I)/Y(I)
      DY2(I) = D(I)*D(I)/(Y(I)*Y(I))
      SUMDY2 = SUMDY2 + DY2(I)
    3 CONTINUE
      DENOM = N - 2
      OK2 = SUMDY2/DENOM
      OK = SQRT(OK2)
      DO 4 I = 1,N
      FY2(I) = F(I)*F(I)/(Y(I)*Y(I))
      GY2(I) = G(I)*G(I)/(Y(I)*Y(I))
      SUMFY2 = SUMFY2 + FY2(I)
      SUMGY2 = SUMGY2 + GY2(I)
    4 CONTINUE
      VALPHA = OK2*SUMFY2/(Q*Q)
      EALPHA = SQRT(VALPHA)
      VBETA = OK2*SUMGY2/(Q*Q)
      EBETA = SQRT(VBETA)
      WRITE (6,1002)
 1002 FORMAT (1HO,4X, 4HX(I), 18X, 4HY(I), 18X, 4HW(I), 18X, 8HYCALC(I),
     614X,' 7HDEVY(I))
      DO 5 I = 1,N
      WRITE (6,1003) X(I), Y(I), W(I), YCALC(I), DEVY(I)
 1003 FORMAT (5X, 5(1PE12.5,10X))
    5 CONTINUE
      WRITE (6,1004) ALPHA
 1004 FORMAT (1H0, 1X, 12HINTERCEPT = , G 16.8)
      WRITE (6,1009) EALPHA
 1009 FORMAT (1H0,1X, 34HSTANDARD DEVIATION IN INTERCEPT = , G16.8)
      WRITE (6,1005) BETA
 1005 FORMAT (1H0, 1X, 8HSLOPE = , G16.8)
      WRITE (6,1011) EBETA
 1011 FORMAT (1H0, 1X, 30HSTANDARD DEVIATION IN SLOPE = , G16.8)
      WRITE (6,1007) OK
 1007 FORMAT (1H0, 1X, 24HPERCENTAGE ERROR IN Y = , G16.8)
      WRITE (6,1012) N
 1012 FORMAT (1H0, 1X, 19HNUMBER OF POINTS = , I4)
      WRITE (6,1014) TEMP
 1014 FORMAT (1H0, 1X, 14HTEMPERATURE = , F6.2, 3H OC)
      WRITE (6,3002)
 3002 FORMAT (1H0,1X,1H  // 1X,120(1H*) ///)
   21 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B6

Weighted least squares analysis for the equation

$$y = \alpha + \beta x$$

using a pooled estimate of variance

This programme corresponds to case 5a of appendix A.

```
*****************************************************
*     WATFIV
*
*                                        C.P.J.VUIK
*
*     74/003
*****************************************************

$JOBW   C.P.J.VUIK       30 310YNYNYYY
C WEIGHTED LEAST SQUARES PROGRAMME FOR Y = ALPHA + BETA (X)
C USING POOLED ESTIMATE OF VARIENCE
      REAL*8    X(100),Y(100),W(100),WX(100),WX2(100),F(100),A(100),
     6G(100),B(100),AY(100),BY(100),D(100),DY2(100),DEVY(100),FY2(100),
     6GY2(100),YCALC(100)
      CHARACTER*80 TITLE
      READ (5, 2100) M
 2100 FORMAT(I4)
      WRITE (6,3001)
 3001 FORMAT (1H1,2X,17HLIGAND DEPENDENCE //)
      DO 21 J = 1,M
      READ (5,4000) TITLE
 4000 FORMAT (A80)
      WRITE (6,4001) TITLE
 4001 FORMAT (1H0,2X,A80)
      READ (5,1000) N, TEMP
 1000 FORMAT (I4, F6.2)
      READ (5,3000) DK
 3000 FORMAT (E12.5)
      DK2 = DK*DK
      I = 0
      SUMW = 0.0
      SUMWX = 0.0
      SUMWX2 = 0.0
      SUMAY = 0.0
      SUMBY = 0.0
      SUMDY2 = 0.0
      SUMFY2 = 0.0
      SUMGY2 = 0.0
      DO 1 I = 1,N
      READ (5,1001) X(I), Y(I)
 1001 FORMAT (2(G12.5))
      W(I) = 1.0/(Y(I)*Y(I))
      WX(I) = W(I)*X(I)
      WX2(I) = W(I)*X(I)*X(I)
      SUMW = SUMW + W(I)
      SUMWX = SUMWX + WX(I)
      SUMWX2 = SUMWX2 + WX2(I)
    1 CONTINUE
      D = SUMW*SUMWX2 - SUMWX*SUMWX
      DO 2 I = 1,N
      F(I) = SUMWX2 - X(I)*SUMWX
      A(I) = F(I)*W(I)
      G(I) = X(I)*SUMW - SUMWX
      B(I) = G(I)*W(I)
      AY(I) = A(I)*Y(I)
      BY(I) = B(I)*Y(I)
      SUMAY = SUMAY + AY(I)
      SUMBY = SUMBY + BY(I)
    2 CONTINUE
```

```
      ALPHA = SUMAY/Q
      BETA = SUMBY/Q
      DO 3 I = 1,N
      YCALC(I) = ALPHA + BETA*X(I)
      D(I) = Y(I) - YCALC(I)
      DEVY(I) = D(I)/Y(I)
      DY2(I) = D(I)*D(I)/(Y(I)*Y(I))
      SUMDY2 = SUMDY2 + DY2(I)
    3 CONTINUE
      DENOM = N - 2
      DO 4 I = 1,N
      FY2(I) = F(I)*F(I)/(Y(I)*Y(I))
      GY2(I) = G(I)*G(I)/(Y(I)*Y(I))
      SUMFY2 = SUMFY2 + FY2(I)
      SUMGY2 = SUMGY2 + GY2(I)
    4 CONTINUE
      VALPHA = OK2*SUMFY2/(Q*Q)
      EALPHA = SQRT(VALPHA)
      VBETA = OK2*SUMGY2/(Q*Q)
      EBETA = SQRT(VBETA)
      WRITE (6,1002)
 1002 FORMAT (1H0,4X, 4HX(I), 18X, 4HY(I), 18X, 4HW(I), 18X, 8HYCALC(I),
     614X, 7HDEVY(I))
      DO 5 I = 1,N
      WRITE (6,1003) X(I), Y(I), W(I), YCALC(I), DEVY(I)
 1003 FORMAT (5X, 5(1PE12.5,10X))
    5 CONTINUE
      WRITE (6,1004) ALPHA
 1004 FORMAT (1H0, 1X, 12HINTERCEPT = , G 16.8)
      WRITE (6,1009) EALPHA
 1009 FORMAT (1H0,1X, 34HSTANDARD DEVIATION IN INTERCEPT = , G16.8)
      WRITE (6,1005) BETA
 1005 FORMAT (1H0, 1X, 8HSLOPE = , G16.8)
      WRITE (6,1011) EBETA
 1011 FORMAT (1H0, 1X, 30HSTANDARD DEVIATION IN SLOPE = , G16.8)
      WRITE (6,1007) OK
 1007 FORMAT (1H0, 1X, 24HPERCENTAGE ERROR IN Y = , G16.8)
      WRITE (6,1012) N
 1012 FORMAT (1H0, 1X, 19HNUMBER OF POINTS = , I4)
      WRITE (6,1014) TEMP
 1014 FORMAT (1H0, 1X, 14HTEMPERATURE = , F6.2, 3H OC)
      WRITE (6,3002)
 3002 FORMAT (1H0,1X,1H  // 1X,120(1H*) ///)
   21 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B7

Unweighted least squares analysis for the temperature-dependence of a rate constant according to the Eyring equation

This programme corresponds to case 3a of appendix A.

```
*****************************************
*     WATFIV
*
*                                   C.P.J.VUIK
*
*     74/003
*****************************************************************

$JOBW   C.P.J.VUIK       30 310YNYNYYY
C UNWEIGHTED LEAST SQUARES ANALYSIS FOR LOG10(KOBSD/T) AGAINST (1/T)
      DIMENSION OBSDK(100), TEMP(100), ABSTEM(100),C(100),Y(100),X(100),
     6X2(100),XY(100), D(100),D2(100), F(100), G(100), F2(100), G2(100),
     6YCALC(100)
      CHARACTER*80 TITLE
      READ (5,1001) BOLCON, PLACON, R
 1001 FORMAT (3(E16.8))
      READ (5,2100) M
 2100 FORMAT (I4)
      WRITE (6,4002)
 4002 FORMAT (1H1,2X,22HUNWEIGHTED EYRING PLOT //)
      DO 21 J = 1,M
      READ (5,4000) TITLE
 4000 FORMAT (A80)
      WRITE (6,4001) TITLE
 4001 FORMAT (1H0,2X,A80)
      READ (5,1000) N
 1000 FORMAT (I4)
      I = 0
      SUMX = 0.0
      SUMY = 0.0
      SUMX2 = 0.0
      SUMXY = 0.0
      SUMD2 = 0.0
      SUMF2 = 0.0
      SUMG2  = 0.0
      DO 1 I = 1,N
      READ (5,1002) OBSDK(I), TEMP(I)
 1002 FORMAT (2(E12.5))
      ABSTEM(I) = TEMP(I) + 273.16
      C(I) = OBSDK(I)/ABSTEM(I)
      Y(I) = ALOG10(C(I))
      X(I) = 1.0/ABSTEM(I)
      X2(I) = X(I)*X(I)
      XY(I) = X(I)*Y(I)
      SUMX = SUMX + X(I)
      SUMY = SUMY + Y(I)
      SUMX2 = SUMX2 + X2(I)
      SUMXY = SUMXY + XY(I)
    1 CONTINUE
      P = N
      Q = P*SUMX2 - SUMX*SUMX
      ALPHA = (SUMX2*SUMY - SUMXY*SUMX)/Q
      BETA = (P*SUMXY - SUMY*SUMX)/Q
      DO 2 I = 1,N
      YCALC(I) = ALPHA + BETA*X(I)
      D(I) = Y(I)- YCALC(I)
      D2(I) = D(I)*D(I)
      F(I) = SUMX2 -X(I)*SUMX
      G(I) = P*X(I) - SUMX
```

```
      F2(I) = F(I)*F(I)
      G2(I) = G(I)*G(I)
      SUMD2 = SUMD2 + D2(I)
      SUMF2 = SUMF2 + F2(I)
      SUMG2 = SUMG2 + G2(I)
    2 CONTINUE
      OK2 = SUMD2/(P-2.0)
      OK = SQRT(OK2)
      VALPHA = SUMF2*OK2/(0*0)
      EALPHA = SQRT(VALPHA)
      VBETA = SUMG2*OK2/(0*0)
      EBETA = SQRT(VBETA)
      E = BOLCON/PLACON
      Z = ALOG10(E)
      DELH = -(BETA*R*2.3026)
      DELS = R*2.3026*(ALPHA - Z)
      EDELH = EBETA*R*2.3026
      EDELS = EALPHA*R*2.3026
      WRITE (6,1003)
 1003 FORMAT (1H0,5X,8HOBSDK(I), 14X, 7HTEMP(I),15X, 4HX(I),18X, 4HY(I),
     618X, 8HYCALC(I), 14X, 4HD(I))
      DO 3 I = 1,N
      WRITE (6,1006) OBSDK(I), TEMP(I), X(I), Y(I), YCALC(I), D(I)
 1006 FORMAT (5X, 5(1PE12.5, 10X),1PE12.5)
    3 CONTINUE
      WRITE (6,1016) DELH
 1016 FORMAT (1H0, 1X, 25HENTHALPY OF ACTIVATION = , G16.8)
      WRITE (6,1020) EDELH
 1020 FORMAT (1H0,1X,47HSTANDARD DEVIATION IN ENTHALPY OF ACTIVATION = ,
     6G16.8)
      WRITE (6,1021) DELS
 1021 FORMAT (1H0,1X, 24HENTROPY OF ACTIVATION = , G16.8)
      WRITE (6,1022) EDELS
 1022 FORMAT (1H0,1X, 46HSTANDARD DEVIATION OF ENTROPY OF ACTIVATION = ,
     6G16.8)
      WRITE (6,1019) OK
 1019 FORMAT (1H0, 1X, 26HSTANDARD DEVIATION IN Y = , G16.8)
      WRITE (6,1012) N
 1012 FORMAT (1H0,1X, 19HNUMBER OF POINTS = , I4)
      WRITE (6,4003)
 4003 FORMAT (1H0,2X, 23HEND OF THIS SET OF DATA ////)
   21 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B8

Weighted least squares analysis for the temperature-dependence of a rate constant according to the Eyring equation

This programme corresponds to case 4b of appendix A

```
*************************************************
*     WATFIV
*
*                                   C.P.J.VUIK
*
*     74/003
*************************************************

$JOBW   C.P.J.VUIK       30 310YNYNYYY
C WEIGHTED LEAST SQUARES PROGRAMME FOR LOG10(K/T) VERSUS (1/T)
C ASSUMES UNEQUAL WEIGHTING OF THE POINTS
C SIGK IS CORRECTED FOR THE NUMBER OF DEGREES OF FREEDOM
      DOUBLE PRECISION DLOG10
      REAL*8
     *          OBSDK(100), TEMP(100), SIGK(100), ABSTEM(100), C(100),
     *Y(100), X(100), D(100), SIGY(100), W(100), WX(100), WX2(100),
     *F(100), A(100), G(100), B(100), AY(100), BY(100), F2W(100),
     *G2W(100), YCALC(100)
      REAL*8            SUMW,SUMWX,SUMWX2,SUMAY,SUMBY,SUMF2W,SUMG2W
      CHARACTER*80 TITLE
      READ (5,1001) BOLCON, PLACON, R
 1001 FORMAT (3(E16.8))
      READ (5, 2100) M
 2100 FORMAT (I4)
      DO 21 J = 1,M
      READ (5,4000) TITLE
 4000 FORMAT (A80)
      WRITE (6,8000)
 8000 FORMAT (1H1,2X,60(2H* ) //)
      WRITE (6,4001) TITLE
 4001 FORMAT (1H0,2X,A80 //)
      WRITE (6,8001)
 8001 FORMAT (1H0,2X,60(2H* ) //)
      READ (5,2100) N
      I = 0
      SUMW = 0.0
      SUMWX = 0.0
      SUMWX2 = 0.0
      SUMAY = 0.0
      SUMBY = 0.0
      SUMF2W = 0.0
      SUMG2W = 0.0
      DO 1 I = 1,N
      READ (5,1002) OBSDK(I), TEMP(I), SIGK(I)
 1002 FORMAT (3(E12.5))
      ABSTEM(I) = TEMP(I) + 273.16
      C(I) = OBSDK(I)/ABSTEM(I)
      Y(I) = DLOG10(C(I))
      X(I) = 1.0/ABSTEM(I)
      D(I) = 1.0 + SIGK(I)/OBSDK(I)
      SIGY(I) = DLOG10(D(I))
      W(I) = 1.0/(SIGY(I)*SIGY(I))
      WX(I) = W(I)*X(I)
      WX2(I) = W(I)*X(I)*X(I)
      SUMW = SUMW + W(I)
      SUMWX = SUMWX + WX(I)
      SUMWX2 = SUMWX2 + WX2(I)
    1 CONTINUE
      Q = SUMW*SUMWX2 - SUMWX*SUMWX
```

```
      DO 2 I = 1,N
      F(I) = SUMWX2 - X(I)*SUMWX
      A(I) = F(I)*W(I)
      G(I) = X(I)*SUMW - SUMWX
      B(I) = G(I)*W(I)
      AY(I) = A(I)*Y(I)
      BY(I) = B(I)*Y(I)
      SUMAY = SUMAY + AY(I)
      SUMBY = SUMBY + BY(I)
      F2W(I) = F(I)*F(I)*W(I)
      G2W(I) = G(I)*G(I)*W(I)
      SUMF2W = SUMF2W + F2W(I)
      SUMG2W = SUMG2W + G2W(I)
    2 CONTINUE
      ALPHA = SUMAY/Q
      BETA = SUMBY/Q
      VALPHA = SUMF2W/(Q*Q)
      VBETA = SUMG2W/(Q*Q)
      EALPHA = SQRT(VALPHA)
      EBETA = SQRT(VBETA)
      E = BOLCON/PLACON
      Z = ALOG10(E)
      DELH = -(BETA*R*2.3026)
      DELS = R*2.3026*(ALPHA - Z)
      EDELH = EBETA*R*2.3026
      EDELS = EALPHA*R*2.3026
      WRITE (6,1003)
 1003 FORMAT (1H0, 5X, 8HOBSDK(I), 19X, 7HTEMP(I), 20X, 7HSIGK(I))
      DO 3 I = 1,N
      WRITE (6,1006) OBSDK(I), TEMP(I), SIGK(I)
 1006 FORMAT (5X, 3(1PE12.5, 15X))
    3 CONTINUE
      WRITE (6, 1007)
 1007 FORMAT (1H0, 5X, 4HX(I), 18X, 4HY(I), 18X, 7HSIGY(I), 15X,4HW(I),
     *18X,8HYCALC(I))
      DO 4 I = 1,N
      YCALC(I) = ALPHA + BETA*X(I)
      WRITE (6,1024) X(I), Y(I), SIGY(I), W(I), YCALC(I)
 1024 FORMAT (5X, 5(1PE12.5, 10X))
    4 CONTINUE
      WRITE (6,1016) DELH
 1016 FORMAT (1H0, 1X, 25HENTHALPY OF ACTIVATION = ,G16.8)
      WRITE (6,1020) EDELH
 1020 FORMAT (1H0,1X,47HSTANDARD DEVIATION OF ENTHALPY OF ACTIVATION = ,
     *G16.8)
      WRITE (6,1021) DELS
 1021 FORMAT (1H0, 1X, 24HENTROPY OF ACTIVATION = ,G16.8)
      WRITE (6,1022) EDELS
 1022 FORMAT (1H0,1X, 46HSTANDARD DEVIATION OF ENTROPY OF ACTIVATION = ,
     *G16.8)
      WRITE (6,1012) N
 1012 FORMAT (1H0, 1X, 19HNUMBER OF POINTS = , I4)
      WRITE (6,8002)
 8002 FORMAT (1H0,1H  ///1X,120(1H*) /////)
   21 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B9

Weighted least squares analysis for the variation of an equilibrium constant with temperature according to the equation

$$\ln K = -\Delta H/RT + \Delta S/R$$

This programme is an adaptation of case 4 of appendix A, and although it was not used for the results found in this study, it is given here for the sake of completeness.

```
*************************************************
*     WATFIV
*
*                                   C.P.J.VUIK
*
*     74/003
*************************************************

$JOBW   C.P.J.VUIK       30 310YNYNYYY
C PROGRAMME TO CALCULATE ENTHALPIES & ENTROPIES FROM
C  THE VARIATION OF EQUILIUM CONSTANTS WITH TEMPERATURE
C ASSUMES UNEQUAL WEIGHTING OF THE POINTS
      DOUBLE PRECISION DLOG10
      REAL*8
     *Y(100), X(100), D(100), SIGY(100), W(100), WX(100), WX2(100),
     *F(100), A(100), G(100), B(100), AY(100), BY(100), F2W(100),
     *G2W(100),YCALC(100),EK(100),TEMP(100),SIGK(100),ABSTEM(100)
      REAL*8          SUMW,SUMWX,SUMWX2,SUMAY,SUMBY,SUMF2W,SUMG2W
      CHARACTER*80 TITLE
      READ (5, 2100) M
 2100 FORMAT (I4)
      DO 21 J = 1,M
      READ (5,4002) TITLE
 4002 FORMAT (A80)
      WRITE (6,4001) TITLE
 4001 FORMAT (1H1,2X,A80)
      READ (5,2100) N
      I = 0
      SUMW = 0.0
      SUMWX = 0.0
      SUMWX2 = 0.0
      SUMAY = 0.0
      SUMBY = 0.0
      SUMF2W = 0.0
      SUMG2W = 0.0
      DO 1 I = 1,N
      READ (5,1002) EK(I),TEMP(I),SIGK(I)
 1002 FORMAT (3(E12.5))
      ABSTEM(I) = TEMP(I) + 273.16
      Y(I) = DLOG10(EK(I))
      X(I) = 1.0/ABSTEM(I)
      D(I) = 1.0 + SIGK(I)/EK(I)
      SIGY(I) = DLOG10(D(I))
      W(I) = 1.0/(SIGY(I)*SIGY(I))
      WX(I) = W(I)*X(I)
      WX2(I) = W(I)*X(I)*X(I)
      SUMW = SUMW + W(I)
      SUMWX = SUMWX + WX(I)
      SUMWX2 = SUMWX2 + WX2(I)
    1 CONTINUE
      Q = SUMW*SUMWX2 - SUMWX*SUMWX
      DO 2 I = 1,N
      F(I) = SUMWX2 - X(I)*SUMWX
      A(I) = F(I)*W(I)
      G(I) = X(I)*SUMW - SUMWX
      B(I) = G(I)*W(I)
      AY(I) = A(I)*Y(I)
      BY(I) = B(I)*Y(I)
      SUMAY = SUMAY + AY(I)
```

```
      SUMBY = SUMBY + BY(I)
      F2W(I) = F(I)*F(I)*W(I)
      G2W(I) = G(I)*G(I)*W(I)
      SUMF2W = SUMF2W + F2W(I)
      SUMG2W = SUMG2W + G2W(I)
    2 CONTINUE
      ALPHA = SUMAY/Q
      BETA = SUMBY/Q
      VALPHA = SUMF2W/(Q*Q)
      VBETA = SUMG2W/(Q*Q)
      EALPHA = SQRT(VALPHA)
      EBETA = SQRT(VBETA)
      R = 1.987
      DELH = -(BETA*R*2.3026)
      DELS = R*2.3026*ALPHA
      EDELH = EBETA*R*2.3026
      EDELS = EALPHA*R*2.3026
      WRITE (6,1003)
 1003 FORMAT (1H0,5X,5HEK(I),22X,7HTEMP(I),20X,7HSIGK(I))
      DO 3 I = 1,N
      WRITE (6,1006) EK(I), TEMP(I), SIGK(I)
 1006 FORMAT (5X, 3(1PE12.5, 15X))
    3 CONTINUE
      WRITE (6, 1007)
 1007 FORMAT (1H0,5X,4HX(I),18X,4HY(I),18X,8HYCALC(I),14X,7HSIGY(I),
     * 15X,4HW(I))
      DO 4 I = 1,N
      YCALC(I) = ALPHA + BETA*X(I)
      WRITE (6,1024) X(I),Y(I),YCALC(I),SIGY(I),W(I)
 1024 FORMAT (5X, 5(1PE12.5, 10X))
    4 CONTINUE
      WRITE (6,1016) DELH
 1016 FORMAT (1H0,1X,11HENTHALPY = , G16.8)
      WRITE (6,1020) EDELH
 1020 FORMAT (1H0,1X,33HSTANDARD DEVIATION IN ENTHALPY = , G16.8)
       WRITE (6,1021) DELS
 1021 FORMAT (1H0,1X,10HENTROPY = , G16.8)
      WRITE (6,1022) EDELS
 1022 FORMAT (1H0,1X, 32HSTANDARD DEVIATION IN ENTROPY = , G16.8)
      WRITE (6,1012) N
 1012 FORMAT (1H0, 1X, 19HNUMBER OF POINTS = , I4)
      WRITE (6, 4000)
 4000 FORMAT (1H0,1X,1H  //1X,120(1H*) ///)
   21 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B10

Calculation of the spectra of rhodium(III) complexes

This programme uses the measured absorbance values at a variety of wavelengths of a solution of known concentration to calculate the spectrum of the complex in terms of its extinction coefficients.

```
*************************************************
*     WATFIV
*
*                                        C.P.J.VUIK
*
*     74/003
*************************************************

$JOBW   C.P.J.VUIK       30 310YNYNYYY
C PROGRAMME FOR SPECTRA OF RH(III) COMPLEXES
      DIMENSION L(500), A(500), BL(500), ACOR(500), ET(500)
      READ(5,2100) M
 2100 FORMAT (I4)
      WRITE (6,1010)
 1010 FORMAT (1H1,2X,29HSPECTRUM OF RH(III) COMPLEXES //)
      DO 21 J = 1,M
      WRITE (6,1004)
 1004 FORMAT (1H0,2X,9HLAMBDA(I),11X,5HET(I))
      READ (5,1000) N
 1000 FORMAT (I4)
      READ (5,1001) CT
 1001 FORMAT (E12.5)
      DO 1I = 1,N
      READ (5,1002) L(I), A(I), BL(I)
 1002 FORMAT (I4, 2(F6.4))
      ACOR(I) = A(I) - BL(I)
      ET(I) = ACOR(I)/CT
      WRITE (6,1005) L(I), ET(I)
 1005 FORMAT (1H0, 1X, I4, 16X,G16.8)
    1 CONTINUE
      WRITE (6,1011)
 1011 FORMAT (1H0,2X, 23HEND OF THIS SET OF DATA ///)
   21 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B11

Calculation of the fraction of cis-products of a reaction using a mixture which has been separated into its components by ion-exchange

For this programme the total concentration of rhodium(III) species is known, as is the spectrum of one of the isomeric products. (In this case the spectrum of the trans-isomer is known). The absorbances at reference wavelengths of the trans- and cis-fractions are used to calculate the mole fraction of cis-products and the extinction coefficients of the cis-isomer at the reference wavelengths. The particular programme appended is for a mixture of cis- and trans-$[Rhen_2Cl_2]^+$.

```
*************************************************
*     WATFIV
*
*                                   C.P.J.VUIK
*
*     74/003
*************************************************

$JOBW   C.P.J.VUIK      30,310YNYNYYY
C STEREOCHEMICAL CHANGE PROGRAMME
C CALCULATION OF FRACTION OF CIS PRODUCTS & OF ECIS
C USING SEPARATED CIS & TRANS SOLUTIONS
C TRANS RHEN2CL2 + OH   ION EXCHANGE ANALYSIS OF PRODUCT
      DIMENSION AT(500),LT(500),VT(500),AC(500),LC(500),VC(500),
     *ACORT(500),CT(500),TMOLE(500),ACORC(500),EQUIVA(500),CC(500),
     *CMOLE(500),NFRACT(500),CAB(500)
      STMOLE = 0.0
      READ (5,1000) TOTMOL
 1000 FORMAT (E12.5)
      READ (5,1001) NT
 1001 FORMAT (I4)
      READ (5,1002) BLT205,BLT241,BLT250,BLT290
 1002 FORMAT (4(F6.4))
      READ (5,1003) ET205,ET241,ET250,ET290
 1003 FORMAT (4(E12.5))
      DO 1 I = 1,NT
      READ (5,1004)NFRACT(I),AT(I),LT(I),VT(I)
 1004 FORMAT (I4, F6.4, I4, E12.5)
      IF (LT(I).EQ.205) BLT = BLT205
      IF (LT(I).EQ.205) ET = ET205
      IF (LT(I).EQ.241) BLT = BLT241
      IF (LT(I).EQ.241) ET = ET241
      IF (LT(I).EQ.250) BLT = BLT250
      IF (LT(I).EQ.250) ET = ET250
      IF (LT(I).EQ.290) BLT = BLT290
      IF (LT(I).EQ.290) ET = ET290
      ACORT(I) = AT(I) - BLT
      CT(I) = ACORT(I)/ET
      TMOLE(I) = CT(I)*VT(I)
      STMOLE = STMOLE + TMOLE(I)
    1 CONTINUE
      WRITE (6,1005)
 1005 FORMAT (1H1,2X,14HTRANS RHEN2CL2//)
      WRITE (6,1009) TOTMOL
 1009 FORMAT (1H0,2X,24HTOTAL NUMBER OF MOLES = ,G16.8)
      WRITE (6,1008) STMOLE
 1008 FORMAT (1H0,2X,27HNUMBER OF MOLES OF TRANS = ,G16.8)
      WRITE (6,1006)
 1006 FORMAT (1H0,2X,5HFN(I),5X,6HABS(I),14X,9HLAMBDA(I),11X,6HVOL(I),
     *14X,7HCONC(I),13X,8HMOLES(I))
      DO 2 I = 1,NT
      WRITE (6,1007) NFRACT(I), AT(I), LT(I), VT(I),CT(I),TMOLE(I)
 1007 FORMAT (1H0,2X,I4,6X,F6.4,14X,I4,16X,G12.5,8X,G16.8,4X,G16.8)
    2 CONTINUE
      SUMCAB = 0.0
      READ (5,2000)NC
 2000 FORMAT (I4)
      READ (5,2001) BLC230, BLC240, BLC356
 2001 FORMAT (3(F6.4))
```

```
      READ (5,2002) F230, F240, F296, F356
 2002 FORMAT (4(E12.5))
      DO 11 I = 1,NC
      READ (5,2003) NFRACT(I), AC(I), LC(I), VC(I)
 2003 FORMAT (I4, F6.4, I4, E12.5)
      IF (LC(I).EQ.230) BLC = BLC230
      IF (LC(I).EQ.230) F = F230
      IF (LC(I).EQ.240) BLC = BLC240
      IF (LC(I).EQ.240) F = F240
      IF (LC(I).EQ.356) BLC = BLC356
      IF (LC(I).EQ.356) F = F356
      ACORC(I) = AC(I) - BLC
      EQUIVA(I) = ACORC(I)*F
      CAB(I) = EQUIVA(I)*VC(I)
      SUMCAB = SUMCAB + CAB(I)
   11 CONTINUE
      WRITE (6,2004)
 2004 FORMAT (1H1,2X,12HCIS RHEN2CL2//)
      SCMOLE = TOTMOL - STMOLE
      WRITE (6,2005) SCMOLE
 2005 FORMAT (1H0,2X,25HNUMBER OF MOLES OF CIS = ,G16.8)
      EC356 = SUMCAB/SCMOLE
      EC296 = EC356/F296
      EC240 = EC356/F240
      EC230 = EC356/F230
      WRITE (6,2006) EC356, EC296, EC240, EC230
 2006 FORMAT (1H0,2X,32HEXTINCTION COEFFICIENT AT 356 = ,G16.8/ 2X,32HEX
     *TINCTION COEFFICIENT AT 296 = ,G16.8/ 2X, 32HEXTINCTION COEFFICIEN
     *T AT 240 = , G16.8/ 2X,32HEXTINCTION COEFFICIENT AT 230 = ,G16.8)
      WRITE (6,1006)
      DO 12 I = 1,NC
      CC(I) = EQUIVA(I)/EC356
      CMOLE(I) = CC(I)*VC(I)
      WRITE (6,1007) NFRACT(I), AC(I), LC(I), VC(I), CC(I), CMOLE(I)
   12 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B12

Calculation of the spectrum of a cis-complex from the spectrum of a cis- and trans-complex mixture

For this programme the total concentration of rhodium(III) species, the spectrum of the trans-isomer and the mole fraction of the cis-isomer present are all known. The absorbances of the mixture at a variety of wavelengths are used to calculate the spectrum of the cis-isomer in terms of its extinction coefficients.

```
*****************************************************
*     MATFIV
*
*                                        C.P.J.VUIK
*
*     74/003
*****************************************************


$JOBM   C.P.J.VUIK       30 310YNYNYYY
C PROGRAMME FOR UV SPECTRUM OF CIS COMPLEXES
C USING UNSEPARATED CIS & TRANS MIXTURES
      DIMENSION A(500),BL(500),ETRANS(500),L(500),ACOR(500),EAPP(500),
     *ECIS(500)
      READ (5,2100) M
 2100 FORMAT (I4)
      WRITE (6,1015)
 1015 FORMAT (1H1,2X,24HSPECTRA OF CIS COMPLEXES //)
      DO 21 J = 1,M
      READ (5,2100) N
      READ (5,1000) XC, CONTOT
 1000 FORMAT (2(E12.5))
      WRITE (6,1004) XC
 1004 FORMAT (1H0,2X,26HFRACTION OF CIS PRODUCT = , E16.8)
      XT = 1.0 - XC
      WRITE (6,1003)
 1003 FORMAT (1H0,2X,9HLAMBDA(I),5X,7HEAPP(I),19X,9HETRANS(I),17X,
     *7HECIS(I))
      DO 1 I = 1,N
      READ (5,1001) A(I), BL(I), L(I), ETRANS(I)
 1001 FORMAT (2(F6.4), I4, E12.5)
      ACOR(I) = A(I) - BL(I)
      EAPP(I) = ACOR(I)/CONTOT
      ECIS(I) = (EAPP(I) - ETRANS(I)*XT)/XC
      WRITE (6,1002) L(I), EAPP(I), ETRANS(I), ECIS(I)
 1002 FORMAT (1H0, 1X,I4,10X,3(G16.8,10X))
    1 CONTINUE
      WRITE (6,1014)
 1014 FORMAT (1H0,2X, 23HEND OF THIS SET OF DATA ///)
   21 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B13

Calculation of the fraction of cis-products of a reaction using the unseparated mixture of cis- and trans-complexes

In this programme the spectra of both the trans- and cis-complexes are known, and are used to calculate the mole fraction of the cis-isomer present from the observed spectrum of a mixture of cis- and trans-complexes of known total rhodium(III) concentration.

```
*************************************************************
*     WATFIV
*
*                                        C.P.J.VUIK
*
*     74/003
*************************************************************
```

```
$JOBW   C.P.J.VUIK       30 310YNYNYYY
C PROGRAMME TO CALCULATE FRACTION OF CIS PRODUCTS
C USING UNSEPARATED CIS & TRANS MIXTURES
      DIMENSION A(500),BL(500),ETRANS(500),ECIS(500),L(500),ACOR(500),
     *EAPP(500),X(500)
      READ (5,2100) M
 2100 FORMAT (I4)
      WRITE (6,3001)
 3001 FORMAT (1H1,2X,37HTO CALCULATE FRACTION OF CIS PRODUCTS //)
      DO 21 J = 1,M
      READ (5,1000) N
 1000 FORMAT (I4)
      READ (5,1002) CONTOT
 1002 FORMAT (E12.5)
      WRITE (6,1003)
 1003 FORMAT (1H0,2X,9HLAMBDA(I),5X,7HEAPP(I),14X,9HETRANS(I),12X,
     *7HECIS(I),14X,4HX(I))
      DO 1 I = 1,N
      READ (5,1001) L(I),A(I),BL(I),ETRANS(I),ECIS(I)
 1001 FORMAT (I4, 2(F6.4),2(E12.5))
      ACOR(I) = A(I) - BL(I)
      EAPP(I) = ACOR(I)/CONTOT
      X(I) = (EAPP(I) - ETRANS(I))/(ECIS(I) - ETRANS(I))
      WRITE (6,1004) L(I),EAPP(I),ETRANS(I),ECIS(I),X(I)
 1004 FORMAT (1H0,1X,I4,10X,4(G16.8,5X))
    1 CONTINUE
      WRITE (6,3000)
 3000 FORMAT (1H0,2X,23HEND OF THIS SET OF DATA ///)
   21 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B14

Calculation of the spectrum of a mixture of cis- and trans-isomers

This programme uses the known spectra of the *cis*- and *trans*-complexes, and the known mole fraction of the *cis*-complex to predict the spectrum of the mixture of *cis*- and *trans*-isomers, and to compare it with the observed spectrum.

```
*************************************************
*     WATFIV
*
*                                        C.P.J.VUIK
*
*     74/003
*************************************************

$JOBW   C.P.J.VUIK       30 310YNYNYYY
C PROGRAMME TO CALCULATE SPECTRA FROM XCIS, ECIS, ETRANS
      DIMENSION A(500),BL(500),ETRANS(500),ECIS(500),L(500),ACOR(500),
     *EAPP(500),ECALC(500)
      CHARACTER*80 TITLE
      READ (5,2100) M
 2100 FORMAT (I4)
      WRITE (6,3001)
 3001 FORMAT (1H1,2X,43HCOMPARISON OF OBSERVED & CALCULATED SPECTRA //)
      DO 21 J = 1,M
      READ (5,3002) TITLE
 3002 FORMAT (A80)
      WRITE (6,3003) TITLE
 3003 FORMAT (1H0,2X,A80)
      READ (5,1002) XCIS
 1002 FORMAT (E12.5)
      WRITE (6,1005) XCIS
 1005 FORMAT (1H0,2X,7HXCIS = , E12.5 /)
      READ (5,2100) N
      READ (5,1002) CONTOT
      XTRANS = 1.0 - XCIS
      WRITE (6,1003)
 1003 FORMAT (1H0,2X,9HLAMBDA(I),5X,7HEAPP(I),14X,9HETRANS(I),12X,
     *7HECIS(I),14X,8HECALC(I))
      DO 1 I = 1,N
      READ (5,1001) L(I),A(I),BL(I),ETRANS(I),ECIS(I)
 1001 FORMAT (I4, 2(F6.4),2(E12.5))
      ACOR(I) = A(I) - BL(I)
      EAPP(I) = ACOR(I)/CONTOT
      ECALC(I) = ETRANS(I)*XTRANS + ECIS(I)*XCIS
      WRITE (6,1004) L(I),EAPP(I),ETRANS(I),ECIS(I),ECALC(I)
 1004 FORMAT (1H0,1X,I4,10X,4(G16.8,5X))
    1 CONTINUE
      WRITE (6,3000)
 3000 FORMAT (1H0,2X,1H //1X,120(1H*) ///)
   21 CONTINUE
      STOP
      END

$DATA
```

PROGRAMME B15

Calculation of elution curves

For this programme the spectra of the various components of the original mixture must be known. The absorbances at reference wavelengths of the different fractions of an ion-exchange separation are used to calculate elution curves for the components, together with the percentage composition of the original mixture. The particular programme appended is for the ion-exchange separation of trans-$[Rhen_2ClOH]^+$ and trans-$[Rhen_2Cl_2]^+$.

```
*****************************************************
*     WATFIV
*
*                                        C.P.J.VUIK
*
*     74/003
*****************************************************

$JOBW    C.P.J.VUIK       30 310YNYNYYY
C PROGRAMME TO CALCULATE ELUTION CURVES
C TRANS RHEN2CL0H SEPARATION FROM TRANS RHEN2CL2
      DIMENSION NFRACT(500),A(500),L(500),ACOR(500),CONC(500),VOL(500)
      CHARACTER*80 TITLE, TF1, TF2
      SUMC1 = 0.0
      SUMC2 = 0.0
      VF = 0.0145
      READ (5,1000) TITLE
 1000 FORMAT (A80)
      WRITE (6,1001) TITLE
 1001 FORMAT (1H1,2X,A80 //)
      READ (5,1000) TF1
      WRITE (6,1002) TF1
 1002 FORMAT (1H0,2X,A80 /)
      WRITE (6,1003)
 1003 FORMAT (1H0,2X,5HFN(I),5X,6HABS(I),14X,9HLAMBDA(I),11X,7HCONC(I),
     *13X,4HV(I))
      READ (5,1004) N1
 1004 FORMAT (I4)
      DO 1 I = 1, N1
      READ (5,1005) NFRACT(I), A(I), L(I)
 1005 FORMAT (I4,F6.4,I4)
      IF (L(I).EQ.205) BL = 0.116
      IF (L(I).NE.205) BL = 0.065
      IF (L(I).EQ.205) E = 39100.0
      IF (L(I).EQ.241) E = 1690.0
      IF (L(I).EQ.250) E = 1130.0
      IF (L(I).EQ.290) E = 121.0
      BL = 0.065
      ACOR(I) = A(I) - BL
      CONC(I) = ACOR(I)/E
      VOL(I) = 14.5*NFRACT(I)
      SUMC1 = SUMC1 + CONC(I)
      WRITE (6,1006) NFRACT(I),A(I),L(I),CONC(I),VOL(I)
 1006 FORMAT (1H0,2X,I4,6X,F6.4,14X,I4,16X,2(G12.5,8X))
    1 CONTINUE
      WRITE (6,1010) SUMC1
 1010 FORMAT (1H0,2X,8HSUMC1 = ,G16.8)
      TM1 = VF*SUMC1
      WRITE (6,1008) TM1
 1008 FORMAT (1H0,1X,1H  /2X,31HTOTAL MOLES OF THIS FRACTION = ,
     *G16.8 //)
      READ (5,1000) TF2
      WRITE (6,1002) TF2
      WRITE (6,1003)
      READ (5,1004) N2
      DO 2 I = 1,N2
      READ (5,1005) NFRACT(I),A(I),L(I)
      IF (L(I).EQ.240) E = 267.0
      IF (L(I).EQ.293) E = 134.0
```

```
      IF (L(I).EQ.370) E = 93.5
      ACOR(I) = A(I) - BL
      CONC(I) = ACOR(I)/E
      VOL(I) = 14.5*NFRACT(I)
      SUMC2 = SUMC2 + CONC(I)
      WRITE (6,1006) NFRACT(I),A(I),L(I),CONC(I),VOL(I)
    2 CONTINUE
      WRITE (6,1011) SUMC2
 1011 FORMAT (1H0,2X,8HSUMC2 = , G16.8)
      TM2 = VF*SUMC2
      WRITE (6,1008) TM2
      WRITE (6,1007)
 1007 FORMAT (1H0,1X,1H  //1X,120(1H*) ///)
      STOP
      END

$DATA
```

Appendix C

Possible Mechanisms for the Bromide Anation of *trans*-$[Pt(CN)_4BrOH_2]^-$

For the formulae given in all mechanisms, $L^- = CN^-$, and the geometry of all Pt(IV) species is assumed to be *trans*. Moreover, the rate laws have been derived assuming that the pH is sufficiently low that the substrate is completely in the form $[Pt(CN)_4BrOH_2]^-$, and no $[Pt(CN)_4BrOH]^{2-}$ is present. If the pH is not sufficiently low for this to be true, then the equilibrium

$$[PtL_4BrOH_2]^- \overset{K_A}{\rightleftharpoons} [PtL_4BrOH]^{2-} + H^+ \qquad (C.1)$$

must be considered.

Since

$$K_A = \frac{[PtL_4BrOH][H^+]}{[PtL_4BrOH_2]} \qquad (C.2)$$

and from a mass balance on the substrate species

$$[PtL_4BrOH_2]^- + [PtL_4BrOH]^{2-} = C_t \qquad (C.3)$$

where C_t is the total concentration of substrate species, it follows that

$$[PtL_4BrOH_2]^- = \frac{[H^+]}{K_A + [H^+]} C_t \qquad (C.4)$$

Thus at pH values such that less than 100% of the substrate is in the bromo-aquo-form, it is necessary to multiply the values of k_{obsd} in this appendix by the factor $[H^+]/(K_A+[H^+])$.

(i) Mechanism A: Adaptation of Mason's Mechanism

$$\underset{S}{Br^-} + [BrPtL_4OH_2]^- \overset{K_{IP}}{\rightleftharpoons} \underset{A}{\{Br,BrPtL_4OH_2\}^{2-}} \qquad (C.5)$$

$$Br^- + \{Br,BrPtL_4OH_2\}^{2-} \underset{}{\overset{K_{IT}}{\rightleftharpoons}} \underset{B}{\{2Br,BrPtL_4OH_2\}^{3-}} \qquad (C.6)$$

$$\underset{A}{\{Br,BrPtL_4OH_2\}^{2-}} + Br^- \xrightarrow{k_1} Br^- + [BrPtL_4Br]^{2-} + H_2O \qquad (C.7)$$

$$\underset{B}{\{2Br,BrPtL_4OH_2\}^{3-}} + Br^- \xrightarrow{k_2} 2Br^- + [BrPtL_4Br]^{2-} + H_2O \qquad (C.8)$$

Assumptions

Steps C.5, C.6 are rapid pre-equilibria and steps C.7, C.8 are rate determining.

Prediction of the rate law

$$K_{IP} = \frac{[A]}{[S][Br^-]} \qquad (C.9)$$

$$K_{IT} = \frac{[B]}{[A][Br^-]} \qquad (C.10)$$

From C.9

$$[A] = K_{IP}[Br^-][S] \qquad (C.11)$$

From C.11, C.10

$$[B] = K_{IP}K_{IT}[Br^-]^2[S] \qquad (C.12)$$

From a mass balance on the substrate species

$$[S] + [A] + [B] = C_t \qquad (C.13)$$

where C_t is the total concentration of unreacted $[BrPtL_4OH_2]^-$ species.

From C.13, C.12, C.11

$$[S](1 + K_{IP}[Br^-] + K_{IP}K_{IT}[Br^-]^2) = C_t \qquad (C.14)$$

Hence

$$[S] = \frac{C_t}{1 + K_{IP}[Br^-] + K_{IP}K_{IT}[Br^-]^2} \qquad (C.15)$$

$$\frac{d[BrPtL_4Br]}{dt} = k_1[A][Br^-] + k_2[B][Br^-] \qquad (C.16)$$

From C.16, C.15, C.12, C.11

$$\frac{d[BrPtL_4Br]}{dt} = \frac{(k_1K_{IP}[Br^-]^2 + k_2K_{IP}K_{IT}[Br^-]^3)[S]}{1 + K_{IP}[Br^-] + K_{IP}K_{IT}[Br^-]^2} \qquad (C.17)$$

Remembering that

$$[C_t] + [BrPtL_4Br] = C^\circ \qquad (C.18)$$

where C° is the total concentration of Pt(IV) species present, we obtain

$$\frac{d[BrPtL_4Br]}{dt} = \frac{(k_1K_{IP}[Br^-]^2 + k_2K_{IP}K_{IT}[Br^-]^3)(C^\circ - [BrPtL_4Br])}{1 + K_{IP}[Br^-] + K_{IP}K_{IT}[Br^-]^2} \qquad (C.19)$$

assuming a pseudo-first order excess of Br^-, equation C.19 gives

$$k_{obsd} = \frac{k_1K_{IP}[Br^-]^2 + k_2K_{IP}K_{IT}[Br^-]^3}{1 + K_{IP}[Br^-] + K_{IP}K_{IT}[Br^-]^2} \qquad (C.20)$$

which is equivalent to

$$k_{obsd} = \frac{a[Br^-]^2 + b[Br^-]^3}{1 + c[Br^-] + d[Br^-]^2} \qquad (C.21)$$

where

$$a = k_1K_{IP} \qquad (C.22)$$

$$b = k_2K_{IP}K_{IT} \qquad (C.23)$$

$$c = K_{IP} \qquad (C.24)$$

$$d = K_{IP}K_{IT} \qquad (C.25)$$

Proof that according to this rate law the graph of $k_{obsd}/[Br^-]^2$ against $[Br^-]$ will not have a minimum

For ease of computation, let

$$y = \frac{k_{obsd}}{[Br^-]^2} \tag{C.26}$$

$$x = [Br^-] \tag{C.27}$$

From C.27, C.26, C.21

$$y = \frac{a + bx}{1 + cx + dx^2} \tag{C.28}$$

At a point of inflection*,

$$\frac{dy}{dx} = 0 \tag{C.29}$$

From C.28

$$\frac{dy}{dx} = \frac{(1+cx+dx^2)b - (a+bx)(c+2dx)}{D} \tag{C.30}$$

where

$$D = (1+cx+dx^2)^2 \tag{C.31}$$

$$\frac{dy}{dx} = \frac{b - ac - 2adx - bdx^2}{D} \tag{C.32}$$

From C.32, C.29, at the point of inflection

$$bdx^2 + 2adx + ac - b = 0 \tag{C.33}$$

So there are points of inflection at

$$x = \frac{-2ad \pm \sqrt{4a^2d^2 - 4bd(ac-b)}}{2bd} \tag{C.34}$$

---

*The term "point of inflection" is used in the general sense of maximum, minimum or point of inflection.

Since x represents a concentration, the negative root has no physical significance, and the only point of inflection is found at

$$x = \frac{-2ad + 2\sqrt{a^2d^2 - bd(ac-b)}}{2bd} \tag{C.35}$$

i.e., at

$$x = \frac{-ad + \sqrt{a^2d^2 - bd(ac-b)}}{bd} \tag{C.36}$$

For a minimum, the sign of $\frac{d^2y}{dx^2}$ at the point of inflection must be positive. From C.32

$$\frac{dy}{dx} = \frac{N}{D} \tag{C.37}$$

where

$$N = b - ac - 2adx - bdx^2 \tag{C.38}$$

$$\frac{d^2y}{dx^2} = \frac{D(\frac{dN}{dx}) - N(\frac{dD}{dx})}{D^2} \tag{C.39}$$

at the point of inflection,

$$N = 0 \tag{C.40}$$

Hence

$$\left(\frac{d^2y}{dx^2}\right)_{N=0} = \frac{1}{D}\left(\frac{dN}{dx}\right)_{N=0} \tag{C.41}$$

D is a perfect square (equation C.31), and x is a concentration so it must be a real number, hence D must be positive, and the sign of $(d^2y/dx^2)_{N=0}$ is given by the sign of $(dN/dx)_{N=0}$

$$\frac{dN}{dx} = -2ad - 2bdx \tag{C.42}$$

Substituting from C.36,

$$\left(\frac{dN}{dx}\right)_{N=0} = 2\sqrt{a^2d^2 - bd(ac-b)} \qquad (C.43)$$

Hence the point of inflection is a maximum, and not a minimum, and the rate law of equation C.20 does not predict the experimentally-found minimum in the graph of $k_{obsd}/[Br^-]^2$ against $[Br^-]$.

(ii) Mechanism B; Id anation of an ion-pair and an ion-triplet

$$Br^- + \underset{S}{[BrPtL_4OH_2]^-} \rightleftharpoons \underset{A}{\{Br^-,BrPtL_4OH_2\}^{2-}} \qquad (C.5)$$

$$Br^- + \underset{A}{\{Br,BrPtL_4OH_2\}^{2-}} \rightleftharpoons \underset{B}{\{2Br^-,BrPtL_4OH_2\}^{3-}} \qquad (C.6)$$

$$\underset{A}{\{Br^-,BrPtL_4OH_2\}^{2-}} + Br^- \rightleftharpoons \underset{C}{\{Br^-,BrPtL_4OH_2,Br\}^{3-}} \qquad (C.44)$$

$$\underset{C}{\{Br^-,BrPtL_4OH_2,Br\}^{3-}} \longrightarrow Br^- + [BrPtL_4Br]^{2-} + H_2O \qquad (C.45)$$

$$\underset{B}{\{2Br^-,BrPtL_4OH_2\}^{2-}} + Br^- \rightleftharpoons \underset{D}{\{2Br^-,BrPtL_4OH_2,Br\}^{4-}} \qquad (C.46)$$

$$\underset{D}{\{2Br^-,BrPtL_4OH_2,Br\}^{4-}} \longrightarrow 2Br^- + [BrPtL_4Br]^{2-} + H_2O \qquad (C.47)$$

Assumptions

Steps C.5, C.6, C.44, C.46 are all fast pre-equilibria; steps C.45 and C.47 are rate-determining.

Calculation of the Predicted Rate Law

$$K_{IP} = \frac{[A]}{[S][Br^-]} \qquad (C.9)$$

$$K_{IT} = \frac{[B]}{[A][Br^-]} \qquad (C.10)$$

$$K_1 = \frac{[C]}{[A][Br^-]} \tag{C.48}$$

$$K_2 = \frac{[D]}{[B][Br^-]} \tag{C.49}$$

From C.9

$$[A] = K_{IP}[S][Br^-] \tag{C.11}$$

From C.10 and C.11

$$[B] = K_{IT}K_{IP}[S][Br^-]^2 \tag{C.12}$$

From C.48 and C.11

$$[C] = K_1K_{IP}[S][Br^-]^2 \tag{C.50}$$

From C.49 and C.12

$$[D] = K_2K_{IT}K_{IP}[S][Br^-]^3 \tag{C.51}$$

$$\frac{d[BrPtL_4Br]}{dt} = k_1[C] + k_2[D] \tag{C.52}$$

$$\frac{d[BrPtL_4Br]}{dt} = k_1K_1K_{IP}[S][Br^-]^2 + k_2K_2K_{IT}K_{IP}[S][Br^-]^3 \tag{C.53}$$

From a mass balance on the substrate species

$$[A] + [B] + [C] + [D] + [S] = C_t \tag{C.54}$$

where C_t is the total concentration of unreacted $[BrPtL_4OH_2]^-$ species.

From C.54, C.51, C.50, C.12, C.11

$$[S]\left(1 + K_{IP}[Br^-] + (K_{IT}K_{IP}+K_1K_{IP})[Br^-]^2 + K_2K_{IP}K_{IT}[Br^-]^3\right) = C_t \tag{C.55}$$

Hence

$$[S] = \frac{C_t}{1 + K_{IP}[Br^-] + (K_{IT}K_{IP}+K_1K_{IP})[Br^-]^2 + K_2K_{IP}K_{IT}[Br^-]^3} \tag{C.56}$$

From C.56 and C.55, and remembering that

$$C_t = C^\circ - [BrPtL_4Br] \qquad (C.18)$$

where C° is the total concentration of all Pt(IV) species present, we obtain

$$\frac{d[BrPtL_4Br]}{dt} = \frac{K_{IP}[Br^-]^2(k_1K_1+k_2K_{IT}K_2[Br^-])(C^\circ-[BrPtL_4Br])}{1 + K_{IP}[Br^-] + (K_{IT}K_{IP}+K_1K_{IP})[Br^-]^2 + K_2K_{IP}K_{IT}[Br^-]^3} \qquad (C.57)$$

Assuming a pseudo-first order excess of Br^-, equation C.57 gives

$$k_{obsd} = \frac{k_1K_{IP}K_1[Br^-]^2 + k_2K_{IP}K_{IT}K_2[Br^-]^3}{1 + K_{IP}[Br^-] + (K_{IT}K_{IP}+K_1K_{IP})[Br^-]^2 + K_2K_{IP}K_{IT}[Br^-]^3} \qquad (C.58)$$

which is equivalent to

$$k_{obsd} = \frac{a[Br^-]^2 + b[Br^-]^3}{1 + c[Br^-] + d[Br^-]^2 + e[Br^-]^3} \qquad (C.59)$$

where

$$a = k_1K_{IP}K_1 \qquad (C.60)$$

$$b = k_2K_{IP}K_{IT}K_2 \qquad (C.61)$$

$$c = K_{IP} \qquad (C.62)$$

$$d = K_{IP}(K_{IT}+K_1) \qquad (C.63)$$

$$e = K_2K_{IP}K_{IT} \qquad (C.64)$$

(iii) Mechanism C: Adaptation of Morgan and Jones' Mechanism

$$Br^- + \underset{S}{[BrPtL_4OH_2]^-} \overset{K_{IP}}{\rightleftharpoons} \underset{A}{\{Br,BrPtL_4OH_2\}^{2-}} \qquad (C.5)$$

$$Br^- + \underset{A}{\{Br,BrPtL_4OH_2\}^{2-}} \overset{K_{IT}}{\rightleftharpoons} \underset{B}{\{2Br,BrPtL_4OH_2\}^{3-}} \qquad (C.6)$$

$$\underset{A}{\{Br,BrPtL_4OH_2\}^{2-}} \overset{K_1}{\rightleftharpoons} \underset{C}{\{Br,BrPtL_4\}^{2-}} + OH_2 \qquad (C.65)$$

$$\underset{C}{\{Br,BrPtL_4\}}^{2-} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (C.66)$$

$$\underset{B}{\{2Br,PtL_4OH_2\}}^{3-} \rightleftharpoons \underset{D}{\{2Br,PtL_4\}}^{3-} + H_2O \qquad (C.67)$$

$$\underset{D}{\{2Br,PtL_4\}}^{3-} + Br^- \xrightarrow{k_4} 2Br^- + [BrPtL_4Br]^{2-} \qquad (C.68)$$

Assumptions

Steps C.5, C.6, C.65, C.67 are all fast pre-equilibria and steps C.66 and C.68 are rate-determining. The ion association constants K_{IP} and K_{IT} are considered to be very much less than 1, and the dissociation constants, K_1 and K_2, are similarly presumed to be very small.

Prediction of the Rate Law

$$K_{IP} = \frac{[A]}{[S][Br^-]} \qquad (C.9)$$

$$K_{IT} = \frac{[B]}{[A][Br^-]} \qquad (C.10)$$

$$K_1 = \frac{[C]}{[A]} \qquad (C.69)$$

$$K_3 = \frac{[D]}{[B]} \qquad (C.70)$$

From C.9

$$[A] = K_{IP}[S][Br^-] \qquad (C.11)$$

From C.11, C.10

$$[B] = K_{IT}K_{IP}[S][Br^-]^2 \qquad (C.12)$$

From C.11, C.69

$$[C] = K_1K_{IP}[S][Br^-] \qquad (C.71)$$

From C.12, C.70

$$[D] = K_3K_{IP}K_{IT}[S][Br^-]^2 \qquad (C.72)$$

$$\frac{d[BrPtL_4Br]}{dt} = k_2[C][Br^-] + k_4[D][Br^-] \qquad (C.73)$$

From C.73, C.72, C.71

$$\frac{d[BrPtL_4Br]}{dt} = (k_2K_1K_{IP}[Br^-] + k_4K_3K_{IP}K_{IT}[Br^-]^2)[S][Br^-] \qquad (C.74)$$

But

$$[S] + [BrPtL_4Br] = C^\circ \qquad (C.75)$$

where C° is the total concentration of Pt(IV) species present.

From C.75, C.74

$$\frac{d[BrPtL_4Br]}{dt} = (k_2K_1K_{IP}[Br^-]^2 + k_4K_3K_{IP}K_{IT}[Br^-]^3)(C^\circ-[BrPtL_4Br]) \qquad (C.76)$$

Assuming a pseudo-first order excess of Br^-, equation C.76 gives

$$k_{obsd} = k_2K_1K_{IP}[Br^-]^2 + k_4K_3K_{IP}K_{IT}[Br^-]^3 \qquad (C.77)$$

which is of the form

$$k_{obsd} = a[Br^-]^2 + b[Br^-]^3 \qquad (C.78)$$

where

$$a = k_2K_1K_{IP} \qquad (C.79)$$

$$b = k_4K_3K_{IP}K_{IT} \qquad (C.80)$$

(iv) Mechanism D; D anation of an ion-pair and an ion-triplet

$$Br^- + [BrPtL_4OH_2]^- \overset{K_{IP}}{\rightleftharpoons} \underset{A}{\{Br,BrPtL_4OH_2\}^{2-}} \qquad (C.5)$$

$$\underset{A}{\{Br,BrPtL_4OH_2\}^{2-}} + Br^- \overset{K_{IT}}{\rightleftharpoons} \underset{C}{\{2Br,BrPtL_4OH_2\}^{3-}} \qquad (C.6)$$

$$\{Br,BrPtL_4OH_2\}^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{Br,BrPtL_4\}^{2-} + H_2O \qquad (C.65)$$

$$\{Br,BrPtL_4\}^{2-} + Br^- \xrightarrow{k_2} [BrPtL_4Br]^{2-} \qquad (C.66)$$

$$\{2Br,BrPtL_4OH_2\} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \{2Br,BrPtL_4\}^{3-} + H_2O \qquad (C.67)$$

$$\{2Br,BrPtL_4\} + Br^- \xrightarrow{k_4} 2Br^- + [BrPtL_4Br]^{2-} \qquad (C.68)$$

Assumptions

Steps C.5 and C.6 are rapid pre-equilibria: equation C.66 and the reverse of equation C.65 represent competition by Br^- and H_2O respectively for the intermediate C, and equation C.68 and the reverse of equation C.67 represent competition by Br^- and H_2O respectively for the intermediate D.

Prediction of the Rate Law

Equations C.9, C.10, C.11, C.12, C.52, C.75 still hold, but it is now necessary to apply the steady state assumption to the concentrations of the intermediates C and D.

Thus

$$\frac{d[C]}{dt} = 0 = k_1[A] - k_{-1}[C] - k_2[C][Br^-] \qquad (C.81)$$

$$\frac{d[D]}{dt} = 0 = k_3[B] - k_{-3}[D] - k_4[D][Br^-] \qquad (C.82)$$

From C.81 and C.11

$$[C] = \frac{k_1K_{IP}[S][Br^-]}{k_{-1} + k_2[Br^-]} \qquad (C.83)$$

From C.82 and C.12

$$[D] \approx \frac{k_3 K_{IT} K_{IP} [S][Br^-]^2}{k_{-3} + k_4[Br^-]} \qquad (C.84)$$

From C.84, C.83, C.52

$$\frac{d[BrPtL_4Br]}{dt} = \frac{k_1 k_2 K_{IP} [Br^-]^2 [S]}{k_{-1} + k_2[Br^-]} + \frac{k_3 k_4 K_{IT} K_{IP} [Br^-]^3 [S]}{k_{-3} + k_4[Br^-]} \qquad (C.85)$$

From C.85 and C.75

$$\frac{d[BrPtL_4Br]}{dt} = \left(\frac{k_1 k_2 K_{IP} [Br^-]^2}{k_{-1} + k_2[Br^-]} + \frac{k_3 k_4 K_{IT} K_{IP} [Br^-]^3}{k_{-3} + k_4[Br^-]} \right) (C^\circ - [BrPtL_4Br]) \qquad (C.86)$$

Assuming a pseudo-first order excess of Br^-, equation C.86 gives

$$k_{obsd} = \frac{k_1 k_2 K_{IP} [Br^-]^2}{k_{-1} + k_2[Br^-]} + \frac{k_3 k_4 K_{IT} K_{IP} [Br^-]^3}{k_{-3} + k_4[Br^-]} \qquad (C.87)$$

which is of the form

$$k_{obsd} = \frac{a[Br^-]^2}{1 + b[Br^-]} + \frac{c[Br^-]^3}{1 + d[Br^-]} \qquad (C.88)$$

where

$$a = \frac{k_1 k_2 K_{IP}}{k_{-1}} \qquad (C.89)$$

$$b = \frac{k_2}{k_{-1}} \qquad (C.90)$$

$$c = \frac{k_3 k_4 K_{IT} K_{IP}}{k_{-3}} \qquad (C.91)$$

$$d = \frac{k_4}{k_{-3}} \qquad (C.92)$$

(v) Mechanism E; Redox reaction between Br^- and the substrate and equilibration of the Br_2 intermediate with Br_3^-

$$Br^- + \underset{S}{[BrPtL_4OH_2]^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br_2 + \underset{A}{[PtL_4]^{2-}} + OH_2 \qquad (C.93)$$

$$Br_2 + Br^- \overset{K_{Br}}{\rightleftharpoons} Br_3^- \qquad (C.94)$$

$$Br_2 + \underset{A}{[PtL_4]^{2-}} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (C.95)$$

$$Br_3^- + \underset{A}{[PtL_4]^{2-}} + OH_2 \xrightarrow{k_3} 2Br^- + [BrPtL_4OH_2]^- \qquad (C.96)$$

$$Br_3^- + \underset{A}{[PtL_4]^{2-}} + Br^- \xrightarrow{k_4} 2Br^- + [BrPtL_4Br]^{2-} \qquad (C.97)$$

Assumptions

Step C.94 is a very rapid equilibrium and $[PtL_4]^{2-}$ (A) is a reactive intermediate.

Prediction of the rate law

Applying the steady state assumption to the [A]

$$\frac{d[A]}{dt} = 0 = k_1[S][Br^-] - k_{-1}[Br_2][A] - k_2[Br_2][A][Br^-] - k_3[Br_3^-][A] - k_4[Br_3^-][A][Br^-] \qquad (C.98)$$

but

$$K_{Br} = \frac{[Br_3^-]}{[Br_2][Br^-]} \qquad (C.99)$$

From C.99

$$[Br_3^-] = K_{Br}[Br_2][Br^-] \qquad (C.100)$$

Substituting C.100 in C.98

$$k_1[S][Br^-] - k_{-1}[Br_2][A] - k_2[Br_2][A][Br^-] - k_3K_{Br}[Br_2][A][Br^-]$$

$$-k_4K_{Br}[Br_2][A][Br^-]^2 = 0 \qquad (C.101)$$

From C.101

$$[A][Br_2] = \frac{k_1[S][Br^-]}{k_{-1} + (k_2+k_3K_{Br})[Br^-] + k_4K_{Br}[Br^-]^2} \qquad (C.102)$$

$$\frac{d[BrPtL_4Br]}{dt} = k_2[Br_2][A][Br^-] + k_4[Br_3^-][A][Br^-] \qquad (C.103)$$

From C.103, C.102, C.100

$$\frac{d[BrPtL_4Br]}{dt} = \frac{k_1k_2[S][Br^-]^2 + k_1k_4K_{Br}[S][Br^-]^3}{k_{-1} + (k_2+k_3K_{Br})[Br^-] + k_4K_{Br}[Br^-]^2} \qquad (C.104)$$

Because

$$[S] + [BrPtL_4Br] = C^\circ \qquad (C.75)$$

where C° is the total concentration of all Pt(IV) species present,

$$\frac{d[BrPtL_4Br]}{dt} = \frac{k_1k_2[Br^-]^2 + k_1k_4K_{Br}[Br^-]^3}{k_{-1} + (k_2+k_3K_{Br})[Br^-] + k_4K_{Br}[Br^-]^2} (C^\circ-[BrPtL_4Br]) \qquad (C.105)$$

Assuming a pseudo-first order excess of Br^-, equation C.105 gives

$$k_{obsd} = \frac{k_1k_2[Br^-]^2 + k_1k_4K_{Br}[Br^-]^3}{k_{-1} + (k_2+k_3K_{Br})[Br^-] + k_4K_{Br}[Br^-]^2} \qquad (C.106)$$

which is equivalent to

$$k_{obsd} = \frac{a[Br^-]^2 + b[Br^-]^3}{1 + c[Br^-] + d[Br^-]^2} \qquad (C.107)$$

where

$$a = \frac{k_1 k_2}{k_{-1}} \qquad (C.108)$$

$$b = \frac{k_1 k_4 K_{Br}}{k_{-1}} \qquad (C.109)$$

$$c = \frac{k_2 + k_3 K_{Br}}{k_{-1}} \qquad (C.110)$$

$$d = \frac{k_4 K_{Br}}{k_{-1}} \qquad (C.111)$$

(vi) Mechanism F

$$Br^- + [BrPtL_4OH_2]^- \overset{K}{\rightleftharpoons} \{Br...BrPtL_4OH_2\}^{2-} \qquad (C.112)$$

$$\underset{A}{\{Br...BrPtL_4OH_2\}^{2-}} \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} Br_2 + \underset{B}{[PtL_4]^{2-}} + OH_2 \qquad (C.113)$$

$$Br^- + \{Br...BrPtL_4OH_2\}^{2-} \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} Br_3^- + \underset{B}{[PtL_4]^{2-}} + OH_2 \qquad (C.114)$$

$$Br^- + Br_2 \overset{k_{Br}}{\underset{k_{-Br}}{\rightleftharpoons}} Br_3^- \qquad (C.94)$$

$$Br_2 + \underset{B}{[PtL_4]^{2-}} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (C.95)$$

$$Br_3^- + \underset{B}{[PtL_4]^{2-}} + Br^- \xrightarrow{k_4} 2Br + [BrPtL_4Br]^{2-} \qquad (C.97)$$

Assumptions

Equilibria C.112, C.90 are very fast. K is very small, so that even at the highest $[Br^-]$ used the [A] is negligible compared with the [S]. Br_2, Br_3^- and Species B are reactive intermediates to which the steady state approximations can be applied.

Prediction of the rate law

Equation C.75 still holds

$$K = \frac{[A]}{[S][Br^-]} \tag{C.115}$$

From C.115

$$[A] = K[S][Br^-] \tag{C.116}$$

Applying the steady state assumption to $[Br_2]$

$$\frac{d[Br_2]}{dt} = 0 = k_1[A] - k_{-1}[B][Br_2] - k_2[B][Br_2][Br^-] - k_{Br}[B][Br^-] + k_{-Br}[Br_3^-] \tag{C.117}$$

But

$$K_{Br} = \frac{k_{Br}}{k_{-Br}} = \frac{[Br_3^-]}{[Br_2][Br^-]} \tag{C.118}$$

From C. 118

$$[Br_3^-] = \frac{k_{Br}}{k_{-Br}}[Br_2][Br^-] \tag{C.119}$$

From C.119, C.117

$$k_1[A] - k_{-1}[B][Br_2] - k_2[B][Br_2][Br^-] = 0 \tag{C.120}$$

whence

$$[B][Br_2] = \frac{k_1[A]}{k_{-1} + k_2[Br^-]} \tag{C.121}$$

Applyirg the steady state assumption to $[Br_3^-]$

$$\frac{d[Br_3^-]}{dt} = 0 = k_3[A][Br^-] - k_{-3}[B][Br_3^-] - k_4[B][Br_3^-][Br^-] + k_{Br}[Br_2][Br^-] - k_{-Br}[Br_3^-] \quad (C.122)$$

From C.122, C.119

$$k_3[A][Br^-] - k_{-3}[B][Br_3^-] - k_4[B][Br_3^-][Br^-] = 0 \quad (C.123)$$

whence

$$[B][Br_3^-] = \frac{k_3[A][Br^-]}{k_{-3} + k_4[Br^-]} \quad (C.124)$$

But from C.124, C.121, C.118

$$K_{Br} = \frac{k_3 k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])}{k_1 k_{-3}(1 + \frac{k_4}{k_{-3}}[Br^-])} \quad (C.125)$$

Since K_{Br} must be independent of the $[Br^-]$,

$$\frac{k_2}{k_{-1}} = \frac{k_4}{k_{-3}} \quad (C.126)$$

and

$$K_{Br} = \frac{k_3}{k_{-3}} \times \frac{k_{-1}}{k_1} \quad (C.127)$$

$$\frac{d[BrPtL_4Br]}{dt} = k_2[B][Br_2][Br^-] + k_4[B][Br_3^-][Br^-] \quad (C.128)$$

From C.128, C.121, C.116

$$\frac{d[BrPtL_4Br]}{dt} = \frac{k_2 k_1 K[S][Br^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} + \frac{k_4 k_3 K[S][Br^-]^3}{k_{-3}(1 + \frac{k_4}{k_{-3}}[Br^-])} \quad (C.129)$$

From C.129, C.126, C.75

$$\frac{d[BrPtL_4Br]}{dt} = \left(\frac{k_2k_1k_{-3}K[Br^-]^2 + k_4k_3k_{-1}K[Br^-]^3}{k_{-1}k_{-3}(1 + \frac{k_2}{k_{-1}}[Br^-])} \right) (C^\circ - [BrPtL_4Br]) \quad (C.130)$$

Assuming a pseudo-first order excess of Br^-, equation C.126 gives

$$k_{obsd} = \frac{k_2k_1k_{-3}K[Br^-]^2 + k_4k_3k_{-1}K[Br^-]^3}{k_{-1}k_{-3}(1 + \frac{k_2}{k_{-1}}[Br^-])} \quad (C.131)$$

which by equation C.127 simplifies to

$$k_{obsd} = \frac{k_1K(k_2 + k_4K_{Br}[Br^-])[Br^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} \quad (C.132)$$

This is of the form

$$k_{obsd} = \frac{a[Br^-]^2 + b[Br^-]^3}{1 + c[Br^-]} \quad (C.133)$$

where

$$a = \frac{k_2k_1}{k_{-1}}K \quad (C.134)$$

$$b = \frac{k_4k_1K}{k_{-1}}K_{Br} \quad (C.135)$$

$$c = \frac{k_2}{k_{-1}} = \frac{k_4}{k_{-3}} \quad (C.136)$$

Proof that according to this rate law the graph of $k_{obsd}/[Br^-]^2$ against $[Br^-]$ will not have a minimum

For ease of computation, let

$$y = \frac{k_{obsd}}{[Br^-]^2} \quad (C.26)$$

$$x = [Br^-] \quad (C.27)$$

From C.133, C.27, C.26

$$y = \frac{a + bx}{1 + cx} \qquad (C.137)$$

at a point of inflection*

$$\frac{dy}{dx} = 0 \qquad (C.29)$$

From C.137

$$\frac{dy}{dx} = \frac{(1+cx)b - (a+bx)c}{(1+cx)^2} \qquad (C.138)$$

$$\frac{dy}{dx} = \frac{b - ac}{(1+cx)^2} \qquad (C.139)$$

From C.139 there will only be a point of inflection if

$$b = ac \qquad (C.140)$$

Substituting equation C.140 in equation C.137 we find there is only a point of inflection for the function y if

$$y = a \qquad (C.141)$$

Since equation C.141 shows y to be independent of x, the rate law of C.133 will clearly not predict the observed minimum in the graph of $k_{obsd}/[Br^-]^2$ against $[Br^-]$.

(vii) Mechanism G

$$Br^- + [BrPtL_4OH_2]^- \overset{K}{\rightleftharpoons} \underset{A}{\{Br...BrPtL_4OH_2\}^{2-}} \qquad (C.112)$$

$$\{Br...BrPtL_4OH_2\}^{2-} \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} \underset{B}{\{Br_2...PtL_4\}^{2-}} + OH_2 \qquad (C.142)$$

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* See footnote on page 414

$$Br^- + \{Br...BrPtL_4OH_2\}^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{C}{\{Br_3^-...PtL_4\}^{3-}} + OH_2 \qquad (C.143)$$

$$Br^- + \underset{B}{\{Br_2...PtL_4\}^{2-}} \underset{k'_{-Br}}{\overset{k'_{Br}}{\rightleftharpoons}} \underset{C}{\{Br_3^-...PtL_4\}^{3-}} \qquad (C.144)$$

$$\{Br_2...PtL_4\}^{2-} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (C.145)$$

$$\{Br_3^-...PtL_4\}^{3-} + Br^- \xrightarrow{k_4} 2Br^- + [BrPtL_4Br]^{2-} \qquad (C.146)$$

Assumptions

Equation C.112 is a fast pre-equilibrium and K is very small so that even at the highest $[Br^-]$ used, the concentration of A is negligible compared to that of S. Equation C.143 is assumed to be a very fast equilibrium so that although B and C are very reactive intermediates they are readily interconvertible.

Prediction of the rate law

Equations C.116, C.115, C.75 still hold.

Applying the steady state assumption to [B]

$$\frac{d[B]}{dt} = 0 = k_1[A] - k_{-1}[B] - k_2[B][Br^-] - k'_{Br}[B][Br^-] + k'_{-Br}[C] \qquad (C.147)$$

But

$$K'_{Br} = \frac{k'_{Br}}{k'_{-Br}} = \frac{[C]}{[B][Br^-]} \qquad (C.148)$$

From C.148

$$[C] = \frac{k'_{Br}}{k'_{-Br}}[B][Br^-] \qquad (C.149)$$

From C.149, C.147

$$k_1[A] - k_{-1}[B] - k_2[B][Br^-] = 0 \qquad (C.150)$$

whence

$$[B] = \frac{k_1[A]}{k_{-1} + k_2[Br^-]} \qquad (C.151)$$

Applying the steady state assumption to [C]

$$\frac{d[C]}{dt} = 0 = k_3[A][Br^-] - k_{-3}[C] - k_4[C][Br^-] + k'_{Br}[B][Br] - k'_{-Br}[C] \qquad (C.152)$$

From C.152, C.149

$$k_3[A][Br^-] - k_{-3}[C] - k_4[C][Br^-] = 0 \qquad (C.153)$$

whence

$$[C] = \frac{k_3[A][Br^-]}{k_{-3} + k_4[Br^-]} \qquad (C.154)$$

From C.154, C.149, C.148

$$K'_{Br} = \frac{k_3k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])}{k_{-3}k_1(1 + \frac{k_4}{k_{-3}}[Br^-])} \qquad (C.155)$$

But K'_{Br} must be independent of the $[Br^-]$.

Hence

$$\frac{k_2}{k_{-1}} = \frac{k_4}{k_{-3}} \qquad (C.156)$$

and

$$K'_{Br} = \frac{k_3}{k_{-3}} \times \frac{k_{-1}}{k_1} \qquad (C.157)$$

$$\frac{d[BrPtL_4Br]}{dt} = k_2[B][Br^-] + k_4[C][Br^-] \qquad (C.158)$$

From C.158, C.154, C.151, C.112

$$\frac{d[BrPtL_4Br]}{dt} = \frac{k_2k_1K[S][Br^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} + \frac{k_4k_3K[S][Br^-]^3}{k_{-3}(1 + \frac{k_4}{k_{-3}}[Br^-])} \qquad (C.159)$$

From C.159, C.157, C.156

$$\frac{d[BrPtL_4Br]}{dt} = \frac{k_1K(k_2 + k_4K'_{Br}[Br^-])[Br^-]^2[S]}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} \qquad (C.160)$$

From C.160, C.75

$$\frac{d[BrPtL_4Br]}{dt} = \frac{k_1K(k_2 + k_4K'_{Br}[Br^-])[Br^-]^2(C^\circ - [BrPtL_4Br])}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} \qquad (C.161)$$

Assuming a pseudo-first order excess of Br^-, equation C.161 gives

$$k_{obsd} = \frac{k_1K(k_2 + k_4K'_{Br}[Br^-])[Br^-]^2}{k_{-1}(1 + \frac{k_2}{k_{-1}}[Br^-])} \qquad (C.162)$$

which is of the form

$$k_{obsd} = \frac{a[Br^-]^2 + b[Br^-]^3}{1 + c[Br^-]} \qquad (C.163)$$

where

$$a = \frac{k_1k_2K}{k_{-1}} \qquad (C.164)$$

$$b = \frac{k_1k_4KK'_{Br}}{k_{-1}} \qquad (C.165)$$

$$c = \frac{k_2}{k_{-1}} = \frac{k_4}{k_{-3}} \qquad (C.166)$$

(viii) Mechanism II

$$\underset{S}{Br^-} + [BrPtL_4OH_2]^- \overset{K}{\rightleftharpoons} \{\underset{A}{Br...BrPtL_4OH_2}\}^{2-} \qquad (C.112)$$

$$\{\underset{A}{Br...BrPtL_4OH_2}\}^{2-} \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} \{\underset{B}{Br_2...PtL_4}\}^{2-} + OH_2 \qquad (C.142)$$

$$Br^- + \{\underset{A}{Br...BrPtL_4OH_2}\}^{2-} \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} \{\underset{C}{Br_3^-...PtL_4}\}^{3-} + OH_2 \qquad (C.143)$$

$$\{\underset{B}{Br_2...PtL_4}\}^{2-} + Br^- \xrightarrow{k_2} Br^- + [BrPtL_4Br]^{2-} \qquad (C.145)$$

$$\{\underset{C}{Br_3^-...PtL_4}\}^{3-} + Br^- \xrightarrow{k_4} 2Br^- + [BrPtL_4Br]^{2-} \qquad (C.146)$$

Assumptions

Equation C.112 is a fast pre-equilibrium and K is very small, so that even at the highest $[Br^-]$ used, the [A] is negligible compared with the [S]. Species B and C are distinct, reactive intermediates which are not interconvertible.

Prediction of the rate law

$$K = \frac{[A]}{[S][Br^-]} \qquad (C.115)$$

From C.115

$$[A] = K[S][Br^-] \qquad (C.116)$$

Applying the steady state assumption to [B]

$$\frac{d[B]}{dt} = 0 = k_1[A] - k_{-1}[B] - k_2[B][Br^-] \qquad (C.167)$$

From C.167, C.116

$$[B] = \frac{k_1K[S][Br^-]}{k_{-1} + k_2[Br^-]} \qquad (C.168)$$

Applying the steady state assumption to [C]

$$\frac{d[C]}{dt} = 0 = k_3[A][Br^-] - k_{-3}[C] - k_4[C][Br^-] \quad (C.169)$$

From C.169, C.116

$$[C] = \frac{k_3K[S][Br^-]^2}{k_{-3} + k_4[Br^-]} \quad (C.170)$$

$$\frac{d[BrPtL_4Br]}{dt} = k_2[B][Br^-] + k_4[C][Br^-] \quad (C.171)$$

From C.171, C.170, C.168

$$\frac{d[BrPtL_4Br]}{dt} = \left(\frac{k_1k_2K[Br^-]^2}{k_{-1} + k_2[Br^-]} + \frac{k_3k_4K[Br^-]^3}{k_{-3} + k_4[Br^-]}\right)[S] \quad (C.172)$$

Since

$$[S] + [BrPtL_4Br] = C^\circ \quad (C.75)$$

Where C° is the total concentration of Pt(IV) species present

$$\frac{d[BrPtL_4Br]}{dt} = \left(\frac{k_1k_2K[Br^-]^2}{k_{-1} + k_2[Br^-]} + \frac{k_3k_4[Br^-]^3}{k_{-3} + k_4[Br^-]}\right)(C^\circ - [BrPtL_4Br]) \quad (C.173)$$

Assuming a pseudo-first order excess of Br^-, equation C.173 gives

$$k_{obsd} = \frac{k_1k_2K[Br^-]^2}{k_{-1} + k_2[Br^-]} + \frac{k_3k_4K[Br^-]^3}{k_{-3} + k_4[Br^-]} \quad (C.174)$$

which is of the form

$$k_{obsd} = \frac{a[Br^-]^2}{1 + b[Br^-]} + \frac{c[Br^-]^3}{1 + d[Br^-]} \quad (C.175)$$

where

$$a = \frac{k_1k_2K}{k_{-1}} \quad (C.176)$$

$$b = \frac{k_2}{k_{-1}} \quad (C.177)$$

$$c = \frac{k_3 k_4 K}{k_{-3}} \qquad (C.178)$$

$$d = \frac{k_4}{k_{-3}} \qquad (C.179)$$

(ix) Mechanism proposed for the hydrolysis of trans-$[Pt(CN)_4Br_2]^{2-}$ in the presence of Br^- or OH^-.

$$\underset{S_1}{Br^- + [BrPtL_4Br]^{2-}} \rightleftharpoons^{K'} \underset{A_1}{\{Br...BrPtL_4Br\}^{3-}} \qquad (C.180)$$

$$\underset{A_1}{\{Br...BrPtL_4Br\}^{3-}} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \underset{B}{\{Br_2...PtL_4\}^{2-}} + Br^- \qquad (C.181)$$

$$Br^- + \underset{A_1}{\{Br...BrPtL_4Br\}^{3-}} \underset{k_4}{\overset{k_{-4}}{\rightleftharpoons}} \underset{C}{\{Br_3^-...PtL_4\}^{3-}} + Br^- \qquad (C.182)$$

$$\underset{B}{\{Br_2...PtL_4\}^{2-}} + OH_2 \xrightarrow{k_{-1}} Br^- + [BrPtL_4OH_2]^- \qquad (C.183)$$

$$\underset{C}{\{Br_3^-...PtL_4\}^{3-}} + OH_2 \xrightarrow{k_{-3}} 2Br^- + [BrPtL_4OH_2]^- \qquad (C.184)$$

$$HO^- + \underset{S_1}{[BrPtL_4Br]^{2-}} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \underset{D}{\{HOBr...PtL_4\}^{2-}} + Br^- \qquad (C.185)$$

$$\underset{D}{\{HOBr...PtL_4\}^{2-}} + OH_2 \xrightarrow{k_6} HO^- + [BrPtL_4OH_2]^- \qquad (C.186)$$

Assumptions

K' is very small, so that at all concentrations of Br^- used, the $[A_1]$ is negligible compared with the $[S_1]$. Species B, C and D are distinct, reactive intermediates which are not interconvertible.

Prediction of the rate law

$$K' = \frac{[A_1]}{[S_1][Br^-]} \qquad (C.187)$$

From C.187

$$[A_1] = K'[Br^-][S_1] \qquad (C.188)$$

Applying the steady state assumption to [B]

$$\frac{d[B]}{dt} = 0 = k_{-2}[A_1] + k_2[B][Br^-] - k_{-1}[B] \qquad (C.189)$$

From C.189

$$[B] = \frac{k_{-2}[A_1]}{k_{-1} + k_2[Br^-]} \qquad (C.190)$$

Applying the steady state assumption to [C]

$$\frac{d[C]}{dt} = 0 = k_{-4}[A_1][Br^-] - k_4[C][Br^-] - k_{-3}[C] \qquad (C.191)$$

From C.191

$$[C] = \frac{k_{-4}[A_1][Br^-]}{k_{-3} + k_4[Br^-]} \qquad (C.192)$$

Applying the steady state assumption to [D]

$$\frac{d[D]}{dt} = 0 = k_5[S_1][OH^-] - k_{-5}[D][Br^-] - k_6[D] \qquad (C.193)$$

From C.193

$$[D] = \frac{k_5[S][OH^-]}{k_6 + k_{-5}[Br^-]} \qquad (C.194)$$

$$\frac{d[BrPtL_4OH_2]}{dt} = k_6[D] + k_{-1}[B] + k_{-3}[C] \qquad (C.195)$$

From C.195, C.194, C.192, C.190, C.188

$$\frac{d[BrPtL_4OH_2]}{dt} = \frac{k_5k_6[OH^-][S_1]}{k_6 + k_{-5}[Br^-]} + \frac{k_{-1}k_{-2}K'[Br^-][S_1]}{k_{-1} + k_2[Br^-]} + \frac{k_{-3}k_{-4}K'[S_1][Br^-]^2}{k_{-3} + k_4[Br^-]} \qquad (C.196)$$

Since

$$[S_1] + [BrPtL_4OH_2] = C^\circ \qquad (C.197)$$

where C° is the total concentration of Pt(IV) species present, it follows that

$$\frac{d[BrPtL_4OH_2]}{dt} = (C^\circ - [BrPtL_4OH_2])\left\{\frac{k_5k_6[OH^-]}{k_6 + k_{-5}[Br^-]} + \frac{k_{-1}k_{-2}K'[Br^-]}{k_{-1} + k_2[Br^-]} + \frac{k_{-3}k_{-4}K'[Br^-]^2}{k_{-3} + k_4[Br^-]}\right\} \qquad (C.198)$$

Assuming a pseudo-first order concentration of Br^- and OH^-, equation C.198 gives

$$k_{obsd} = \frac{k_5k_6[OH^-]}{k_6 + k_{-5}[Br^-]} + \frac{k_{-1}k_{-2}K'[Br^-]}{k_{-1} + k_2[Br^-]} + \frac{k_{-3}k_{-4}K'[Br^-]^2}{k_{-3} + k_4[Br^-]} \qquad (C.199)$$

which is of the form

$$k_{obsd} = \frac{a'[Br]}{1 + b[Br^-]} + \frac{c'[Br^-]^2}{1 + d[Br^-]} + \frac{e[OH^-]}{1 + f[Br^-]} \qquad (C.200)$$

where

$$a' = k_{-2}K' \qquad (C.201)$$

$$b = \frac{k_2}{k_{-1}} \qquad (C.202)$$

$$c' = k_{-4}K' \qquad (C.203)$$

$$d = \frac{k_4}{k_{-3}} \qquad (C.204)$$

$$e = k_5 \qquad (C.205)$$

$$f = \frac{k_{-5}}{k_6} \qquad (C.206)$$

APPENDIX D

Statistical Analysis of Experimental Data in Part II

Case 1 ; The weighted least squares analysis of the bromide-dependence of the pseudo-first-order rate constant for anation of trans-$[Pt(CN)_4BrOH]^-$

As indicated in chapter 7, the bromide-dependence of the pseudo-first-order rate constant, k_{obsd} , was assumed to be of the form

$$k_{obsd} = \frac{a[Br^-]^2}{1 + b[Br^-]} + \frac{c[Br^-]^3}{1 + d[Br^-]} \qquad (D.1)$$

If we define

$$y = k_{obsd} \qquad (D.2)$$

$$x = [Br^-] \qquad (D.3)$$

then equation D.1 becomes

$$y = \frac{ax^2}{1 + bx} + \frac{cx^3}{1 + dx} \qquad (D.4)$$

In accordance with the Berkson model, all the error of an individual observation is assumed to reside in the value of y. Furthermore, it is assumed that there is a constant percentage error, P , in y, so that the standard deviation, σ_i , of the "i" th observation, y_i , is given by

$$\sigma_i = \frac{Py_i}{100} \qquad (D.5)$$

Equation D.4 can be "linearised" by expansion of y in a truncated Taylor's series about the approximate value, y^0 , of y given by equation D.6

$$y^0 = \frac{a^0x^2}{1 + b^0x} + \frac{c^0x^3}{1 + d^0x} \tag{D.6}$$

where a^0 , b^0 , c^0 , d^0 are approximate values of a, b, c, d. This expansion gives

$$y - y^0 = \left(\frac{\partial y}{\partial a}\right)_0 (a - a^0) + \left(\frac{\partial y}{\partial b}\right)_0 (b - b^0) + \left(\frac{\partial y}{\partial c}\right)_0 (c - c^0) + \left(\frac{\partial y}{\partial d}\right)_0 (d - d^0) \tag{D.7}$$

where the subscripts zero (0) on the partial derivatives indicate that they are evaluated at $a = a^0$, $b = b^0$, $c = c^0$, $d = d^0$. Thus

$$\left(\frac{\partial y}{\partial a}\right)_0 = \frac{x^2}{1 + b^0x} \tag{D.8}$$

$$\left(\frac{\partial y}{\partial b}\right)_0 = \frac{-a^0x^3}{(1 + b^0x)^2} \tag{D.9}$$

$$\left(\frac{\partial y}{\partial c}\right)_0 = \frac{x^3}{1 + d^0x} \tag{D.10}$$

$$\left(\frac{\partial y}{\partial d}\right)_0 = \frac{-c^0x^4}{(1 + d^0x)^2} \tag{D.11}$$

If we define

$$\Delta j = j - j^0 \tag{D.12}$$

$$F_j = \left(\frac{\partial y}{\partial j}\right)_0 \tag{D.13}$$

where j = a, b, c or d, equation D.7 becomes

$$\Delta y = \Delta a F_a + \Delta b F_b + \Delta c F_c + \Delta d F_d \tag{D.14}$$

Equation D.14 is linear in Δa, Δb, Δc, Δd, and hence is amenable to a least squares treatment to determine the "best" values, $\Delta\hat{a}$, $\Delta\hat{b}$, $\Delta\hat{c}$, $\Delta\hat{d}$, of Δa, Δb, Δc, Δd.

By the law of propagation of errors, the standard deviation, $\sigma_{\Delta i}$, associated with a given value, Δy_i , of Δy will be given by

$$\sigma_{\Delta i} = \sigma_i = \frac{P y_i}{100} \tag{D.15}$$

since y^0 is a constant. Since P/100 is also a constant, the weighting factor, w_i , associated with Δy_i is given by

$$w_i = \frac{1}{y_i^2} \tag{D.16}$$

For a least squares analysis of the data accordinggg to equation D.14, $\Delta\hat{a}$, $\Delta\hat{b}$, $\Delta\hat{c}$, $\Delta\hat{d}$ are chosen so that

$$S = \sum_i w_i r_i^2 = \text{a minimum} \tag{D.17}$$

where $\sum_i$ denotes summation over all values of i from i = 1 to i = N, the total number of observations, and the residual, r_i , is given by

$$r_i = \Delta y_i - \Delta a F_{ai} - \Delta b F_{bi} - \Delta c F_{ci} - \Delta d F_{di} \tag{D.18}$$

where F_{ai}, F_{bi}, F_{ci}, F_{di} are values of F_a, F_b, F_c, F_d at $x = x_i$ and $y = y_i$. To fulfill the condition of equation D.17,

$$\left(\frac{\partial S}{\partial \Delta a}\right) = 0 \tag{D.19}$$

$$\left(\frac{\partial S}{\partial \Delta b}\right) = 0 \tag{D.20}$$

$$\left(\frac{\partial S}{\partial \Delta c}\right) = 0 \tag{D.21}$$

$$\left(\frac{\partial S}{\partial \Delta d}\right) = 0 \tag{D.22}$$

The conditions of equations D.19 to D.22 will be obeyed at

$$\Delta a = \Delta\hat{a} \tag{D.23}$$

$$\Delta b = \Delta\hat{b} \tag{D.24}$$

$$\Delta c = \Delta\hat{c} \tag{D.25}$$

$$\Delta d = \Delta\hat{d} \tag{D.26}$$

Application of equations D.19 to D.26 to equations D.17 and D.18 gives the four normal equations D.27 to D.30.

$$\Delta\hat{a}\sum_i w_i F_{ai}^2 + \Delta\hat{b}\sum_i w_i F_{ai}F_{bi} + \Delta\hat{c}\sum_i w_i F_{ai}F_{ci} + \Delta\hat{d}\sum_i w_i F_{ai}F_{di} = \sum_i w_i F_{ai}\Delta y_i \tag{D.27}$$

$$\Delta\hat{a}\sum_i w_i F_{ai}F_{bi} + \Delta\hat{b}\sum_i w_i F_{bi}^2 + \Delta\hat{c}\sum_i w_i F_{bi}F_{ci} + \Delta\hat{d}\sum_i w_i F_{bi}F_{di} = \sum_i w_i F_{bi}\Delta y_i \tag{D.28}$$

$$\Delta\hat{a}\sum_i w_i F_{ai}F_{ci} + \Delta\hat{b}\sum_i w_i F_{bi}F_{ci} + \Delta\hat{c}\sum_i w_i F_{ci}^2 + \Delta\hat{d}\sum_i w_i F_{ci}F_{di} = \sum_i w_i F_{ci}\Delta y_i \tag{D.29}$$

$$\Delta\hat{a}\sum_i w_i F_{ai}F_{di} + \Delta\hat{b}\sum_i w_i F_{bi}F_{di} + \Delta\hat{c}\sum_i w_i F_{ci}F_{di} + \Delta\hat{d}\sum_i w_i F_{di}^2 = \sum_i w_i F_{di}\Delta y_i \tag{D.30}$$

Equations D.27 to D.30 can be solved using determinants (see reference 5) to give the values of $\Delta\hat{a}$, $\Delta\hat{b}$, $\Delta\hat{c}$, $\Delta\hat{d}$. The "corrected" values, $\hat{a}$, $\hat{b}$, $\hat{c}$, $\hat{d}$, of a, b, c, d are then given by

$$\hat{a} = a^0 + \Delta\hat{a} \tag{D.31}$$

$$\hat{b} = b^0 + \Delta\hat{b} \tag{D.32}$$

$$\hat{c} = c^0 + \Delta\hat{c} \tag{D.33}$$

$$\hat{d} = d^0 + \Delta\hat{d} \tag{D.34}$$

The value of the percentage deviation, P , in y is given by

$$P = 100\sqrt{\frac{\sum_i w_i\left\{y_i - \frac{\hat{a}x_i^2}{1+\hat{b}x_i} - \frac{\hat{c}x_i^3}{1+\hat{d}x_i}\right\}^2}{N-4}} \qquad (D.35)$$

where N is the number of observations. The standard deviation, $\sigma_{\hat{a}}$, of $\Delta\hat{a}$, which by the law of propagation of errors applied to equation D.12 is also the standard deviation of $\hat{a}$, is given by

$$\sigma_{\hat{a}} = \frac{P}{100}\sqrt{\frac{M_{aa}}{D}} \qquad (D.36)$$

where

$$D = \begin{vmatrix} \sum wF_aF_a & \sum wF_aF_b & \sum wF_aF_c & \sum wF_aF_d \\ \sum wF_aF_b & \sum wF_bF_b & \sum wF_bF_c & \sum wF_bF_d \\ \sum wF_aF_c & \sum wF_bF_c & \sum wF_cF_c & \sum wF_cF_d \\ \sum wF_aF_d & \sum wF_bF_d & \sum wF_cF_d & \sum wF_dF_d \end{vmatrix} \qquad (D.37)$$

In equation D.37

$$\sum wF_jF_k = \sum_i w_iF_{ji}F_{ki} \qquad (D.38)$$

where j, k = a, b, c, d.

M_{aa} denotes the cofactor of $\sum_i w_iF_{ai}F_{ai}$ in D.

The standard deviations, $\sigma_{\hat{b}}$, $\sigma_{\hat{c}}$, $\sigma_{\hat{d}}$, of $\hat{b}$, $\hat{c}$, $\hat{d}$ are similarly given by

$$\sigma_{\hat{b}} = \frac{P}{100}\sqrt{\frac{M_{bb}}{D}} \qquad (D.39)$$

$$\sigma_{\hat{c}} = \frac{P}{100}\sqrt{\frac{M_{cc}}{D}} \qquad (D.40)$$

$$\sigma_{\hat{d}} = \frac{P}{100}\sqrt{\frac{M_{dd}}{D}} \tag{D.41}$$

where M_{jj} (j = b, c, d) is the cofactor of $\sum_i w_i F_{ji} F_{ji}$ in D. The covariance, $\sigma_{\hat{ab}}$, of $\hat{a}$ and $\hat{b}$ is given by

$$\sigma_{\hat{ab}} = \frac{P^2 \; M_{ab}}{10^4 \; D} \tag{D.42}$$

where M_{ab} is the cofactor of $\sum_i w_i F_{ai} F_{bi}$ in D. Similarly

$$\sigma_{\hat{ac}} = \frac{P^2 \; M_{ac}}{10^4 \; D} \tag{D.43}$$

$$\sigma_{\hat{ad}} = \frac{P^2 \; M_{ad}}{10^4 \; D} \tag{D.44}$$

$$\sigma_{\hat{bc}} = \frac{P^2 \; M_{bc}}{10^4 \; D} \tag{D.45}$$

$$\sigma_{\hat{bd}} = \frac{P^2 \; M_{bd}}{10^4 \; D} \tag{D.46}$$

$$\sigma_{\hat{cd}} = \frac{P^2 \; M_{cd}}{10^4 \; D} \tag{D.47}$$

where $\sigma_{\hat{jk}}$ denotes the covariance between j and k and M_{jk} is the cofactor of $\sum_i w_i F_{ji} F_{ki}$ in D. (j = a, b, c, d ; k = b, c, d and k $\neq$ j).

The least squares treatment was then repeated, taking

$$a^0 = \hat{a} \tag{D.48}$$

$$b^0 = \hat{b} \tag{D.49}$$

$$c^0 = \hat{c} \tag{D.50}$$

$$d^0 = \hat{d} \tag{D.51}$$

until the "n" th iteration gave values of $\hat{a}$, $\hat{b}$, $\hat{c}$, $\hat{d}$ which differed by less than 0.5% from the corresponding values found in the "(n-1)" th iteration. When this condition was met, the values of $\hat{a}$, $\hat{b}$, $\hat{c}$, $\hat{d}$, P, $\sigma_{\hat{a}}$, $\sigma_{\hat{b}}$, $\sigma_{\hat{c}}$, $\sigma_{\hat{d}}$, $\sigma_{\hat{a}\hat{b}}$, $\sigma_{\hat{a}\hat{c}}$, $\sigma_{\hat{a}\hat{d}}$, $\sigma_{\hat{b}\hat{c}}$, $\sigma_{\hat{b}\hat{d}}$, $\sigma_{\hat{c}\hat{d}}$ obtained were taken as the final estimates of these parameters.

Case 2 ; Calculation of the standard deviation of a quantity g which is a function of a, b, c, d

If

$$g = f(a,b,c,d) \tag{D.52}$$

then the standard deviation, σ_g , of g is given by

$$\sigma_g^2 = \left(\frac{\partial g}{\partial a}\right)^2\sigma_a^2 + \left(\frac{\partial g}{\partial b}\right)^2\sigma_b^2 + \left(\frac{\partial g}{\partial c}\right)^2\sigma_c^2 + \left(\frac{\partial g}{\partial d}\right)^2\sigma_d^2 + 2\left(\frac{\partial g}{\partial a}\right)\left(\frac{\partial g}{\partial b}\right)\sigma_{ab} + 2\left(\frac{\partial g}{\partial a}\right)\left(\frac{\partial g}{\partial c}\right)\sigma_{ac} + 2\left(\frac{\partial g}{\partial a}\right)\left(\frac{\partial g}{\partial d}\right)\sigma_{ad} + 2\left(\frac{\partial g}{\partial b}\right)\left(\frac{\partial g}{\partial c}\right)\sigma_{bc} + 2\left(\frac{\partial g}{\partial b}\right)\left(\frac{\partial g}{\partial d}\right)\sigma_{bd} + 2\left(\frac{\partial g}{\partial c}\right)\left(\frac{\partial g}{\partial d}\right)\sigma_{cd} \tag{D.53}$$

where σ_j is the standard deviation of j (j = a,b,c,d) and σ_{jk} is the covariance between j and k (k = b,c,d and k ≠ j).

Case 2a ; Calculation of the standard deviation of the function, u

$$u = \frac{[Br^-]}{k_{obsd} - k_B} \tag{D.54}$$

where

$$k_B = \frac{c[Br^-]^3}{1 + d[Br^-]} \tag{D.55}$$

From equations D.54, D.55, D.2, D.3

$$u = \frac{x}{y - k_B} \tag{D.56}$$

$$k_B = \frac{cx^3}{1 + dx} \tag{D.57}$$

The standard deviation, σ_u , of u is given by

$$\sigma_u^2 = \left(\frac{\partial u}{\partial y}\right)^2\sigma_y^2 + \left(\frac{\partial u}{\partial k_B}\right)^2\left\{\left(\frac{\partial k_B}{\partial c}\right)^2\sigma_c^2 + \left(\frac{\partial k_B}{\partial d}\right)^2\sigma_d^2 + 2\left(\frac{\partial k_B}{\partial c}\right)\left(\frac{\partial k_B}{\partial d}\right)\sigma_{cd}\right\} \tag{D.58}$$

The terms in equation D.58 are given by

$$\sigma_y = \frac{Py}{100} \tag{D.59}$$

$$\left(\frac{\partial u}{\partial y}\right) = \frac{-x}{(y - k_B)^2} \tag{D.60}$$

$$\left(\frac{\partial u}{\partial k_B}\right) = \frac{x}{(y - k_B)^2} \tag{D.61}$$

$$\left(\frac{\partial k_B}{\partial c}\right) = \frac{x^3}{1 + dx} \tag{D.62}$$

$$\left(\frac{\partial k_B}{\partial d}\right) = \frac{-cx^4}{(1 + dx)^2} \tag{D.63}$$

Case 2b ; Calculation of the standard deviation of the function, v

$$v = \frac{[Br^-]^2}{k_{obsd} - k_A} \tag{D.64}$$

where

$$k_A = \frac{a[Br^-]^2}{1 + b[Br^-]} \tag{D.65}$$

From equations D.64, D.65, D.2, D.3

$$v = \frac{x^2}{y - k_A} \tag{D.66}$$

where

$$k_A = \frac{ax^2}{1 + bx} \tag{D.67}$$

The standard deviation, σ_v , of v is given by

$$\sigma_v^2 = \left(\frac{\partial v}{\partial y}\right)^2 \sigma_y^2 + \left(\frac{\partial v}{\partial k_A}\right)^2 \left\{ \left(\frac{\partial k_A}{\partial a}\right)^2 \sigma_a^2 + \left(\frac{\partial k_A}{\partial b}\right)^2 \sigma_b^2 + 2\left(\frac{\partial k_A}{\partial a}\right)\left(\frac{\partial k_A}{\partial b}\right)\sigma_{ab} \right\} \tag{D.68}$$

σ_y is given by equation D.59 and the other terms in equation D.68 are given by

$$\left(\frac{\partial v}{\partial y}\right) = \frac{-x^2}{(y - k_A)^2} \tag{D.69}$$

$$\left(\frac{\partial v}{\partial k_A}\right) = \frac{x^2}{(y - k_A)^2} \tag{D.70}$$

$$\left(\frac{\partial k_A}{\partial a}\right) = \frac{x^2}{1 + bx} \tag{D.71}$$

$$\left(\frac{\partial k_A}{\partial b}\right) = \frac{-ax^3}{(1 + bx)^2} \tag{D.72}$$

<u>Case 2c</u> ; <u>Calculation of the standard deviation of the function R</u>

$$R = \frac{bc}{ad} \tag{D.73}$$

The standard deviation, σ_R , of R is given by equation D.74.

$$\sigma_R^2 = \left(\frac{\partial R}{\partial a}\right)^2\sigma_a^2 + \left(\frac{\partial R}{\partial b}\right)^2\sigma_b^2 + \left(\frac{\partial R}{\partial c}\right)^2\sigma_c^2 + \left(\frac{\partial R}{\partial d}\right)^2\sigma_d^2$$
$$+ 2\left(\frac{\partial R}{\partial a}\right)\left(\frac{\partial R}{\partial b}\right)\sigma_{ab} + 2\left(\frac{\partial R}{\partial a}\right)\left(\frac{\partial R}{\partial c}\right)\sigma_{ac} + 2\left(\frac{\partial R}{\partial a}\right)\left(\frac{\partial R}{\partial d}\right)\sigma_{ad}$$
$$+ 2\left(\frac{\partial R}{\partial b}\right)\left(\frac{\partial R}{\partial c}\right)\sigma_{bc} + 2\left(\frac{\partial R}{\partial b}\right)\left(\frac{\partial R}{\partial d}\right)\sigma_{bd} + 2\left(\frac{\partial R}{\partial c}\right)\left(\frac{\partial R}{\partial d}\right)\sigma_{cd} \qquad (D.74)$$

The terms in equation D.74 are given by

$$\left(\frac{\partial R}{\partial a}\right) = \frac{-bc}{a^2d} \qquad (D.75)$$

$$\left(\frac{\partial R}{\partial b}\right) = \frac{c}{ad} \qquad (D.76)$$

$$\left(\frac{\partial R}{\partial c}\right) = \frac{b}{ad} \qquad (D.77)$$

$$\left(\frac{\partial R}{\partial d}\right) = \frac{-bc}{ad^2} \qquad (D.78)$$

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(4) E. Whittaker and G. Robinson, "The Calculus of Observations", 4th edn., Blackie and Son, Glascow, 1965, pages 239 to 243

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APPENDIX E

Computer programmes used in Part II

PROGRAMME E1

Weighted least squares analysis for the equation

$$y = ax^2/(1 + bx) + cx^3/(1 + dx)$$

This programme corresponds to case 1 of appendix D.

```
*****************************************************
*     WATFIV
*
*                                        C.P.J.VUIK
*
*     74/003
*****************************************************

$JOBW   C.P.J.VUIK       30 310YNYNYYY
C WEIGHTED LEAST SQUARES PROGRAMME FOR
C KOBSD = A*X*X/(1.0+B*X)  +  C*X*X*X/(1.0+D*X)
      DIMENSION X(230),Y(230),A(230),B(230),C(230),D(230),W(230),
     6WA2(230),WAB(230),WAC(230),WAD(230),WB2(230),WBC(230),WBD(230),
     6WC2(230),WCD(230),WD2(230),WAY(230),WBY(230),WCY(230),WDY(230),
     6PART1(230),PART2(230),YCALC(230),RESID(230),WTRES(230),
     *YPRED(230),DELY(230)
      DIMENSION PCENT(230)
      CHARACTER*80 TITLE
      READ (5,6000) TITLE
 6000 FORMAT (A80)
      WRITE (6,6002)
 6002 FORMAT (1H1,1X,120(1H*) //)
      WRITE (6,6001) TITLE
 6001 FORMAT (1H0,5X,A80 //)
      WRITE (6,6003)
 6003 FORMAT (1H0,1X,120(1H*) //)
      READ (5,1000) AK,BK,CK,DK
 1000 FORMAT (4(F12.5))
      READ (5,1001) N
 1001 FORMAT (I4)
      SUMW = 0.0
      SUMWA2 = 0.0
      SUMWAB = 0.0
      SUMWAC = 0.0
      SUMWAD = 0.0
      SUMWB2 = 0.0
      SUMWBC = 0.0
      SUMWBD = 0.0
      SUMWC2 = 0.0
      SUMWCD = 0.0
      SUMWD2 = 0.0
      SUMWAY = 0.0
      SUMWBY = 0.0
      SUMWCY = 0.0
      SUMWDY = 0.0
      SUMWTR = 0.0
      DO 1 I = 1,N
      READ (5,1002) Y(I), X(I)
 1002 FORMAT(2(E12.5))
      A(I) = X(I)*X(I)/(1.0 + BK*X(I))
      B(I) = -AK*A(I)*X(I)/(1.0+BK*X(I))
      C(I) = X(I)*X(I)*X(I)/(1.0+DK*X(I))
      D(I) = -CK*X(I)*C(I)/(1.0+DK*X(I))
      YPRED(I) = AK*A(I) + CK*C(I)
      DELY(I) = Y(I) - YPRED(I)
      W(I) = 1.0/(Y(I)*Y(I))
      SUMW = SUMW + W(I)
      WA2(I) = A(I)*A(I)*W(I)
      SUMWA2 = SUMWA2 + WA2(I)
```

```
      WAB(I) = A(I)*B(I)*W(I)
      SUMWAB = SUMWAB + WAB(I)
      WAC(I) = A(I)*C(I)*W(I)
      SUMWAC = SUMWAC + WAC(I)
      WAD(I) = A(I)*D(I)*W(I)
      SUMWAD = SUMWAD + WAD(I)
      WB2(I) = B(I)*B(I)*W(I)
      SUMWB2 = SUMWB2 + WB2(I)
      WBC(I) = B(I)*C(I)*W(I)
      SUMWBC = SUMWBC + WBC(I)
      WBD(I) = B(I)*D(I)*W(I)
      SUMWBD = SUMWBD + WBD(I)
      WC2(I) = C(I)*C(I)*W(I)
      SUMWC2 = SUMWC2 + WC2(I)
      WCD(I) = C(I)*D(I)*W(I)
      SUMWCD = SUMWCD + WCD(I)
      WD2(I) = D(I)*D(I)*W(I)
      SUMWD2 = SUMWD2 + WD2(I)
      WAY(I) = W(I)*A(I)*DELY(I)
      SUMWAY = SUMWAY + WAY(I)
      WBY(I) = W(I)*B(I)*DELY(I)
      SUMWBY = SUMWBY + WBY(I)
      WCY(I) = W(I)*C(I)*DELY(I)
      SUMWCY = SUMWCY + WCY(I)
      WDY(I) = W(I)*D(I)*DELY(I)
      SUMWDY = SUMWDY + WDY(I)
    1 CONTINUE
      E1 = SUMWA2
      E2 = SUMWAB
      E3 = SUMWAC
      E4 = SUMWAD
      F1 = SUMWAB
      F2 = SUMWB2
      F3 = SUMWBC
      F4 = SUMWBD
      G1 = SUMWAC
      G2 = SUMWBC
      G3 = SUMWC2
      G4 = SUMWCD
      H1 = SUMWAD
      H2 = SUMWBD
      H3 = SUMWCD
      H4 = SUMWD2
      P1 = SUMWAY
      P2 = SUMWBY
      P3 = SUMWCY
      P4 = SUMWDY
      CALL DETMT (E1,E2,E3,E4,F1,F2,F3,F4,G1,G2,G3,G4,H1,H2,H3,H4,
     6ANSWER)
      DENOM = ANSWER
      CALL DETMT (P1,P2,P3,P4,F1,F2,F3,F4,G1,G2,G3,G4,H1,H2,H3,H4,
     6ANSWER)
      ANUM = ANSWER
      CALL DETMT (E1,E2,E3,E4,P1,P2,P3,P4,G1,G2,G3,G4,H1,H2,H3,H4,
     6ANSWER)
      BNUM = ANSWER
      CALL DETMT (E1,E2,E3,E4,F1,F2,F3,F4,P1,P2,P3,P4,H1,H2,H3,H4,
     6ANSWER)
      CNUM = ANSWER
      CALL DETMT (E1,E2,E3,E4,F1,F2,F3,F4,G1,G2,G3,G4,P1,P2,P3,P4,
```

```
     6ANSWER)
       DNUM = ANSWER
       DELA = ANUM/DENOM
       DELB = BNUM/DENOM
       DELC = CNUM/DENOM
       DELD = DNUM/DENOM
       ANEW = AK + DELA
       BNEW = BK + DELB
       CNEW = CK + DELC
       DNEW = DK + DELD
       DO 2 I = 1,N
       PART1(I) = ANEW*X(I)*X(I)/(1.0 + BNEW*X(I))
       PART2(I) = CNEW*X(I)*X(I)*X(I)/(1.0 + DNEW*X(I))
       YCALC(I) = PART1(I) + PART2(I)
       RESID(I) = Y(I) - YCALC(I)
       PCENT(I) = 100.0*RESID(I)/Y(I)
       WTRES(I) = W(I)*RESID(I)*RESID(I)
       SUMWTR = SUMWTR + WTRES(I)
     2 CONTINUE
       P = N
       OK2 = SUMWTR/(P - 4.0)
       OK = SQRT(OK2)
       WRITE (6,1003) ANEW
1003 FORMAT (1H0,5X,7HANEW = , G16.8)
       WRITE (6,1004) BNEW
1004 FORMAT(1H0, 5X, 7HBNEW = , G16.8)
       WRITE(6,1005) CNEW
1005 FORMAT (1H0, 5X, 7HCNEW = , G16.8)
       WRITE (6,1006) DNEW
1006 FORMAT (1H0, 5X, 7HDNEW = , G16.8)
       WRITE (6,1011) AK, BK, CK, DK
1011 FORMAT (1H0,5X,5HAK = ,G16.8,5X,5HBK = ,G16.8,5X,5HCK = ,G16.8,
     65X,5HDK = ,G16.8)
       WRITE (6,1010) DELA, DELB, DELC, DELD
1010 FORMAT(1H0,5X,7HDELA = ,G16.8,3X,7HDELB = ,G16.8,3X,7HDELC = ,
     6G16.8,3X,7HDELD = ,G16.8)
       WRITE (6,1009) OK
1009 FORMAT(1H0,5X,24HPERCENTAGE ERROR IN Y = , G16.8)
       CALL DET3 (F2,F3,F4,G2,G3,G4,H2,H3,H4,RESULT)
       COEFFA = RESULT/DENOM
       CALL DET3 (E1,E3,E4,G1,G3,G4,H1,H3,H4,RESULT)
       COEFFB = RESULT/DENOM
       CALL DET3 (E1,E2,E4,F1,F2,F4,H1,H2,H4,RESULT)
       COEFFC = RESULT/DENOM
       CALL DET3 (E1,E2,E3,F1,F2,F3,G1,G2,G3,RESULT)
       COEFFD = RESULT/DENOM
       CALL DET3 (E2,E3,E4,G2,G3,G4,H2,H3,H4,RESULT)
       COEFAB = -RESULT/DENOM
       CALL DET3 (E2,E3,E4,F2,F3,F4,H2,H3,H4,RESULT)
       COEFAC = RESULT/DENOM
       CALL DET3 (E2,E3,E4,F2,F3,F4,G2,G3,G4,RESULT)
       COEFAD = -RESULT/DENOM
       CALL DET3 (E1,E3,E4,F1,F3,F4,H1,H3,H4,RESULT)
       COEFBC = -RESULT/DENOM
       CALL DET3 (E1,E3,E4,F1,F3,F4,G1,G3,G4,RESULT)
       COEFBD = RESULT/DENOM
       CALL DET3 (E1,E2,E4,F1,F2,F4,G1,G2,G4,RESULT)
       COEFCD = -RESULT/DENOM
       VA = COEFFA*OK2
       SIGA = SQRT(VA)
```

```
      VB = COEFFB*OK2
      SIGB = SQRT(VB)
      VC = COEFFC*OK2
      SIGC = SQRT(VC)
      VD = COEFFD*OK2
      SIGD = SQRT(VD)
      COVAB = COEFAB*OK2
      COVAC = COEFAC*OK2
      COVAD = COEFAD*OK2
      COVBC = COEFBC*OK2
      COVBD = COEFBD*OK2
      COVCD = COEFCD*OK2
      COCOAB = COVAB/(SIGA*SIGB)
      COCOAC = COVAC/(SIGA*SIGC)
      COCOAD = COVAD/(SIGA*SIGD)
      COCOBC = COVBC/(SIGB*SIGC)
      COCOBD = COVBD/(SIGB*SIGD)
      COCOCD = COVCD/(SIGC*SIGD)
      RATIO = BNEW*CNEW/(ANEW*DNEW)
      DRA = -BNEW*CNEW/(ANEW*ANEW*DNEW)
      DRB = CNEW/(ANEW*DNEW)
      DRC = BNEW/(ANEW*DNEW)
      DRD = -BNEW*CNEW/(ANEW*DNEW*DNEW)
      SRA = DRA*DRA*VA + DRB*DRB*VB
      SRB = DRC*DRC*VC + DRD*DRD*VD
      SRC = 2.0*DRA*DRB*COVAB + 2.0*DRA*DRC*COVAC
      SRD = 2.0*DRA*DRD*COVAD + 2.0*DRB*DRC*COVBC
      SRE = 2.0*DRB*DRD*COVBD + 2.0*DRC*DRD*COVCD
      SIG2R = SRA + SRB + SRC + SRD + SRE
      SIGR = SQRT(SIG2R)
      WRITE (6,1013) VA, VB, VC, VD
1013  FORMAT (1H0,2X,5HVA = ,G16.8/ 2X,5HVB = ,G16.8/ 2X,5HVC = ,G16.8/
     *2X,5HVD = ,G16.8)
      WRITE (6,1014) SIGA, SIGB, SIGC, SIGD
1014  FORMAT (1H0,2X,26HSTANDARD DEVIATION IN A = ,G16.8/ 2X,26HSTANDARD
     * DEVIATION IN B = ,G16.8/ 2X,26HSTANDARD DEVIATION IN C = ,G16.8/
     *2X,26HSTANDARD DEVIATION IN D = ,G16.8)
      WRITE (6,1015) COVAB,COVAC,COVAD,COVBC,COVBD,COVCD
1015  FORMAT (1H0,2X,22HCOVARIANCE OF A & B = ,G12.5/3X,22HCOVARIANCE OF
     * A & C = ,G12.5/3X,22HCOVARIANCE OF A & D = ,G12.5/3X,22HCOVARIANC
     *E OF B & C = ,G12.5/3X,22HCOVARIANCE OF B & D = ,G12.5/3X,22HCOVAR
     *IANCE OF C & D = ,G12.5/)
      WRITE (6,1016) COCOAB,COCOAC,COCOAD,COCOBC,COCOBD,COCOCD
1016  FORMAT (1H0,2X,9HCOCOAB = ,G12.5/3X,9HCOCOAC = ,G12.5/3X,
     *9HCOCOAD = ,G12.5/3X,9HCOCOBC = ,G12.5/3X,9HCOCOBD = ,G12.5/3X,
     *9HCOCOCD = ,G12.5/)
      WRITE (6,1020) RATIO, SIGR
1020  FORMAT (1H0,2X,8HRATIO = ,G12.5 /3X,7HSIGR = G12.5//)
      WRITE (6,1007)
1007  FORMAT (1H0,5X,4HX(I),16X,4HY(I),16X,8HYCALC(I),12X,8HPCENT(I),
     *12X,4HW(I))
      DO 3 I = 1,N
      WRITE (6,1008) X(I),Y(I),YCALC(I),PCENT(I),W(I)
1008  FORMAT (1H0,5X,5(G12.5,8X))
    3 CONTINUE
      WRITE(6,1012) SUMWA2,SUMWAB,SUMWAC,SUMWAD,SUMWB2,SUMWBC,SUMWBD,
     6SUMWC2,SUMWCD,SUMWD2,SUMWAY,SUMWBY,SUMWCY,SUMWDY
1012  FORMAT(1H0,5X,9HSUMWA2 = ,G16.8,5X,9HSUMWAB = ,G16.8,5X,9HSUMWAC =
     6 ,G16.8/5X,9HSUMWAD = ,G16.8,5X,9HSUMWB2 = ,G16.8,5X,9HSUMWBC = ,
     6G16.8/5X,9HSUMWBD = ,G16.8,5X,9HSUMWC2 = ,G16.8,5X,9HSUMWCD = ,
```

```
     6G16.8/5X,9HSUMWD2 = ,G16.8,5X,9HSUMWAY = ,G16.8,5X,9HSUMWBY = ,
     6G16.8/5X,9HSUMWCY = ,G16.8,5X,9HSUMWDY = ,G16.8)
      WRITE (6,2001)
2001  FORMAT (1H0,1X,1H  //1X,120(1H*) ///)
      STOP
      END

      SUBROUTINE DETMT (R1,R2,R3,R4,S1,S2,S3,S4,T1,T2,T3,T4,U1,U2,U3,U4,
     6ANSWER)
      A1 = T3*U4 - T4*U3
      A2 = T3*U4 - T4*U3
      A3 = T2*U4 - T4*U2
      A4 = T2*U3 - T3*U2
      B1 = T2*U4 - T4*U2
      B2 = T1*U4 - T4*U1
      B3 = T1*U4 - T4*U1
      B4 = T1*U3 - T3*U1
      C1 = T2*U3 - T3*U2
      C2 = T1*U3 - T3*U1
      C3 = T1*U2 - T2*U1
      C4 = T1*U2 - T2*U1
      D1 = S2*A1 - S3*B1 + S4*C1
      D2 = S1*A2 - S3*B2 + S4*C2
      D3 = S1*A3 - S2*B3 + S4*C3
      D4 = S1*A4 - S2*B4 + S3*C4
      ANSWER = R1*D1 - R2*D2 + R3*D3 - R4*D4
      RETURN
      END

      SUBROUTINE DET3 (X1,X2,X3,Y1,Y2,Y3,Z1,Z2,Z3,RESULT)
      W1 = Y2*Z3 - Y3*Z2
      W2 = Y1*Z3 - Y3*Z1
      W3 = Y1*Z2 - Y2*Z1
      RESULT = X1*W1 - X2*W2 + X3*W3
      RETURN
      END

$DATA
```

PROGRAMME E2

Calculation of functions of y and x for the equation

$$y = ax^2/(1 + bx) + cx^3/(1 + dx)$$

This programme corresponds in part to cases 2a, 2b, 2c of appendix D. It was used to calculate the functions plotted in Fig. 7.4 to Fig. 7.8.

```
*****************************************************
*     WATFIV
*
*                                        C.P.J.VUIK
*
*     74/003
*****************************************************


$JOBW    C.P.J.VUIK       30 310YNYNYYY
C  ***************************************************************************
C                                                                             C
C                                                                             C
C                                                                             C
C   TRANS PT(CN)4BROH2  +  BR                                                 C
C   CALCULATION OF KOBSD/(BR) & KOBSD/(BR)2  V  (BR) PLOTS                    C
C   CALCULATION OF (BR)2/(KOBSD-PART1) & (BR)/(KOBSD-PART2) V 1/(BR)          C
C   USING AVERAGE VALUES OF KOBSD                                             C
C                                                                             C
C                                                                             C
C                                                                             C
C  ***************************************************************************
      DIMENSION X(230),Y(230),YCALC(230),PART1(230),PART2(230),M(230),
     *YPLOT1(230),YCALP1(230),YPLOT2(230),YCALP2(230)
      DIMENSION G(230),H(230),F(230),GCALC(230),HCALC(230)
      DIMENSION A(230),B(230),C(230),D(230),VKA(230),VKB(230),VK(230),
     *SK(230),VKZ(230),SKZ(230),SIGH(230),HLIMU(230),HLIML(230),
     *SIGG(230),GLIMU(230),GLIML(230)
      DIMENSION SYP1(230),YP1U(230),YP1L(230),SYP2(230),YP2U(230),
     *YP2L(230)
      CHARACTER*80 TITLE
      READ (5,1000) TITLE
 1000 FORMAT (A80)
      WRITE (6,2004)
 2004 FORMAT (1H1,1X,60(2H* ) /)
      WRITE (6,1006) TITLE
 1006 FORMAT (1H0,2X,A80)
      WRITE (6,2002)
 2002 FORMAT (1H0,1X,1H / 1X,60(2H* ) /)
      READ (5,1001) AK, BK, CK, DK
 1001 FORMAT (4E12.5)
      WRITE (6,5000) AK,BK,CK,DK
 5000 FORMAT (1H0,2X,5HAK = ,G12.5/3X,5HBK = ,G12.5/3X,5HCK = ,
     *G12.5/3X,5HDK = ,G12.5)
      READ (5,1011) VA,VB,COVAB
 1011 FORMAT (3E12.5)
      READ (5,1011) VC,VD,COVCD
      READ (5,1010) DK
 1010 FORMAT (E12.5)
      WRITE (6,1019) VA,VB,COVAB,VC,VD,COVCD,DK
 1019 FORMAT (1H0,2X,5HVA = ,G12.5/3X,5HVB = ,G12.5/3X,8HCOVAB = ,G12.5/
     *3X,5HVC = ,G12.5/3X,5HVD = ,G12.5/3X,8HCOVCD = ,G12.5/3X,5HDK = ,
     *G12.5/)
      DK2 = DK*DK
      READ (5,2100) N
 2100 FORMAT (I4)
      DO 1 I = 1,N
      READ (5,1002) Y(I),X(I),M(I)
 1002 FORMAT (2E12.5, I4)
      PART1(I) = AK*X(I)*X(I)/(1.0 + BK*X(I))
```

```
      PART2(I) = CK*X(I)*X(I)*X(I)/(1.0 + DK*X(I))
      YCALC(I) = PART1(I) + PART2(I)
      YPLOT1(I) = Y(I)/X(I)
      YPLOT2(I) = YPLOT1(I)/X(I)
      YCALP1(I) = YCALC(I)/X(I)
      YCALP2(I) = YCALP1(I)/X(I)
      F(I) = 1.0/X(I)
      G(I) = X(I)/(Y(I)-PART2(I))
      GCALC(I) = X(I)/PART1(I)
      H(I) = X(I)*X(I)/(Y(I)-PART1(I))
      HCALC(I) = X(I)*X(I)/PART2(I)
      A(I) = X(I)*X(I)/(1.0 + BK*X(I))
      B(I) = -AK*A(I)*X(I)/(1.0 + BK*X(I))
      VKA(I) = A(I)*A(I)*VA + B(I)*B(I)*VB + 2.0*A(I)*B(I)*COVAB
      VK(I) = DK2*Y(I)*Y(I) + VKA(I)
      SK(I) = SQRT(VK(I))
      SIGH(I) = H(I)*SK(I)/(Y(I) - PART1(I))
      HLIMU(I) = H(I) + SIGH(I)
      HLIML(I) = H(I) - SIGH(I)
      C(I) = X(I)*X(I)*X(I)/(1.0 + DK*X(I))
      D(I) = -CK*C(I)*X(I)/(1.0 + DK*X(I))
      VKB(I) = C(I)*C(I)*VC + D(I)*D(I)*VD + 2.0*C(I)*D(I)*COVCD
      VKZ(I) = DK2*Y(I)*Y(I) + VKB(I)
      SKZ(I) = SQRT(VKZ(I))
      SIGG(I) = G(I)*SKZ(I)/(Y(I) - PART2(I))
      GLIMU(I) = G(I) + SIGG(I)
      GLIML(I) = G(I) - SIGG(I)
      SYP1(I) = YPLOT1(I)*DK
      SYP2(I) = YPLOT2(I)*DK
      YP1U(I) = YPLOT1(I) + SYP1(I)
      YP1L(I) = YPLOT1(I) - SYP1(I)
      YP2U(I) = YPLOT2(I) + SYP2(I)
      YP2L(I) = YPLOT2(I) - SYP2(I)
    1 CONTINUE
      WRITE (6,2002)
      WRITE (6,1003)
1003  FORMAT (1H0,2X,4HX(I),16X,9HYPLOT1(I),11X,9HYCALP1(I),11X,
     *9HYPLOT2(I),11X,9HYCALP2(I),11X,4HM(I))
      DO 3 I = 1,N
      WRITE (6,1004) X(I),YPLOT1(I),YCALP1(I),YPLOT2(I),YCALP2(I),M(I)
1004  FORMAT (1H0,2X,5(G12.5,8X),I4)
    3 CONTINUE
      WRITE (6,2002)
      WRITE (6,2000)
2000  FORMAT (1H0,1X,4HG(I),16X,8HGCALC(I),12X,4HF(I),16X,4HH(I),16X,
     *8HHCALC(I),12X,4HF(I))
      DO 4 I = 1,N
      WRITE (6,2001) G(I),GCALC(I),F(I),H(I),HCALC(I),F(I)
2001  FORMAT (1H0,1X,6(G12.5,8X))
    4 CONTINUE
      WRITE (6,2002)
      WRITE (6,1008)
1008  FORMAT (1H0,2X,7HSIGG(I),13X,8HGLIMU(I),12X,8HGLIML(I),12X,7HSIGH(
     *I),13X,8HHLIMU(I),12X,8HHLIML(I))
      DO 5 I = 1,N
      WRITE (6,1009) SIGG(I),GLIMU(I),GLIML(I),SIGH(I),HLIMU(I),HLIML(I)
1009  FORMAT (3X,6(G12.5,8X))
    5 CONTINUE
      WRITE (6,2002)
      WRITE (6,1020)
```

```
 1020 FORMAT (1H0,2X,7HSYP1(I),13X,7HYP1U(I),13X,7HYP1L(I), 13X,
     *7HSYP2(I),13X,7HYP2U(I),13X,7HYP2L(I))
       DO 6 I = 1,N
       WRITE (6,1009) SYP1(I),YP1U(I),YP1L(I),SYP2(I),YP2U(I),YP2L(I)
    6  CONTINUE
       WRITE (6,1007)
 1007  FORMAT (1H0,1X,1H  ////1X,120(1H*) //////////)
       STOP
        END

$DATA
```

PROGRAMME E3

Comparison of all data for the bromide-anation of trans-$[Pt(CN)_4BrOH_2]^-$

This programme re-interprets all previous data for this reaction in terms of the rate law found in the present study. It was used to calculate the parameters given in Table 7.7 and the functions plotted in Fig. 7.9 and 7.10.

```
*************************************************
*     WATFIV
*
*                                   C.P.J.VUIK
*
*     74/003
*************************************************

$JOBW    C.P.J.VUIK       30 310YNYNYYY
C PROGRAMME TO COMPARE ALL PT(CN)4BROH2 + BR DATA
      DIMENSION X(500),OBSDK(500),PART1(500),PART2(500),Z(500),D2(500),
     *D(500),CORRK(500),FACTOR(500),CALCK(500),PCENT(500),G(500),
     *ZOBS(500),Y(500),YCALC(500),YPLOT1(500),YPLOT2(500),
     *YCALP1(500),YCALP2(500),XPLOT(500)
      READ (5,1001) AK, BK, CK, DK
 1001 FORMAT (4(E12.5))
      WRITE (6,2000)
 2000 FORMAT (1H1,2X, 23HTRANS PT(CN)4BROH2 + BR //)
      WRITE (6,3000) AK, BK, CK, DK
 3000 FORMAT (1HO,1X,5HAK = ,E12.5,5X,5HBK = ,G12.5,5X,5HCK = ,G12.5,5X,
     *5HDK = ,G12.5)
      READ(5,2100) M
 2100 FORMAT (I4)
      DO 21 J = 1,M
      READ (5,1000) N, IDENT, HC, OK1
 1000 FORMAT (2I4,2E12.5)
      IF (IDENT.EQ.1) WRITE (6,1002)
      IF (IDENT.EQ.2) WRITE (6,1003)
      IF (IDENT.EQ.3) WRITE (6,1004)
 1002 FORMAT (1HO,2X, 42HSKINNER AND JONES, J.A.C.S. 1969, 91, 4405)
 1003 FORMAT (1HO,2X, 26HMASON, I.C. 1971, 10, 1914)
 1004 FORMAT (1HO,2X, 40HMORGAN AND JONES, J.I.N.C. 6972, 34, 275)
      WRITE (6,1009) HC
 1009 FORMAT (1HO,2X,21HCONCENTRATION OF H = ,E12.5)
      WRITE (6,1006)
 1006 FORMAT (1HO,2X,4HX(I),16X,9HFACTOR(I),11X,8HCORRK(I),12X,
     *8HCALCK(I),12X,8HPCENT(I))
      SUMF = 0.0
      SUMD2 = 0.0
      DO 1 I = 1, N
      READ (5,1005) X(I), OBSDK(I)
 1005 FORMAT (2(E12.5))
      PART1(I) = AK*X(I)*X(I)/(1.0+BK*X(I))
      PART2(I) = CK*X(I)*X(I)*X(I)/(1.0+DK*X(I))
      Z(I) = PART1(I) + PART2(I)
      CORRK(I) = OBSDK(I) - OK1
      FACTOR(I) = Z(I)/CORRK(I)
      SUMF = SUMF + FACTOR(I)
    1 CONTINUE
      P = N
      FMEAN = SUMF/P
      DO 2 I = 1,N
      CALCK(I) = Z(I)/FMEAN
      D(I) = CORRK(I) - CALCK(I)
      PCENT(I) = D(I)/CORRK(I)
      D2(I) = PCENT(I)*PCENT(I)
      SUMD2 = SUMD2 + D2(I)
      WRITE (6,1007) X(I),FACTOR(I),CORRK(I),CALCK(I),PCENT(I)
 1007 FORMAT (1HO,1X,5(G16.8,4X))
```

```
    2 CONTINUE
      WRITE (6,4000)
 4000 FORMAT (1H0,2X,8HXPLOT(I),12X,9HYPLOT1(I),11X,9HYCALP1(I),11X,
     *9HYPLOT2(I),11X,9HYCALP2(I),11X,8HXPLOT(I))
      DO 3 I = 1,N
      ZOBS(I) = CORRK(I)*FMEAN
      Y(I) = ZOBS(I)
      YCALC(I) = Z(I)
      YPLOT1(I) = X(I)/(Y(I)-PART2(I))
      YPLOT2(I) = X(I)*X(I)/(Y(I)-PART1(I))
      XPLOT(I) = 1.0/X(I)
      YCALP1(I) = X(I)/(YCALC(I)-PART2(I))
      YCALP2(I) = X(I)*X(I)/(YCALC(I)-PART1(I))
      WRITE (6,4001) XPLOT(I),YPLOT1(I),YCALP1(I),YPLOT2(I),YCALP2(I),
     *XPLOT(I)
 4001 FORMAT (1H0,1X,6(G12.5,8X))
    3 CONTINUE
      OK2 = SUMD2/(P-1.0)
      OK = SQRT(OK2)
      WRITE (6,1008) FMEAN
 1008 FORMAT (1H0,2X,26HAVERAGE VALUE OF FACTOR = , G12.5)
      WRITE (6,1010) OK
 1010 FORMAT (1H0,2X,34HPERCENTAGE ERROR IN CORRECTED K = , G16.8)
      WRITE (6,2001)
 2001 FORMAT (1H0,1X,1H  //1X,120(1H*)///)
   21 CONTINUE
      STOP
      END

$DATA
```