A THESIS

entitled

THE METAL CATALYSED OXIDATION OF THIOLS IN GAS-LIQUID SYSTEMS

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ABSTRACT

This thesis describes an investigation into the oxidation by gaseous oxygen of thiols (mercaptans) in alkaline solution, both in the nominal absence and in the presence of metal salts and complexes.

In the Introductory section a survey is made of previous work published on this subject. With the exception of certain papers published since 1962, the majority of published work has been concerned with the oxidation of carboxy-thiols such as cysteine.

The Experimental section describes the apparatus used in the investigation and the procedure by which experiments were performed. Most kinetic results were obtained by measurement of oxygen uptake as a function of time, the oxygen pressure being maintained at a constant pre-set value.

The Results section contains details of experimental measurements obtained both in kinetic and in non-kinetic experiments. The majority of kinetic results were obtained using 2 M aqueous solutions of sodium hydroxide which were 0.5 M in thiol and 10^{-3} M in metal (where added), under a constant oxygen pressure of 75 cm.Hg at 30° C. The solubility, stability and structure of added metal complexes are shown to be important in the determination of the mode of action of metal-containing homogeneous catalysts.

The experimental results are critically examined in the Discussion section. Rates of reaction are compared for (i) a variety of metals, (ii) a series of complexes of one metal and (iii) a variety of thiols. Reaction mechanisms are proposed which involve the

transfer of an electron from a co-ordinated thiol anion to the metal complex, which is then re-oxidised by molecular oxygen. At the same time thiolic ligands dimerise and disulphide is eliminated. It is suggested that, in certain circumstances, a second reaction resulting in the formation of thiyl free radicals becomes important. The mechanisms are shown to account satisfactorily for all the principal experimental observations made in this work.

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INTRODUCTION

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INTRODUCTION

A INTRODUCTION

One of the most important and characteristic reactions of the thiol group is the ready oxidation to disulphide:

$$2RSH \xrightarrow{[O]} RSSR \qquad (1)$$

The oxidation can be brought about by mild reagents, such as air or oxygen, and by a variety of chemical reagents. The reaction can usually be stopped at the disulphide stage, but more vigorous conditions can convert the disulphide into more highly oxidised products, leading finally to the sulphonic acid, RSO_3H.

Large numbers of research workers have been concerned with the oxidation of thiols, and there have been few periods in the past century when some work in this field has not been in progress. The mechanism has proved surprisingly difficult to elucidate, much of the data having been in conflict, a trend which has continued in some of the more recently published work. This confusion appears chiefly to be due to the extreme sensitivity of the systems to traces of metals, and real progress has been made only when the catalytic role of such impurities has been appreciated.

The first published work on the subject appeared in 1865, when Maercker[1] prepared some sulphur derivatives of toluene, and noted that what is now known as phenylmethanethiol (α-toluenethiol, or benzyl mercaptan) was oxidised by air faster if ammonia was present. Subsequent papers published before 1900 include the work of Klason[2], who studied the oxidation of thioglycolic acid by iron and copper salts, and by iodine and gaseous oxygen.

Investigations were also carried out on the catalysis by ferric chloride of the autoxidation of potassium thioglycolate, and on the autoxidation of sodium ethanethiolate in aqueous and alcoholic solution.[3]

Thiol autoxidation has provided biochemists with an excellent model system for studying the role of metals as catalysts in physiological systems. Following the papers of Matthews and Walker[4], a plethora of data has been published on the catalytic oxidation of acidic thiols such as cysteine and thioglycolic acid in the pH region of 6-8, which is comparable to conditions existing in vivo. The oxidation of simple weakly acidic thiols which require a highly alkaline medium for the formation of the thiol anion has, however, been almost wholly neglected.

A certain amount of work on the subject has been carried out in connection with the rubber industry[5], although here the emphasis has naturally been placed on factors contributing to the deterioration of vulcanised rubber, such as the oxidation of sulphur-sulphur bonds in disulphides.

B THE SWEETENING OF PETROLEUM

Crude oils contain trace amounts of a variety of sulphur compounds which may be removed during the refining process to yield "sweetened" petroleum distillates. The sulphur compounds which are removed are objectionable on account of their obnoxious odour, their potential corrosiveness, and their reduction of the antiknock characteristics of tetraethyllead[6]. Furthermore, the oxidation of such compounds leads to colour and sediment formation

in distillate fuels, resulting in blocked fuel filters and deposit problems. Among the sulphur compounds normally present in petroleum, hydrogen sulphide and thiols are particularly offensive, and while hydrogen sulphide may readily be removed, the ease of removal of thiols depends upon their molecular structure.

Each petroleum distillate fraction contains thiols boiling in the same range as the hydrocarbon material, different fractions requiring different thiol removal or sweetening treatments. The methods available for sweetening petroleum feedstocks may be loosely categorised as either non-catalytic or catalytic in nature.

B.1 Non-catalytic methods

Non-catalytic methods of sweetening petroleum involve reaction of the thiol with a chemical reagent, which may in some cases be regenerated.

One of the earliest non-catalytic sweetening processes was the plumbite or "doctor" process[7], which involved agitation of a sour distillate with an alkaline solution of sodium plumbite. The initial reaction consisted of the formation of lead mercaptides, which were then converted into lead sulphide and the corresponding dialkyl disulphides by the addition of carefully controlled amounts of elemental sulphur. Regeneration of the "doctor" solution was effected by treatment of the lead sulphide with sodium hydroxide[8]. A modification of the "doctor" process involves reaction of thiols with lead sulphide[9], agitated with air in a solution of sodium hydroxide. This process is in current use,

and is known as the Bender process.

The hypochlorite process[10] differed from the plumbite process in that oxidation of the thiols proceeded to some extent past the disulphide stage to yield water-soluble products such as sulphonic acids, thus resulting in a drop in the total sulphur content of the petroleum without the necessity of purification by distillation. The process consisted essentially in agitation of the sour distillate with an aqueous solution of sodium or calcium hypochlorite, and had the advantage that the spent wash was entirely valueless and contained no objectionable products; no recovery was necessary and the effluent could be disposed of without difficulty.

In order not to affect adversely the octane number and lead susceptibility of petroleum distillate fuels, it is desirable to extract thiols from the fuel, rather than to convert them to other petroleum-soluble sulphur compounds. This is accomplished by the Solutizer process[11], which consists of treating the distillate with a caustic solution to which has been added a suitable organic solvent or salt, resulting in a greatly improved extracting power for thiols. Salts of isobutyric acid and of alkyl phenols are used for this purpose. Regeneration of the Solutizer solution can be effected by steam stripping at elevated temperatures, or by direct oxidation of the thiols to disulphides by air blowing, occasionally in the presence of tannin.

Apart from the Solutizer process and the Bender process, non-catalytic methods of sweetening are not used widely at the

present time, catalytic methods being used instead.

B.2 Catalytic methods

The catalytic oxidation of thiols is a sweetening technique that has reached practical fruition in the last decade. The oxidation is carried out in alkaline solution using an oxidation-reduction catalyst together with air or oxygen as the oxidising agent.

Perhaps the most widely used technique involves copper ions and compounds, and various sweetening processes involving the use of these compounds have been patented[12-15]. Copper salts possess several characteristics which make them useful in sweetening processes, particularly the ease with which they may be reduced and oxidised. The sweetening reaction may be expressed as follows:

$$2CuCl_2 + 4RSH \longrightarrow 2CuSR + RSSR + 4HCl \quad (2)$$

$$2CuSR + 2CuCl_2 \longrightarrow RSSR + 4CuCl \quad (3)$$

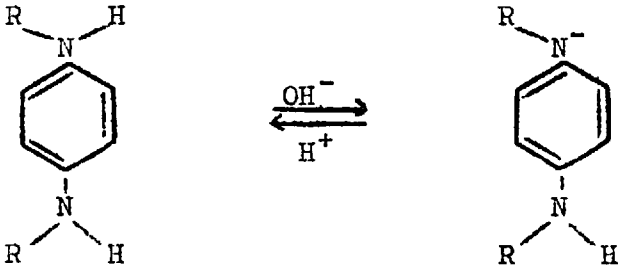
$$4CuCl + 4HCl + O_2 \longrightarrow 4CuCl_2 + 2H_2O \quad (4)$$

Since the catalyst is regenerated during the sweetening process, chemical costs are low. The ease with which copper compounds catalyse the oxidation of thiols to disulphides has promoted investigation into oil-soluble copper compounds such as naphthenates, and more obscure complexes such as the dye Dark Green Sulfanol B[15]. The dye, whose structure has not been determined, is prepared by fusion of p-aminophenol with sodium sulphide, sulphur and copper salts.

Under certain conditions, it is better to use a catalyst such as an N,N' dialkyl aromatic amine ("antioxidant" or "inhibitor"

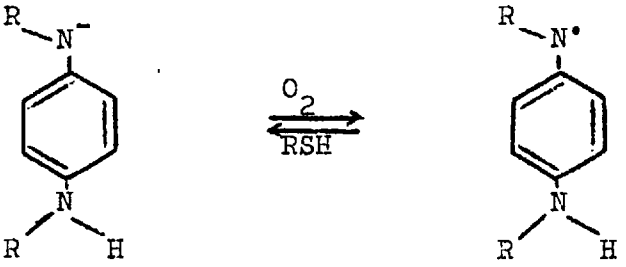
sweetening)[16]. These catalysts are used in particular where the substrate contains olefins and low molecular weight thiols. The mode of action of the catalyst is complex, but it is possible to formulate a simplified mechanism.

Activation of the catalyst can occur by reaction with the alkali to form an amino anion:



(5)

This anion can be oxidised by oxygen to a semiquinone radical, which can be reduced by the thiol to regenerate the anion.



(6)

In the presence of reactive olefins, the rate of the disappearance of the thiol is increased by co-oxidation of the thiol with the olefin, (see Section C.1).

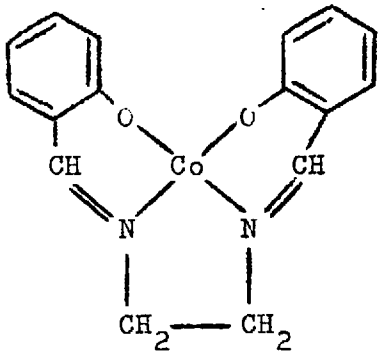
$$RSH \longrightarrow RS^{\bullet} \xrightarrow{CH_2=CR'_2} RS\text{-}CH_2\text{-}\dot{C}R'_2$$

$$\xrightarrow{O_2} RS\text{-}CH_2\text{-}CR'_2\text{-}O_2^{\bullet} \xrightarrow{RSH} RS\text{-}CH_2\text{-}CR'_2\text{-}O_2H$$

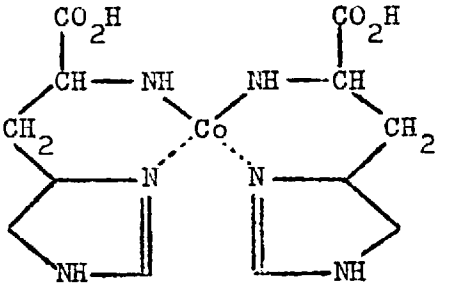
$$\xrightarrow{2RSH} RS\text{-}CH_2\text{-}CR'_2\text{-}OH + RSSR + H_2O \qquad (7)$$

However, the resulting hydroxyalkyl sulphides have a deleterious effect on fuel stability[17]; consequently fuels of high reactive olefin content are seldom sweetened by adding inhibitors. More

recent studies on oxidation-reduction catalysts for sweetening have been concerned with organic chelates such as bis-salicylaldehyde ethylenediimine cobalt (II) and its derivatives[18]



and cobalt (II) histidine chelates[19]



These systems are capable of absorbing up to one molecule of oxygen for every two cobalt atoms[20]. Hence it is not surprising that these substances catalyse the oxidation of thiol anions by oxygen in aqueous sodium hydroxide.

Metal phthalocyanines have been found to catalyse the oxidation of thiols by oxygen, and are used in the Merox process for sweetening petroleum[21]. In order to increase their solubility in the alkaline sweetening solution, the phthalocyanines are normally sulphonated before use. The activity of phthalocyanine catalysts is thought to be due to the enhancement by the ligand environment of the ability of the cation to donate an electron to

oxygen, and to stabilisation by the ligand of each oxidation state of the cation.

C THE OXIDATION OF ORGANIC SULPHUR COMPOUNDS

Work on the oxidation of organic sulphur compounds, and in particular on the oxidation of thiols may conveniently be divided into three classes: firstly, the oxidation at elevated temperatures or in the presence of oxidising agents, secondly the uncatalysed autoxidation of thiols in alkaline media and thirdly the catalysed autoxidation of thiols in alkaline media.

C.1 Introduction

The autoxidation of thiols is a thermodynamically favourable process. On taking the most probable values for the energies of the bonds involved, viz. $D(C_2H_5S\text{-}H)$ = 87 kcal/mole, $D(C_2H_5S\text{-}SC_2H_5)$ = 70 kcal/mole[22], D(O=O) = 118 kcal/mole and D(H-O-H) = 219 kcal/mole[23], the reaction:

$$C_2H_5SH + \tfrac{1}{4}O_2 \longrightarrow \tfrac{1}{2}C_2H_5SSC_2H_5 + \tfrac{1}{2}H_2O \qquad (8)$$

is exothermic by about 30 kcal/mole. Taking $D(C_2H_5O\text{-}H)$ = 110 kcal/mole and $D(C_2H_5O\text{-}OC_2H_5)$ = 40 kcal/mole, the analogous reaction for the oxidation of ethanol would be endothermic by about 10 kcal/mole. It is therefore not surprising that ethanethiol is oxidised to the disulphide under conditions which do not affect ethanol.

The autoxidation of a pure dry thiol to the disulphide has probably not been observed, presumably because the energy of activation is so high that temperatures are required such that the reaction proceeds by a different mechanism, leading to the formation

of more highly oxidised products.

Thus the oxidation of pure thiols by oxygen proceeds at an appreciable rate only at temperatures considerably above room temperature. The gas-phase oxidation of methanethiol and ethanethiol by oxygen was studied by Cullis and Roselaar[24], who found the rate of reaction to be suitable for study only above 210°C, the main product being sulphur dioxide. Alkyl fragments were recovered as carbon monoxide and aldehydes, but the formation of an increasing proportion of dialkyl disulphide was favoured by higher ratios of thiol to oxygen. The results were consistent with a mechanism initiated by hydrogen abstraction of the SH group:

$$RSH + O_2 \longrightarrow RS^{\bullet} + HO_2^{\bullet} \qquad (9)$$

the $HO_2^{\bullet}$ radical probably attacking another thiol molecule to form hydrogen peroxide:

$$RSH + HO_2^{\bullet} \longrightarrow RS^{\bullet} + H_2O_2 \qquad (10)$$

In oxygen-rich mixtures $RS^{\bullet}$ radicals are believed to associate with oxygen to yield sulphur dioxide and an alkyl radical:

$$RS^{\bullet} + O_2 \longrightarrow R^{\bullet} + SO_2 \qquad (11)$$

while in oxygen-lean mixtures disulphide may be produced by radical recombination:

$$RS^{\bullet} + RS^{\bullet} \longrightarrow RSSR \qquad (12)$$

The oxygenated products observed are derived from reactions of the various intermediates, especially $R^{\bullet}$ radicals.

The oxidation of various organic sulphur compounds by a number of reagents including gaseous oxygen has been studied by Bateman, et al.[25, 26, 27]. The initial attack on sulphides

containing allylic or vinyl groups took place on hydrogen atoms attached to the alpha carbon atom, leading to the formation of the corresponding hydroperoxide in a free-radical chain reaction. Similarities thus appear to exist between the autoxidation of such compounds, and that of the hydrocarbons from which they are derived[28, 29] and of the corresponding oxygenated products[30].

A number of studies have been made on the low-temperature oxidation of thiols by oxidants other than molecular oxygen, and a review by Tarbell[31] is available. Thiyl free radicals have again been suggested as reaction intermediates in some cases. For example, the kinetics of the oxidation of some aliphatic thiols by potassium persulphate have been investigated[32], and the results have been found to be in agreement with the existence of two reaction mechanisms, depending upon either the homolysis[32] or heterolysis[33] of the persulphate ion as the rate-determining step. In the latter mechanism, the disulphide is produced through a sulphenyl cation (RS^+) intermediate, and in the former through thiyl radicals ($RS^\bullet$).

The oxidation by hydrogen peroxide of 2-mercaptophenylacetic acid has been studied by Pascal and Tarbell[34]. The addition of ferrous or ferric ions to the system was found to increase the rate of reaction but copper ions and the corresponding disulphide had no effect. The observations did not allow a definitive mechanism to be formulated, but an intermediate with the empirical formula $(H_2O)(RSH)(OH).M_{\frac{1}{2}}$, where M is a heavy metal atom, may be formed during the reaction. The reaction may have some possibilities in the sweetening of petroleum distillates[35] (see above), but the

method has not yet been employed on a commercial scale.

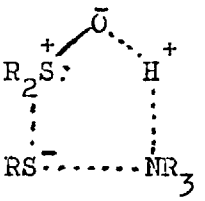
The oxidation of thiols by dimethyl sulphoxide has been investigated by Yiannios and Karabinos[36], and subsequently by Wallace and co-workers[37-42]. The reaction products are disulphides and sulphides (formed by reduction of the sulphoxide). The rate of reaction is markedly dependent on the acidity of the thiol, the order of reactivity being $ArSH > ArCH_2SH > RSH$. It was proposed that the reaction proceeds by a rate-determining step involving the formation of an unstable sulphoxide-thiol adduct, which is rapidly consumed by reaction with another thiol molecule:

$$R_2SO + R'SH \rightleftharpoons \left[R-\overset{+}{S}(OH)-R\right]SR'^- \qquad (13)$$

$$\left[R-\overset{+}{S}(OH)-R\right]SR'^- + R'SH \rightleftharpoons \left[R_2\overset{+}{S}SR'\right]SR'^- + H_2O \qquad (14)$$

$$\left[R_2\overset{+}{S}SR'\right]SR'^- \rightleftharpoons R_2S + R'SSR' \qquad (15)$$

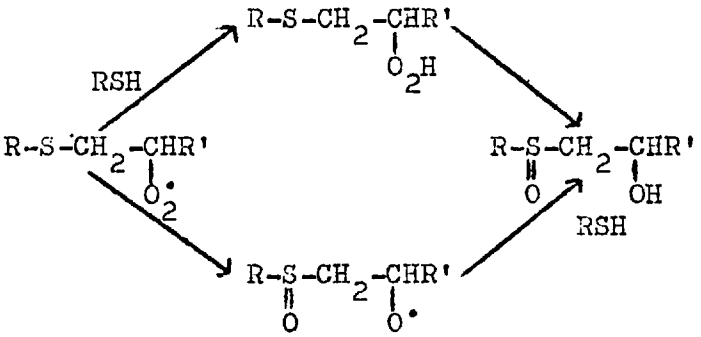
The oxidation of 1-dodecanethiol by tetramethylene sulphoxide was studied in the presence of four amines in an attempt to establish that the reaction is catalysed by acids and bases[41]. In the presence of N,N dimethylaniline and 2,6-lutidine, the rate of oxidation was increased by a factor of only 2 to 3, whereas in the presence of 1-dodecylamine and tri-(n-butyl)amine, a rate increase of 84 to 269 was observed. It was proposed that the amine, thiol and sulphoxide form a transition state of the type



which favours the production of the thiol-sulphoxide adduct formed during the rate-determining step. The low activity of the first two amines was attributed to their decreased basicity in comparison to aliphatic amines.

The co-oxidation reaction between thiols and olefins is one of the few autoxidation reactions which proceed rapidly under mild conditions. Kharasch and co-workers[43] found that thiols and alpha olefins were co-oxidised by molecular oxygen at room temperature, the end products being 2-hydroxyethyl sulphoxides. Kharasch suggested a chain mechanism with two routes for the formation of these compounds:

$$RSH \longrightarrow RS^{\bullet} \xrightarrow{CH_2=CHR'} RS\text{-}CH_2\text{-}\dot{C}HR' \xrightarrow{O_2} RS\text{-}CH_2\text{-}CHR'\text{-}O_2^{\bullet} \qquad (16)$$



(17)

The two routes were termed the "hydroperoxide" route and the "alkoxyl radical" route. In both mechanisms, the first step, after the addition of the thiyl radical to the olefin, is oxygen addition, which is a fast and highly exothermic irreversible reaction. A

good recent review of investigations of the co-oxidation of thiols with olefins is available[44].

The oxidation of thiols with a dye provides a convenient spectrophotometric method for rapid estimation of their relative ease of oxidation. Dixon and Tunnicliffe[45] used methylene blue as the oxidising agent, but the method has been employed more fully in recent work using 2,6-dichlorophenolindophenol at pH 7[46]. The mechanism apparently involves the intermediate production of sulphenyl ions:

$$RSH + H^+ + \underline{D} \longrightarrow RS^+ + \underline{DH}_2 \qquad (18)$$

which can then react to give the sulphenic acid RSOH. In the presence of Cu^{2+}, Ni^{2+} and Fe^{2+} ions, reaction of the RS^+ ion with more thiol is favoured:

$$RS^+ + RSH \longrightarrow RSSR + H^+ \qquad (19)$$

On studying a series of monothiols and dithiols in this system at pH 10, Overberger and Ferraro[47, 48] found aromatic thiols to be considerably more stable to oxidation than saturated aliphatic thiols. This was confirmed by Xan, et al.[49] for the oxidation by molecular oxygen of a series of thiols, among which the rate of oxidation decreased in the order: n-Pr > n-Bu > n-Pen > $PhCH_2$ > Ph. On the other hand, Kharasch, et al.[43], compared the rates of oxidation of thiols by "a variety of reagents", and found the order to be Ar > $HOOC.CH_2$ >> RCH_2 > RR'CH > RR'R"C, thus largely reversing the former order. It should be noted, however, that the latter order is that of the ease of oxidation of thiol molecules (RSH), while the former applies to thiol anions(RS^-) [50, 51].

In contrast to the oxidation of pure dry thiols by molecular

oxygen, the base-catalysed autoxidation of most thiols proceeds at a reasonable rate at room temperature, due to the much lower activation energy needed for the oxidation of the thiol anion RS^-. This reaction is very strongly catalysed by a number of transition metal ions.

The oxidation of thiols in basic media, both in the presence and absence of metallic and other catalysts, will be discussed in detail in the following Sections. For convenience, the reaction in the absence of added catalysts is referred to as the "uncatalysed" reaction.

C.2 Uncatalysed autoxidation of thiols in basic media

Previous work on the uncatalysed oxidation of thiols under alkaline conditions is clearly divided into two classes. Firstly, there are some earlier papers on the oxidation in buffered solutions of carboxy-thiols such as cysteine. Secondly, there is a considerable amount of more recent work on the autoxidation of simple thiols in strongly basic media.

C.2 (a) Carboxy-thiols

Matthews and Walker[4] studied the autoxidation of cysteine, $HOOC.CHNH_2.CH_2SH$, at low alkaline pH values, and found that the rate was highest at pH 8. The autoxidation of three carboxy-thiols was studied by Dixon and Tunnicliffe[45], who investigated reduced glutathione (a dipeptide of cysteine and glutamine), cysteine, and thioglycolic acid. The oxidations were carried out over a wide range of alkaline pH values, the reaction being followed by the decrease in oxygen pressure at constant volume, and by titration of unchanged thiol with iodine, the final solutions being tested for complete oxidation with nitroprusside. The reactions were found

to be catalysed by the addition of disulphides, although in the absence of added disulphides the reactions were not autocatalytic.

At pH 7 to 7.5 the rate of autoxidation of glutathione was highest, whilst outside this pH range the rate fell off rapidly, being less than 10% of the maximum at pH 13.8. The rate of autoxidation of thioglycolic acid, however, increased steadily with pH. It was suggested by Benesch and Benesch[52] that an increase in the pH produced a higher concentration of thiol anions, RS^-, which are the active species, thus favouring autoxidation. This effect is offset above pH 7 with glutathione and cysteine, by the loss of a proton from the substituted ammonium group $>NH_2^+$, which increases the net negative charge on the thiyl radical, and discourages its dimerisation. This explanation is not completely satisfactory, however, since the rate determining step appears to be the reaction producing the radicals, and not their dimerisation.

The probable effect of contaminants on the results of previous workers prompted Gerwe[53] to take special precautions to exclude iron from his reagents. It appears, however, that no special precautions were taken to exclude copper ions, which are about 16 times more effective than iron in promoting the oxidation of cysteine[54].

The results available for the uncatalysed oxidation of carboxythiols are therefore inconclusive, but it is likely that the kinetics are similar to those found more recently for simple thiols, which are discussed in the next section.

C.2 (b) Simple aliphatic and aromatic thiols

Most simple thiols, RSH, where R is an alkyl or aryl group, have pK_a values in the range 10 to 11 and moderately strong basic conditions are necessary for their oxidation. For this reason the uncatalysed oxidation is often referred to as the base-catalysed reaction. The bases most commonly used have been the alkali metal hydroxides and alkoxides, with water, alcohols or binary mixtures as solvents. Highly polar solvents have also been used to increase the basicity, and in certain cases base and solvent properties have been included in the same molecule, such as dimethylformamide (DMF)[51, 55] and tetramethylguanidine (TMG)[56].

The need for strongly alkaline conditions has in general obviated the use of buffers, which have been a constant source of contamination and kinetic irreproducibility in the carboxy-thiol systems. The brief study by Fruton and Clarke[57] of the autoxidation of ethanethiol in solutions buffered to pH 7.5 to 9 gave little simple kinetic data. The rate appeared, however, to be independent of pH, which is perhaps not surprising, since the thiol was unionised over this range of pH.

A more detailed investigation of the oxidation of some simple thiols in aqueous sodium hydroxide solution was published by Xan, et al.[49], who used a very simple apparatus in which a roughly constant pressure was maintained by raising a mercury reservoir manually. The concentrations of sodium hydroxide were between 0.05 and 2.7 N and the ease of oxidation of the different thiols decreased in the order nPr > nBu > nAm > $PhCH_2$ > Ph. The total consumption of

oxygen corresponded to the formation of disulphide at low alkali concentrations, but in the strongest alkali the final uptake was 50% higher. Thiophenol was an exception, and absorbed the theoretical volume of oxygen under all the conditions used. This confirmed the early results of Engler and Broniatowsky[58], who found that thiophenol absorbed 98.2 to 107.9% of the theoretical amount of oxygen in 1N sodium carbonate solution, and 92.3 to 104.8% in 0.2N ammonia. More recently Cole[5] has found that p-nitrothiophenol was oxidised with extensive breakage of the C-S bond. Three times the theoretical quantity of oxygen required for oxidation to disulphide was absorbed, and twice as much monosulphide as disulphide was produced, the remaining sulphur appearing as sulphite and sulphate.

An extensive investigation of the base-catalysed oxidation of simple thiols has been made by Wallace and Schriesheim[51] who suggested that the base-catalysed oxidation of thiols can proceed without the intervention of metal ions according to the scheme:

$$RSH + B \rightleftharpoons RS^- + BH^+ \qquad (20)$$

$$RS^- + O_2 \longrightarrow RS^\bullet + O_2^- \qquad (21)$$

$$RS^- + O_2^- \longrightarrow RS^\bullet + O_2^= \qquad (22)$$

$$2RS^\bullet \longrightarrow RSSR \qquad (23)$$

$$O_2^= + H_2O \longrightarrow 2OH^- + \tfrac{1}{2}O_2 \qquad (24)$$

in which reaction (21) is rate-determining. This mechanism predicts that the rate of oxidation depends upon the proportion of RS^- ions in the solution, and this was confirmed by measurement of the oxidation rates of n-butanethiol with sodium methoxide as the base in (a) strongly basic solvents of low dielectric constant, and (b) polar,

aprotic solvents of high dielectric constant. The oxidation rates (which were not corrected for changes in oxygen solubility) were first order in thiol, and were from 35 to 300 times faster than in methanol. The effect of various alkoxide bases was compared, and again the strongest bases gave the highest rates.

In further investigations, a series of thiols was oxidised under a variety of conditions[55]. The reactivity depended upon the alkyl group in the order: benzyl > n-butyl > p-aminophenyl > cyclohexyl > phenyl > p-nitrophenyl ≈ 0, confirming that the most acidic thiols are most resistant to oxidation, and that the rate-determining step is therefore that in which the anion is destroyed, i.e. reaction (21), and not that in which the anion is produced, i.e. reaction (20). The reactions were followed to 30% conversion and were first order in thiol. Electrophilic substituents in the beta position to the thiol group have been reported to decrease the ease of oxidation of aliphatic thiols[59]; this is probably another case of anion stabilisation.

The nature of the rate-determining transfer of the electron from the thiol anion to the oxygen molecule has been further elucidated[58]. The oxidation of n-butanethiol was investigated in binary solutions of methanol with DMF and with diglyme (diethylene glycol dimethyl ether), using sodium methoxide as the base. The relative rates of oxidation were observed to decrease in the same manner in the two solvent mixtures as the proportion of methanol increased, suggesting that similar transition states operate in each medium. A series of ion-pair complexes was

suggested to explain this; an electron is transferred from the ion-pair complex of the thiol anion with methanol, to an oxygen molecule, less readily than from the complex with DMF or diglyme.

The oxidation of n-octanethiol and of thiophenol in t-butanol containing various proportions of potassium t-butoxide has been studied by Berger[60], who found that the amount of oxygen absorbed, and the corresponding products formed, appeared to depend upon the relative amounts of thiol and base present. Disulphides were formed when the thiol was in excess, but with excess base the products were sulphinic acids ($R.SO_2H$) and sulphonic acids ($R.SO_3H$). It was concluded that disulphides are formed from thiol molecules, RSH, and acids, primarily sulphinic, from the thiol anion RS^-. The higher yields of acids from thiophenol were ascribed to its lower pK_a value. The oxygen uptake rates were zero order in thiol, and the final uptake values varied from the O_2:RSH ratio of 1:4 (theoretical for oxidation to disulphide) with excess thiol to more than 1:1 (theoretical for oxidation to sulphinate) with excess base. In oxidations giving finally about 50% disulphide and 50% sulphinate, the disulphide was the main product until the thiol ceased to be in excess, when sulphinate became the major product. To explain these results a chain mechanism was proposed by Berger:

$$RSO^- + O_2 \longrightarrow RSO.OO^- \qquad (25)$$

$$RSO.OO^- + RS^- \longrightarrow RSO^- + RSO_2^- \qquad (26)$$

$$RSO_2^- + RSH \longrightarrow RSSR + HO_2^- \qquad (27)$$

$$HO_2^- + 2RSH \longrightarrow RSSR + H_2O + OH^- \qquad (28)$$

or alternatively:

$$RS^- + O_2 \rightleftharpoons RSO_2^- \text{ (triplet)} \quad (29)$$

$$RSO_2^- \text{ (triplet)} \longrightarrow RSO_2^- \quad (30)$$

$$2RSH + RSO_2^- \text{ (triplet)} \longrightarrow RSSR + RS^- + H_2O_2 \quad (31)$$

$$2RSH + H_2O_2 \longrightarrow RSSR + 2H_2O \quad (32)$$

It is somewhat surprising that no account was taken of the plausible explanation that the oxygenated acids are not primary products, but are derived from hydrolysis of the disulphide; this would be favoured by excess base. Thus, by varying the basicity of the solution and the temperature, Wallace and Schriesheim[61] have shown that thiols may be oxidised to disulphides or sulphonic acids at will. Excellent yields of sulphonic acids have been obtained by the base catalysed oxidation of several thiols and disulphides, using hexamethylphosphoramide (HMPA) as the solvent[62, 63].

The acceleration of thiol anion oxidations in dipolar solvents has been attributed to a specific cation solvation of the alkali metal associated with the thiol anion (RS^-M^+)[64]. Further, solvent-base and base-reactant agglomeration is apparently at a minimum in these systems. Thus, the anion of the base and the thiol are relatively "free" in comparison to the complex situation which prevails in protic solvents such as alcohol or water, and hence thiol anions are more reactive in these systems, and disulphides are oxidised comparatively readily to sulphonate salts. Nucleophilic attack on the disulphide linkage can occur readily to produce a thiol anion and a sulphenate ion (RSO^-), which is unstable and can either disproportionate to a sulphonate ion and disulphide[65] or be oxidised directly by molecular oxygen.

$$RSSR \xrightarrow{HO^-} RS^- + RSO^- \qquad (33)$$

$$3RSO^- \longrightarrow RSO_3^- + RSSR \qquad (34)$$

$$RSO^- \xrightarrow{O_2} RSO_3^- \qquad (35)$$

It may be concluded that the primary product of the base-catalysed oxidation of simple thiols is the corresponding disulphide, which is produced by a mechanism which is at least similar to that of Wallace and Schriesheim. Under strongly basic conditions, other products may be formed by hydrolysis and oxidation of the disulphide.

A greater understanding of the mechanism of the autoxidation of thiols has resulted from the work of Hopton[66], who studied the kinetics of the oxidation of ethanethiol. Precautions were taken to minimise contamination by metallic impurities. The rate law with ethanethiol was found to be:

$$-\frac{d[EtSH]}{dt} = 4.86 \times 10^{-2} [EtSH][O_2] \text{ mole}^{-1} \text{ l.sec}^{-1}$$

which after 10-30% of the reaction changes to

$$-\frac{d[EtSH]}{dt} = 2.01 \times 10^{-2} [O_2] \text{ sec}^{-1}$$

Investigations were also made into the oxidation of a number of simple thiols, and the order of ease of oxidation was found to be comparable with that found by previous workers[49, 55].

C.3 Catalysed autoxidation of thiols in basic media

C.3 (a) Introduction

The autoxidation of thiols under basic conditions is essentially an electron transfer reaction. Any molecule which can easily absorb an electron and then transfer it to an oxygen molecule

is a potential catalyst. Catalysts will include, then, not only the well known redox transition metal ion systems, but also organic molecules which can accept and donate an electron.

Wallace, et al.[67] have investigated a good example of the latter type of catalysis, namely the oxidation of 1-butanethiol by nitrobenzene in dimethylformamide containing potassium hydroxide. In the absence of oxygen the colour changed to yellow, to red, and then slowly to dark blue. Electron spin resonance and u.v. and visible absorption spectra showed that the nitrobenzene had been reduced to the radical-anion, and analysis of the oxidation products revealed that 99% of the thiol had been oxidised to give the disulphide in 98% yield. The reaction was followed spectrophotometrically for 100 minutes, and first-order kinetics were observed, suggesting a rate-determining transfer of the electron from the thiol anion to the nitrobenzene. In similar experiments toluene α-thiol (benzyl mercaptan) and thiophenol were converted into their disulphides in yields of 81% and 2% respectively. Exposure of the nitrobenzene-butanethiol system to oxygen was found to reduce the absorption at 457 mμ, showing destruction of the radical-anion. This is unlikely to have resulted other than from a simple electron transfer to O_2, allowing recycling of the nitrobenzene as a true catalyst:

$$PhNO_2 + Bu^nS^- \longrightarrow PhNO_2^- + Bu^nS^\bullet \qquad (36)$$

$$PhNO_2^- + O_2 \longrightarrow PhNO_2 + O_2^- \qquad (37)$$

$$2Bu^nS^\bullet \longrightarrow Bu^nSSBu^n \qquad (38)$$

Several similar catalysts for the oxidation have been identified. Thus Wallace, et al.[67] found 2-nitrothiophene,

tetracyanoethylene and 4-nitropyridine-N-oxide to be catalysts for the oxidation of 1-butanethiol, and nitrotoluene has been found to be a catalyst for the oxidation of 1-octanethiol[60]. Similarly, Smentowski[68] studied the effect of organic oxidising agents on the oxidation of 2-naphthalenethiol in DMSO/tert-butanol, and found the order of effectiveness to be: azodicarbonamide > nitrosobenzene > maleic anhydride >> acrylonitrile > nitrobenzene > acrylamide $\approx$ 0.

The quinone-hydroquinone redox system would also be expected to be applicable as a catalyst, and Meguerian[69] studied the oxidation of 1-hexanethiol in the presence of base and of various quinones. With hydroquinone (QH_2) and sodium hydroxide, the kinetics were consistent with the following mechanism:

$$QH_2 + OH^- \rightleftharpoons QH^- + H_2O \qquad (39)$$

$$QH^- + O_2 \longrightarrow QH^\bullet + O_2^- \qquad (40)$$

$$QH^\bullet + RSH \longrightarrow QH_2 + RS^\bullet \qquad (41)$$

$$2RS^\bullet \longrightarrow RSSR \qquad (42)$$

According to this scheme, the hydroquinone catalyses the oxidation of undissociated thiol molecules, but thiol anions may also react to give QH^- and $RS^\bullet$.

Patents have been taken out for oxidations of thiols in which both hydroquinone and a water-soluble iron salt are used as catalysts[70]. The rate of oxidation in the presence of both catalysts was three times higher than the sum of the rates with either used alone. At a constant concentration of hydroquinone the rate seemed to bear a second order relationship to the sodium

hydroxide concentration. No explanation of these facts was advanced.

The rate of oxidation of thiols has also been observed by several workers to be increased by adding an organic disulphide[45], which was not necessarily identical with the disulphide product from the thiol undergoing oxidation[71]. In this case, catalysis again appeared to involve redox reactions which originate as a result of alkaline hydrolysis of disulphides. Thus Harrison[71] found that both the aerobic and anaerobic oxidation of thiol groups were accelerated by the disulphide, dithioglycolic acid, in the complete absence of metals. The catalysis was not inhibited by cyanide, but disappeared when the S-S bond had been destroyed by treatment with bromine. Aware that the disulphide bond was liable to alkaline hydrolysis[72], he proposed that catalysis might be due to the setting up of a sulphenate-sulphinate oxidation-reduction cycle:

$$RSSR + H_2O \rightleftharpoons RSH + RSOH \qquad (43)$$

$$RSOH + O \rightleftharpoons RSOOH \qquad (44)$$

$$2R'SH + RSOOH \rightleftharpoons R'SSR' + RSOH \qquad (45)$$

From studies of the hydrolysis of a number of disulphides, it has been concluded[73] that only disulphides with aryl, carbonyl or alpha-unsaturated groups are susceptible to hydrolytic attack by nucleophilic reagents such as hydroxide ions. However, susceptibility is a matter of degree and some small catalytic effect from dialkyl disulphides might well be expected.

In view of the catalytic nature of disulphides, it is remarkable that an autocatalytic increase in rate is not observed in thiol autoxidation experiments. Autocatalysis has, however, been

discovered in the oxidation of some carboxy-thiols with methylene blue, a system which was also catalysed by added disulphide[45]. Presumably in the case of alkanethiols any such autocatalytic effect would be very small owing to the resistance of the disulphide to hydrolysis.

It has been shown that one of the factors which determines the proportion of disulphides and higher oxidation products in the system is the basicity of the solution. Using comparatively weak basic conditions (e.g. aqueous sodium hydroxide or sodium methoxide in methanol), n- and s-butanethiols and phenylmethanethiol gave 77 to 85% yields, and thiophenol a 67% yield of the respective disulphides[65], whereas solutions of thiols in DMF containing potassium hydroxide gave sulphonic acids in yields of 90% or more[62].

The disulphides which are most liable to hydrolysis are also most liable to oxidation, since both reactions involve initial nucleophilic attack. It is therefore possible that when the hydrolysis necessary for catalysis takes place, the products undergo further oxidation rather than taking part in an oxidation-reduction cycle with oxygen and thiol. In agreement with this, the base-catalysed autoxidation of thiophenol is observed to be a slow non-autocatalytic reaction, which in strongly alkaline media produces larger yields of higher oxidation products than are obtained in the much faster oxidation of alkanethiols[62].

It may be concluded that catalysis and autocatalysis by disulphide requires certain conditions of alkalinity and reactivity in which a redox cycle may be established and maintained. The

requirements are evidently more exacting than those which apply in the case of catalysis by other chemicals described above.

In all of the mechanisms put forward to account for the kinetic features of thiol autoxidation, one stage has necessarily involved electron-transfer on to an oxygen molecule to give a peroxy radical-ion, which then acquires either an electron or a hydrogen atom and becomes a peroxide ion. The peroxide then oxidises more thiol or reacts with water to yield hydroxide ions and oxygen.

Early attempts to show that peroxide was present in autoxidising systems of thiophenol[58] and cysteine[74] were not successful, although the rate of consumption of oxygen in the latter system was increased by the addition of hydrogen peroxide. Schoeberl[75] believed peroxide to be an intermediate in this system, and this was confirmed by Holtz and Triem[76] and by Schales[77], who added luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) and observed luminescence; this test being sensitive to 10^{-5} parts % of peroxide. This evidence is generally accepted by modern workers including Wallace and Schriesheim[50].

The autoxidation of thiols under basic conditions is very sensitive to traces of metals. In some cases the metal may be in the elemental form, but more usually it is present as the aquo-ion or some other complex. The recorded work may conveniently be sub-divided into work on carboxy thiols and work on simple thiols.

C.3 (b) Carboxy-thiols

Earlier workers surveyed the effect of a variety of metals, ions and complexes on the autoxidation of cysteine[4,78],

thioglycolic acid[79, 80] and glutathione[81]. Although there are some differences between the behaviour of these thiols, the ions and, in some cases, the free metals of transition and B sub-group elements are generally catalytic, and among these the catalytic effects of manganese, iron, cobalt, copper and arsenic have repeatedly been demonstrated.

Studies of the iron catalysed oxidation of cysteine in solutions buffered to pH 7 have shown that the rate was first order in iron[82, 83] and zero order in thiol[71]. The catalysis was inhibited by cyanide. In the presence of cupric ions in solutions buffered with pyrophosphate (pH 7.6) the kinetics were zero order in cysteine to over 50% oxidation[84]. Krebs[85] investigated the role of haemin as a catalyst for the oxidation of cysteine, and found the catalysis to be very sensitive to cyanide.

The results showed that the most probable mechanism of this catalysis by metal ions involved the formation of intermediate metal-thiol complexes, and schemes for the iron-catalysed oxidation of cysteine[86] and thioglycolic acid[87] were proposed. The first major work on the problem was that of Michaelis[88, 89], assisted chiefly by Barron and Schubert, who studied the cysteine complexes of iron, cobalt and nickel and their oxidation at pH 7 and 8. The oxygen uptake curves were again zero order in cysteine and it was found that cobalt and nickel were not good catalysts for this system. The conclusion reached was that the difference between iron and the other metals was due to decomposition of the iron-cysteine complex, which allows the iron to take part in an oxidation-reduction cycle.

Since the corresponding cobalt complex, $Co(SCH_2CHNH_2{\cdot}COO)_3H_2$[90] is stable, the cobalt can not be re-cycled, and the sequence of reactions has been suggested[91] to be:

$$Co^{II} + 3RS^- \rightarrow Co^{II}(RS^-)_3 \xrightarrow{O_2} Co^{III}(RS^-)_3$$

$$\rightarrow Co^{II}\left[(RS^-)(RSSR)\right] \qquad (46)$$

With iron replacing the cobalt, the complex reacts further with two molecules of free cysteine to complete the cycle:

$$Fe^{II}\left[(RS^-)(RSSR)\right] + 2RS^- \rightarrow Fe^{II}(RS^-)_3 + RSSR \qquad (47)$$

Nickel was not a good catalyst since "it is inconceivable that the nickelic state would ever be established by exposing the nickelous state to air"[91]. These conclusions were confirmed by the more recent work by Neville[92].

Complexes of iron and cobalt with thioglycolic acid were also studied by Michaelis and Schubert[93]. The stable brown complex formed when solutions of thioglycolic acid containing cobalt ions were aerated was found to have two cobalt atoms and four thioglycolate groups per molecule of the complex. The exact nature of the complex could not be established, but it is possible to write both cobalti-thiol and cobalto-disulphide formulae. The rearrangement of bonds by which the former becomes the latter might be responsible for the catalysis of thioglycolate oxidation by both cobalt and iron[94, 95].

Fruton and Clarke[57] studied the kinetics of the oxidation of cysteine and some derivatives in the presence of 10^{-3} M iron. The reaction was zero order in thiol for cysteine and thioglycolic

acid, but first order for a series of N-acylated cysteines. The solutions were buffered with a series of phosphate, borate and barbiturate buffers at M/15 concentration, which evidently modified the catalytic effect of the iron, since the rates differed sharply from one buffer to the next, whilst little dependence of the rate on pH was found within the range of a single buffer. The metal ions presumably formed complexes with the buffer molecules.

The cysteine-cystine redox system in the presence of iron has been studied polarographically by Kolthoff, et al.[96]. In aerated solutions at pH 10 to 11 an equilibrium exists between the complexes $[Fe(SR)_3]^{3-}$ and $[Fe(OH)(SR)_2]^{2-}$, where R is the group $^-S.CH_2.CHNH_2.COO^-$, but the equilibrium constants show that the ferro-disulphide complex is strongly favoured[97]. There was, however, evidence for a reverse reduction of cystine by ferrous ions, possibly through the equilibrium[98].

$$Fe^{II} + RSSR \rightleftharpoons Fe^{III} + RS^- + RS^{\cdot} \qquad (48)$$

This back-reduction may of course have been induced by the polarographic mercury. The catalytic effect of iron in this system was found to be eliminated by the addition of EDTA, and of much pyrophosphate, but was unaffected by tartrate.

Following Michaelis and Schubert's studies of the thioglycolic acid system in the presence of iron and cobalt, Kharasch et al.[99] have extended their kinetic work to copper and manganese ions. The effect of copper was greatest at pH 6 and 9, presumably due to stepwise ionisation of the thioglycolic acid, but catalysis was found to depend on the nature of the complex in solution.

Phosphates inhibited catalysis by manganese and iron, but accelerated that by copper.

Kolthoff and Leussing[100] made a photometric study of iron-thioglycolate complexes, and observed an intensely coloured ferric complex which was formed from the precipitated ferric hydroxide when thioglycolate was added to alkaline solutions. This complex was found to be $Fe^{III}[(OH)(RS)_2]^{2-}$. Leussing and Newman followed the anaerobic bleaching of the complex[101], and produced an elaborate mechanism involving a succession of one- and two- centred complexes to explain their findings.

The formal mechanism for the iron-catalysed autoxidation of thioglycolate:

$$Fe^{II} + RSH \longrightarrow Fe^{II}[RSH\ complex] \quad (49)$$

$$Fe^{II}[RSH\ complex] + O_2 \longrightarrow Fe^{III}[RSH\ complex] \quad (50)$$

$$Fe^{III}[RSH\ complex] \longrightarrow Fe^{II}[RSH\ complex] + RSSR \quad (51)$$

in which the nature of the complex is uncertain, was rejected by Lamfron and Nielsen[102] on the grounds that the separately measured rates of reactions (49) and (50) were much lower than the overall rate of autoxidation. They proposed further free-radical steps to account for the higher rate of oxidation:

$$Fe^{II}[RSH\ complex] + O_2 \longrightarrow Fe^{III}[RSH\ complex] + O_2^- \quad (52)$$

$$O_2^- + RSH \longrightarrow HO_2^- + RS^\cdot \quad (53)$$

$$RS^\cdot + Fe^{III}[RSH\ complex] \longrightarrow Fe^{II}[RSH\ complex] + RSSR \quad (54)$$

This is one of the few attempts to explain the fate of

the oxygen: the hydroperoxide ion would presumably produce further oxidation. These postulated reactions receive some support from the reported positive effect of hydroquinone and the detection of hydrogen peroxide as an intermediate under certain conditions (Section C.3 (a)).

A little work has been carried out on glutathione, which in contrast to cysteine and thioglycolic acid, was not catalysed by iron at pH 7. However, copper was effective, and this may have been due to the use of pyrophosphate buffers. The kinetics were zero-order in thiol[103]. The effectiveness of copper increased with pH, but haemin had an optimum effect at pH 8, and was insensitive to cyanide, in marked contrast to the corresponding cysteine system. With 1 molar % cuprous chloride in 0.02 mM glutathione at pH 8.7, the oxygen uptake curve was first order in thiol, and the final uptake was theoretical for oxidation to disulphide.

The kinetics and rate of oxidation in any particular system appear to depend upon the formation of a metal-thiol complex, its oxidation to a metal-disulphide complex, and the decomposition of the latter to give disulphide, possibly as a result of further attack by thiols. In such a system the balance may be disturbed by changes of pH, by competing ligands such as cyanide, and by the buffers used to maintain the pH. The wide variety of kinetic results obtained in systems of this type are probably a reflection of the delicacy of this balance.

C.3 (c) Simple aliphatic and aromatic thiols

The catalytic effect of metal salts and complexes on

the oxidation of simple thiols is probably one of the least understood aspects of thiol autoxidation. This is because such reactions take place only under strongly basic conditions, when most of the catalysts are precipitated as hydroxides, which may have an heterogeneous effect, while those metal-thiol complexes which are formed are of uncertain composition and concentration.

As with cysteine and the carboxy-thiols, the catalytic effect of a number of metals and salts has been recorded[104]. Transition metals generally, and especially copper, iron and cobalt have been investigated in detail. In the presence of these ions in aqueous solutions, disulphide is formed as the only detectable product[60, 104]. An oxidation-reduction mechanism has been suggested in which the catalyst is regenerated by electron transfer with the mercaptide ion, RS^-[105].

$$2M^{2+} + O_2 \longrightarrow 2M^{3+} + O_2^{2-} \quad (55)$$

$$2M^{3+} + 2RS^- \longrightarrow 2M^{2+} + 2RS^{\cdot} \quad (56)$$

$$2RS^{\cdot} \longrightarrow RSSR \quad (57)$$

$$O_2^{2-} + H_2O \longrightarrow 2OH^- + \tfrac{1}{2}O_2 \quad (58)$$

The actual catalysis is believed to take place through the formation of some kind of metal-thiol complex[106], but little is known of these or of their stability constants. The kinetic data in these systems are not simple; thus, for example, although ferric ions had a positive effect on the rate of autoxidation of ethanethiol, the rate was almost independent of the iron concentration from 10^{-4} to 10^{-2} M[57].

One of the most comprehensive investigations into the catalytic effect of transition metal ions has been completed by Hopton[66], who studied the kinetics of the oxidation of ethanethiol and a number of other simple thiols in the presence of copper, cobalt, iron and manganese catalysts. Reaction schemes were suggested for copper and cobalt catalysis; in the latter case, two schemes were suggested, respectively involving "inner sphere" and "outer sphere" electron transfer. The effects of various complexing agents on the rates of reaction were also considered, and in particular cyanide ions were found to have a pronounced inhibiting effect on the reaction.

Similar effects have been observed in the oxidation of 1-octanethiol by ferricyanide, which has been studied by Kolthoff, et al.[107, 108] and by Gorin and Godwin[109]. In 60-70% aqueous acetone solution at 50°C, the kinetics were found to be first order in thiol, ferricyanide and hydroxide. In the absence of excess cyanide the reaction proceeds through an intermediate complex in which a thiol anion has displaced a cyanide ligand:

$$Fe(CN)_6^{3-} + RS^- \rightleftharpoons Fe\left[(CN)_5(SR)\right]^{3-} + CN^- \qquad (59)$$

$$Fe\left[(CN)_5(SR)\right]^{3-} \xrightarrow{\text{fast}} Fe(CN)_5^{3-} + RS^{\cdot} \qquad (60)$$

$$Fe(CN)_5^{3-} + CN^- \xrightarrow{\text{fast}} Fe(CN)_6^{4-} \qquad (61)$$

$$2RS^{\cdot} \longrightarrow RSSR \qquad (62)$$

The reaction is slowed by excess cyanide, proceeding under these conditions by electron transfer from the thiol anion to the iron through its intact ligand shell of six cyanide ions:

$$RS^- + Fe(CN)_6^{3-} \longrightarrow Fe(CN)_6^{4-} + RS^\bullet \qquad (63)$$

In the presence of oxygen these reactions could form part of an oxidation-reduction cycle, but no detailed mechanism has been worked out for any practical system.

In addition to inhibition by cyanide, the oxidation of 1-octanethiol by ferricyanide is inhibited by EDTA[109]. This inhibition was ascribed to the removal of catalytic trace metal impurities by complexing with the EDTA. A reaction mechanism was suggested in which the ferricyanide reacts not with the mercaptide ion but with a metal-thiol complex:

$$RSM^+ + Fe(CN)_6^{3-} \longrightarrow RS^\bullet + Fe(CN)_6^{4-} + M^{2+} \qquad (64)$$

in contrast to the mechanism put forward by Kolthoff, et al.

In studies of the oxidation of various thiols with ferric octanoate in xylene in the absence of oxygen, disulphides were produced as the exclusive products[110]. Rate studies in xylene and acetone, indicated that the reactions were rapid and obeyed second order kinetic laws; rate constants for the oxidation of α-toluenethiol and 1-dodecanethiol varied from 7.50×10^{-1} to 5.83×10^{-2} $l.mole^{-1}$ sec^{-1} at 25°. The radical nature of the reactions was confirmed by trapping the thiyl radicals with an olefin.

Similar studies have been made by Overberger, et al.[111], who investigated the oxidation of polyvinyl mercaptan by ferric sulphate in dimethyl sulphoxide, the disulphide being formed as the only product. The rate of oxidation was directly proportional to the iron concentration and was sensitive to the structure of the thiol

substrate. A kinetic scheme was proposed involving rapid formation of a ferric-thiol complex, a slow rate-determining reduction of the complex by thiol, and finally rapid regeneration of the ferric complex by autoxidation.

The investigations discussed above have all involved reactions in which the metal was either added to the solutions, or was present in the solutions as a soluble salt. A number of instances have been recognised where the metal catalyst may have an heterogeneous effect.

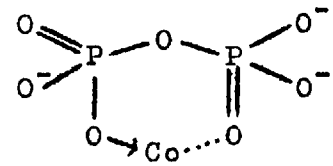
One of the more comprehensive investigations into systems of this type has been made by Wallace, et al.[105, 112, 113, 114], with a view to the use of these catalysts in commercial processes. Investigations with 2M 1-butanethiol and 2M sodium hydroxide in the presence of 100 mg cobalt phthalocyanine (whose commercial use has been patented[21]) showed that essentially quantitative conversion to the disulphide was obtained in 2 hours, whereas in the absence of added catalyst only 18% conversion was obtained in the same period.

In a similar investigation, Yokote, et al.[115] studied the oxidation of thiols by a cobalt phthalocyanine nitrogen isolog (cobalt tetra-2,3-pyridinoporphyrazine) in aqueous sodium hydroxide, and found that this complex was as active as cobalt phthalocyanine for the oxidation of 1-butanethiol. Further experiments were concerned with petroleum feedstocks containing unspecified thiols.

Investigations on the oxidation of 1-butanethiol have shown that cobalt pyrophosphate was of similar catalytic ability to cobalt phthalocyanine and was much greater than that of the

phosphomolybdate, phosphotungstate or phosphate[105, 112, 113]. It was suggested that the catalysts were acting in an heterogeneous manner, since the catalytic activity apparently increased as the catalyst particle size decreased.

The activity of the pyrophosphate catalyst was attributed to the existence of six-membered rings involving the cobalt cation[116]:



This enhances the ability of the cation to donate an electron to oxygen and stabilises each oxidation state of the cation. This situation also exists in cobalt phthalocyanine. For a series of pyrophosphates, the order of activity was Co > Cu > Ni > Fe, and this may be explained in terms of the stability of the 3d-electron shells. Thus the oxidation-reduction of cobalt (II) and copper (I) pyrophosphate would be expected to proceed readily, but the Co^{II} ($3d^7$) would be more easily oxidised than Cu^{I} ($3d^{10}$ or $4p^6$), which is also stable in the Cu^{II} state. Oxidation of Ni^{II} ($3d^8$) to $Ni^{(III)}$ is possible but not as favourable. The Fe^{II} catalyst ($3d^6$) would undergo oxidation to Fe^{III} ($3d^5$), but the reduction step would be difficult due to the stability of the half-filled 3d electron shell.

The oxidation of thiols by four transition metal oxides in xylene has been studied at 55° in the absence of oxygen[114]. In all cases studied, oxidation to disulphide was observed, manganese dioxide being the most active, with ferric oxide, cobaltic

oxide and cupric oxide displaying similar oxidising capabilities. The rate of oxidation was not affected by the thiol structure and acidity but was dependent on the rate of agitation. The rate-determining step is thought to be thiol adsorption on the surface of the metal oxide. Oxidation studies in the presence of an olefin resulted in the formation of sulphides, apparently as a result of a low-temperature, free-radical addition reaction in which the metal oxide functions as an initiator for the production of thiyl radicals:

$$RSH + Mn^{IV}O_2 \longrightarrow RS^{\bullet} + HOMn^{III}O \quad (65)$$

$$RSH + HOMn^{III}O \longrightarrow RS^{\bullet} + Mn^{II}O + H_2O \quad (66)$$

$$2RS^{\bullet} \longrightarrow RSSR \quad (67)$$

$$RCH{=}CH_2 + RS^{\bullet} \longrightarrow R\dot{C}H.CH_2SR \quad (68)$$

$$RSH + R\dot{C}H.CH_2SR \longrightarrow RS^{\bullet} + RCH_2CH_2SR \quad (69)$$

Clearly the metal-catalysed oxidation of simple aliphatic and aromatic thiols in strongly alkaline solutions is the least understood aspect of thiol oxidations.

D THE PRESENT WORK

The previous survey of published work has shown that, although the oxidation of carboxythiols is by no means fully understood, there is even less complete understanding of the oxidation of simple thiols in strongly alkaline solutions.

This thesis therefore describes an investigation of the metal-catalysed oxidation of thiols in aqueous alkaline solutions in the temperature range 20-50°C. Measurements have been made of the rate of oxidation of a variety of aliphatic and aromatic thiols by a

range of transition and non-transition metals, added to the solutions as simple salts and as complexes. The nature of the catalysis has been established for certain systems, and the catalytic species have been elucidated. Mechanisms are proposed in which metal ions promote electron transfer from thiol anions to oxygen in a redox cycle. A number of metal-thiol complexes have been isolated and the catalytic activity of these complexes has been investigated. The kinetics of the reaction of thiols with certain catalysts are compared with the kinetics of the oxidation of thiols in the presence of such catalysts.

EXPERIMENTAL

EXPERIMENTAL

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EXPERIMENTAL

E. APPARATUS

1. Apparatus for measuring oxygen uptake by solutions

All measurements of the gas uptake by solutions were made with the apparatus shown in Plate 1 and diagrammatically in Fig. 1. The system was similar in principle to the apparatus described by Bolland[117]. In so far as the reagents were shaken together in a closed system, the apparatus may be termed static. The reaction was followed by measuring the decrease in the volume of oxygen at a pressure which was automatically maintained at a constant pre-set value.

1(a) Reaction vessel and sampler

The reaction vessel and sampling system are shown schematically in Fig. 2. Tap numbers and ground glass joint letters mentioned in the text refer to these Figures. The reaction vessel consisted of a flattened spherical flask, containing a sampling cup of 4.0 ml capacity, connected to tap 3 and ground glass cone B by a capillary tube through an internal seal at the bottom of the flask. The neck of the flask was closed by a rubber Suba-seal 30 serum cap. The vessel was connected to the working line by means of a flexible glass spiral which consisted of 7 turns of 5 cm diameter, made from 3 mm bore thin walled tubing. The spiral led to microtap 4 and ground joint C, which was used to connect the vessel to the line. The neck of the reaction vessel and part of the sampling tube were clamped to a recessed wooden block to which the shaker was attached. The reaction vessel was designed to give maximum contact between the gaseous and liquid reagents when shaken, and thus to minimise

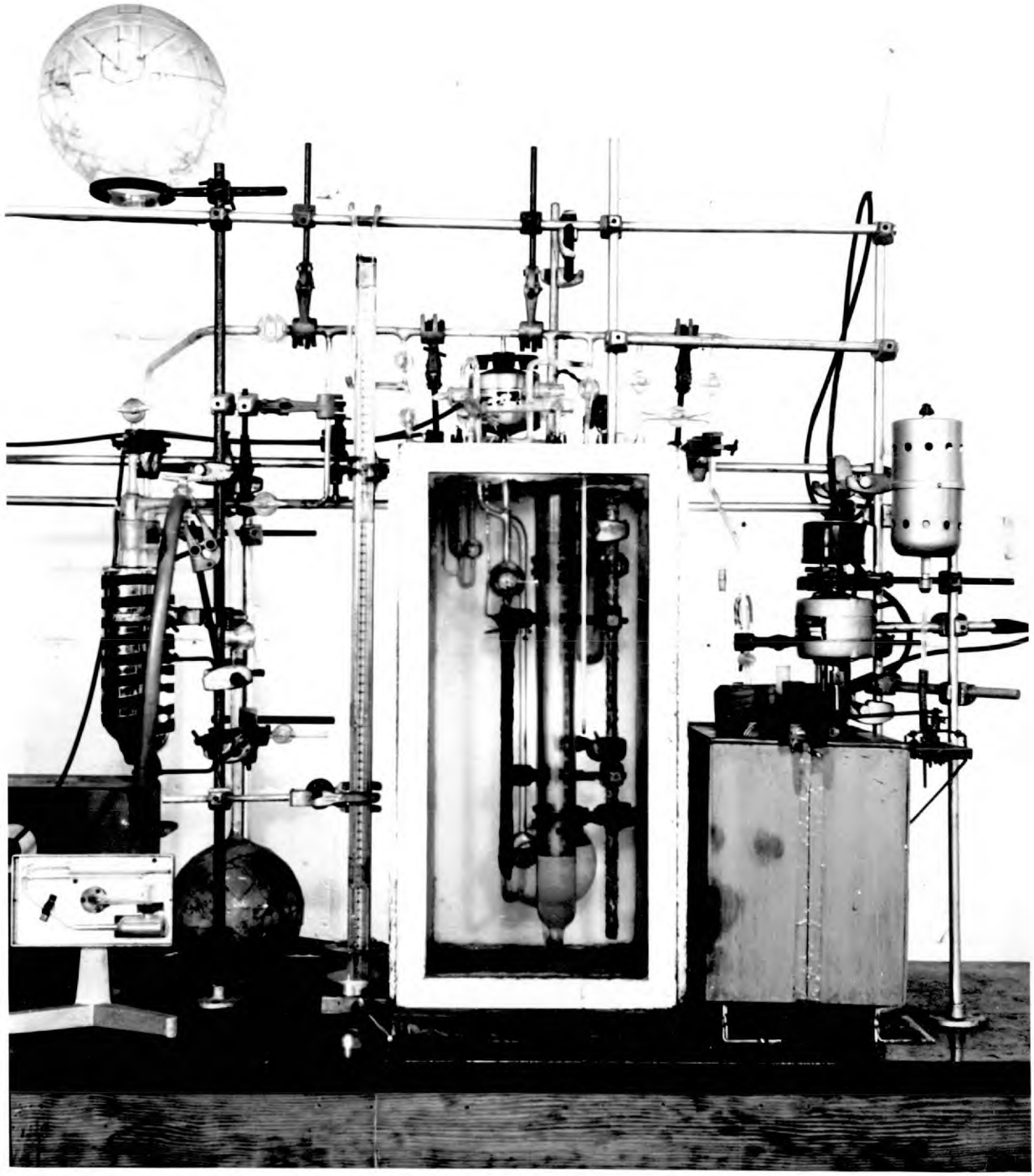


Plate 1. Apparatus for the measurement of oxygen-uptake by solutions

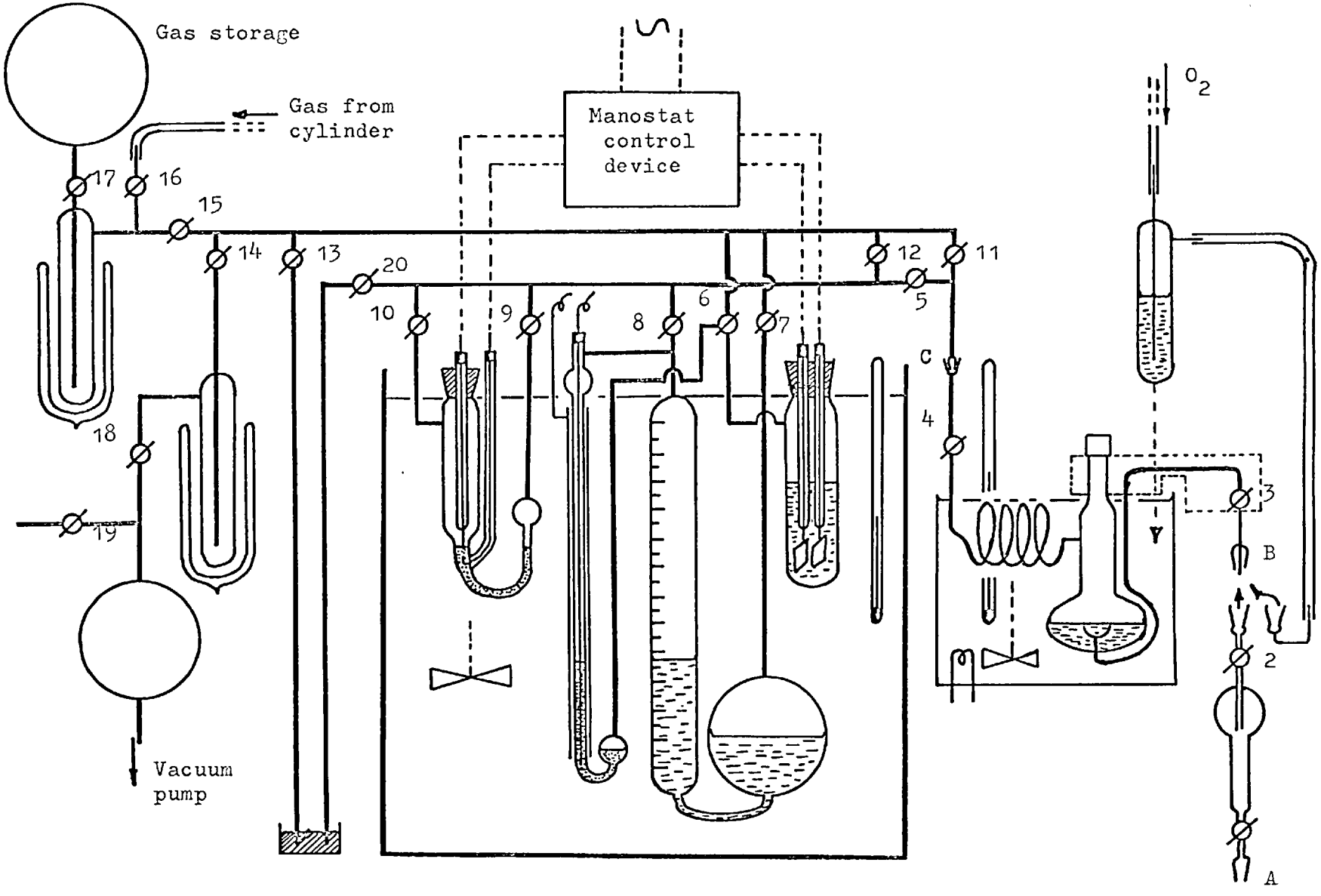


Fig. 1. Apparatus for the measurement of oxygen-uptake by solutions

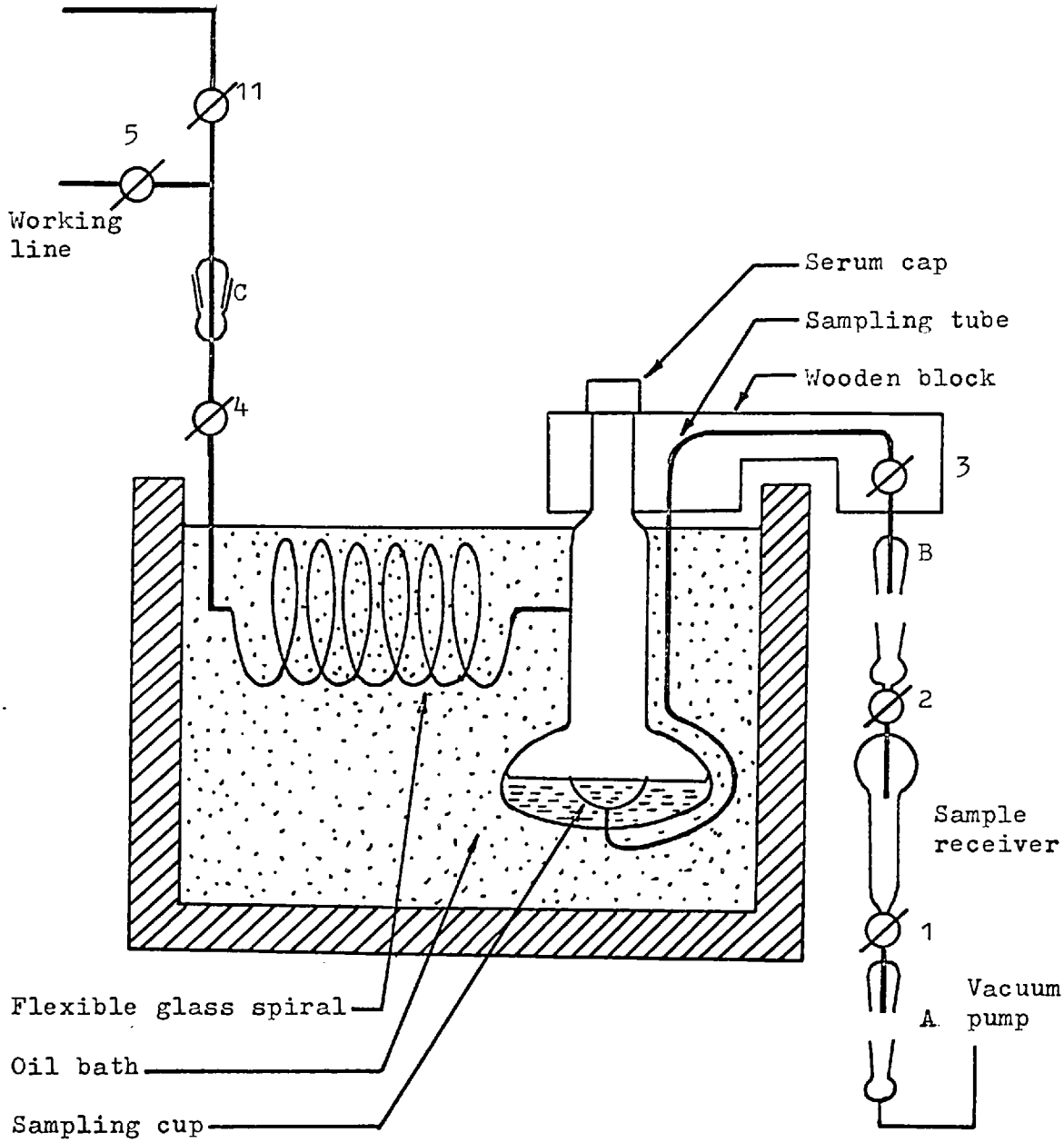


Fig. 2. Reaction vessel and sampling system

diffusion effects. The bulb of the vessel shown in Fig. 2 had a capacity of 50 ml up to its equator, giving a surface/volume ratio of about 0.75 cm^{-1} when the liquid was at rest.

The cup mounted in the reaction vessel was developed as a device for sampling a heterogeneous mixture of liquids in their bulk proportions. The rim of the cup was about 1 mm above the surface of the reactant solution(50 ml) when the vessel was at rest. When the unit was shaken, the homogenised liquid phase slopped into and out of the cup, which therefore collected a representative sample, which was isolated immediately shaking had ceased and the liquid had come to rest. Although the immiscible phases then rapidly settled out, the isolated sample still contained the phases in their bulk proportions. Although the capacity of the cup was 4.0 ml, the actual volume of samples was determined by chance and was usually 1-2 ml.

The reaction vessel and spiral were immersed in a bath of liquid paraffin, the temperature of which was controlled by a Sunvic F 103-S thermostat unit. The temperature could be pre-set to any value from 25 to 70° C and was automatically controlled to within 0.1° C at 30° C.

The reaction vessel was shaken in a direction perpendicular to the plane of Fig. 2 by a device made from Meccano parts. The frequency of shaking could be varied by means of the variable speed control on the electric motor. The motor was geared down and was attached by a crank wheel and connecting rod to the wooden block which held the reaction vessel, thus enabling the vessel to be shaken

with a reciprocating motion. A Meccano beam was attached to one end of the wooden block and was mounted above the glass spiral and parallel to its axis. The vibrating length of the beam was adjusted by means of a slotted wooden block to give a steady resonant frequency of oscillation, thus minimising wear on the moving parts by forced vibrations. The wooden block which held the reaction vessel was mounted on two small rubber tyred wheels, which ran in tandem on the broad smooth rim of the thermostat tank. This reduced the tendency of the reaction vessel to pitch owing to the viscous drag of the oil in which the lower parts of the vessel were immersed.

1(b) Gas burette

The oxygen uptake during kinetic experiments was measured as a decrease in volume at constant pressure by means of the gas burette, which is shown schematically in Fig. 1. The left hand (front) limb of the burette had an etched scale reading to 500 ml by 2 ml divisions, and 1 mm length on the scale corresponded to about 1 ml volume. The burette contained silicone oil type MS 550, which is suitable for this use, having a low density and negligible vapour pressure. Diffuse illumination from the rear produced a sharply contrasted meniscus and permitted reading of the burette to 0.1 ml.

The burette and manostat cells (see Section E.1(c)) were immersed in water in a large glass walled tank (1 ft square, 2 ft high) The water served as a large thermal capacity which damped the effect of variations in the ambient temperature on the gas in the burette and cells. The water in the tank was stirred but not thermostatted, and was insulated on three sides by half-inch sheets of expanded

polystyrene. Variations of 0.5-1° C in the water temperature were observed during day-long experiments, and the burette readings were therefore always corrected to a standard temperature for each experiment. The burette readings were also corrected for the small pressure variations which occurred during the manostat switching cycle. Details of these corrections are given in Appendix 1.

1(c) Manostat

Constant pressure in the working line of the apparatus was maintained during kinetic experiments by means of an automatic manostat, consisting of three parts: the pressure sensing cell, the electronic switching device and the electrolytic gas-generating cell. The two cells are shown in Fig. 1.

When the pressure in the working line fell below a pre-set standard value, the electric circuit through the sensing cell was broken, and the switching device allowed a small current to pass through the electrolytic cell. The pressure of the generated gas was applied to the back limb of the burette, thus raising the level and decreasing the volume in the front limb until the working pressure was restored to the standard value. The circuit in the sensing cell was thereby closed, and gas-generation stopped.

The sensing cell contained an electrolyte consisting of a saturated solution of sodium nitrite in propane-1,3-diol. This electrolyte was chosen because it does not release any gas when passing a current, and it has a negligible vapour pressure. During experiments one limb of the cell was open to the working line, while the other was closed by tap 10, and provided the constant reference

pressure. The closed limb of the cell contained two sealed-in platinum wire electric contacts. One of these was sealed in to the U-tube well below the surface of the electrolyte, while the other was held vertically above the electrolyte surface, and was ground to a point in order to reduce the effect of surface tension. The manostat system was controlled by making and breaking contact between this probe and the electrolyte surface.

The electrolytic cell contained two platinum electrodes each of about 1 cm^2, 1 cm apart, immersed in 50% sulphuric acid. Hydrogen and oxygen were thus generated by the passage of a direct current through the cell.

The circuit diagram for the switching device is shown in Fig. 3. Two separate 12 volt power supplies were used to minimise the voltage drop when current passed through the transistor OC 35. The variable resistor VR1 was used to adjust the current passing through the electrolytic cell. The grid-bias battery B1 was used to overcome the effects of polarisation in the sensing cell, 4.5 to 6 volts being a suitable value for this purpose.

The limits within which the pressure could be controlled with this manostatic arrangement depend chiefly upon the design of the sensing cell and the absolute pressure. If the sensitivity of the cell is defined as the change in the electrolyte level in the reference limb per unit pressure change in the working line, the Boyle's law calculation given in Appendix 2 shows that the sensitivity would be increased by enlarging the volume of the reference limb, and by decreasing the bore of the glass tubing where contact was made and

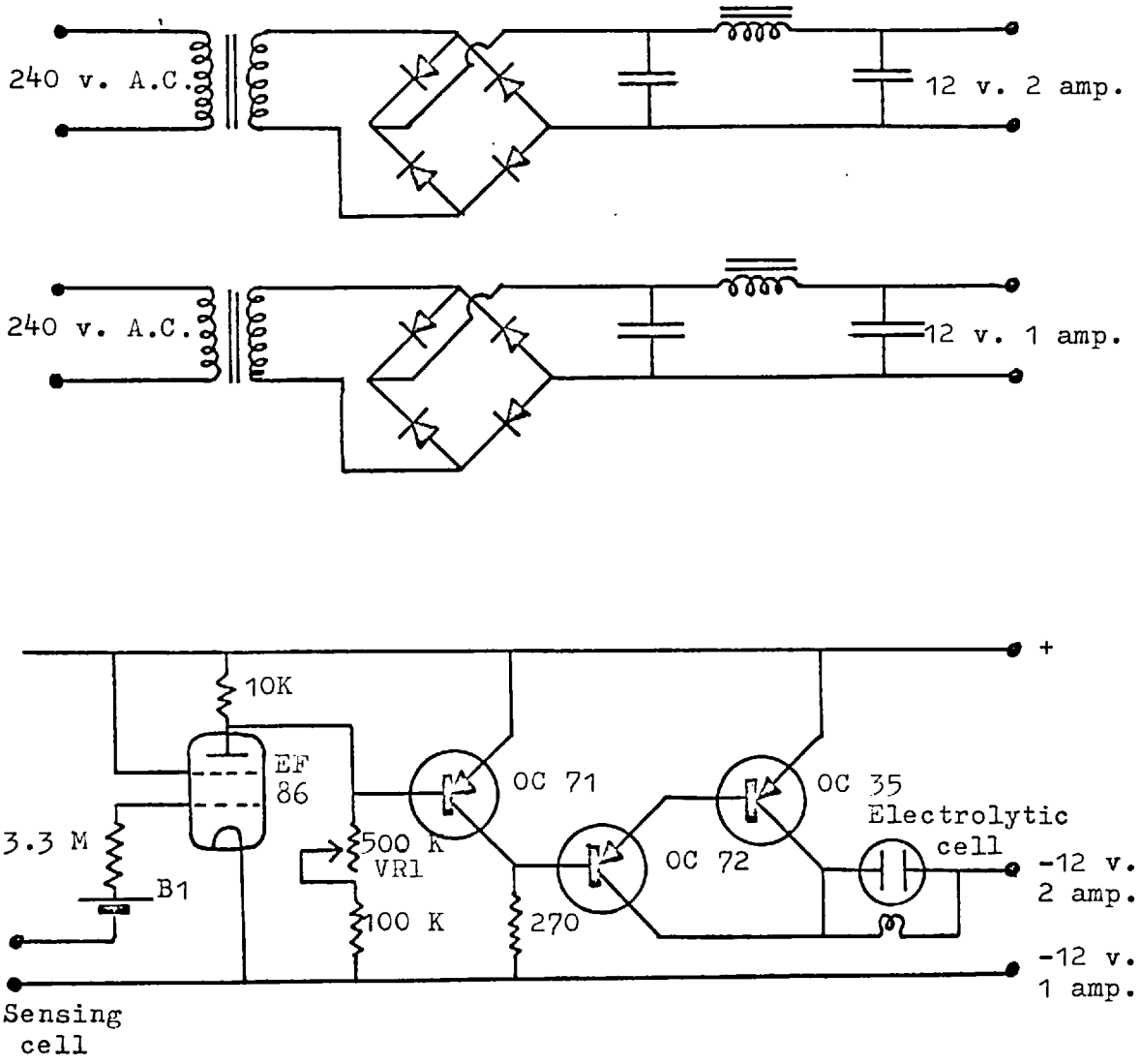


Fig. 3. Circuit diagram for manostat control device

broken in the cell. The cell was designed with these principles in mind, and was found to control the pressure to within ± 0.2 mm at 760 mm.

The two cells of the manostat were immersed in the water tank with the gas burette, thus allowing correction of the burette readings to be made for fluctuations in temperature and pressure.

1(d) Automatic burette level recorder

The oxygen-uptake measuring apparatus included a device for recording automatically the gas burette level. The arrangement is shown in Fig. 1 and in Fig. 4.

Changes in the burette oil level were paralleled by changes in the level of propane-1,3-diol in a U-tube bridging the limbs of the burette, both levels being determined by the same pressure difference. The U-tube was constructed such that changes in the level of propane-1,3-diol produced corresponding changes in electrical capacity. This capacity cell was made the variable arm of a Fielden Electronics "Telstor" capacity bridge unit. The out of balance current was amplified and passed to a Fielden "Servograph" circular chart recorder.

The front limb of the U-tube was blown out into a bulb, so that changes in pressure produced the maximum movement in the level of propane-1,3-diol in the rear limb, which was the capacity limb. This consisted of a piece of glass tubing of uniform bore (9 mm) and wall thickness (1 mm). The tube was surrounded by a sleeve of aluminium foil bound tightly with copper wire. The sleeve formed one plate of the capacity cell, the other being a bronze-welding rod

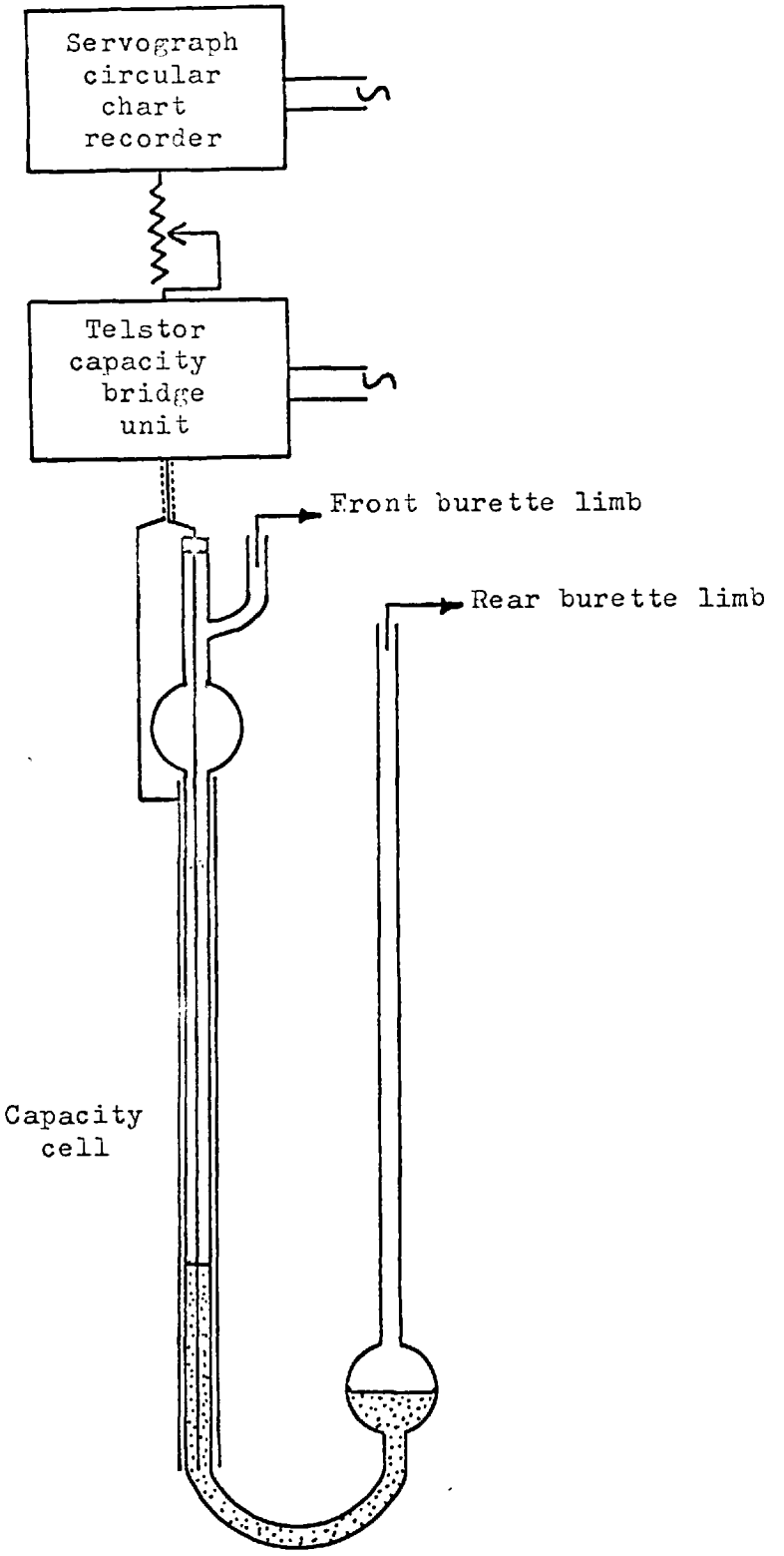


Fig. 4. Automatic burette level recorder (schematic)

of 1/16 inch diameter, which was mounted concentrically in the glass tube, and to which electrical contact was made through a platinum-glass seal. The dielectric material was therefore the 1 mm thick Pyrex wall of the tube, together with oxygen and propane-1,3-diol, the relative amount of the latter being proportional to the oil level in the gas burette. The outer cylindrical metal plate was insulated by a thick coating of Picien wax, and the entire U-tube unit was surrounded by a water-proof polyethylene bag, with spacers of expanded polystyrene to minimise the capacity effect of the water in the earthed tank.

The capacity cell was connected to the Fielden "Telstor" capacity unit type LF3 by coaxial cable. The output from the "Telstor" unit was passed through an attenuating rheostat to the Fielden "Servograph" circular chart recorder type RF1, which had a 24 hour period of rotation. The chart was graduated in 100 arbitrary units.

A full-scale deflection on the "Servograph" was produced by a change of approximately 0 to 350 ml on the burette scale. The calibration curve was very nearly linear between these limits, and the stability of the instruments was found to be good ($\pm$ 1%). The device was used in long experiments, (up to 200 hr.), together with visual checking of the burette level from time to time. The device was not used in short experiments.

1(e) Gas-introduction line

The gas-introduction line consisted of an inlet to which gas storage cylinders could be connected, a combined manometer and

blow-off tube, a trap which could be surrounded by an appropriate coolant, and a 5-litre gas-storage globe. The arrangement is shown in Fig 1. The use of this arrangement to admit, purify, and store gases is described in Section F(f).

1(f) Pumping line

The entire apparatus was served by one Metrovac DR1 two-stage rotary vacuum pump (Fig.1). This enabled the apparatus to be pumped rapidly down to below 0.05 mm pressure.

1(g) Lubricants

All taps and ground joints were greased with Silicone High Vacuum Grease from Edwards High Vacuum Ltd. Taps were cleaned with trichloroethylene or chloroform prior to regreasing.

1(h) Hypodermic needles and syringes

Thiols were extracted and transferred from their storage vessels in measured volumes by means of a hypodermic needle and syringe. This method minimised the exposure of thiols to the atmosphere, and thereby reduced aerial contamination of the thiol and the escape of objectionable odours. In order to minimise contamination of the thiol by the metallic needle, the syringe and needle were stored at -10° C, and the thiol was handled only at 0° C.

All-glass 2 ml and 5 ml "Accoson" brand syringes supplied by McCarthy (Romford) Ltd. were used, together with No. 15 stainless steel needles. The syringes were calibrated to 0.05 ml and allowance was made for the calibrated 0.15 ml volume of the needle and Luer fitting.

2. Apparatus for the preparation of complexes

The existence of metal complexes of carboxy-thiols has

been recognised for many years[88, 89], but much less has been published on similar complexes of simple aliphatic and aromatic thiols. At the time the research reported in this thesis was started, the only information on metal complexes of simple thiols appeared to be provided by the work of Jensen[118] on nickel complexes, Mann and Purdie[119] on palladium complexes and McCormick and Gorin[120] on cobalt complexes.

More recent publications include the work of Hayter and Humiec[121] on nickel and palladium complexes, a number of investigations into cyclic hexameric nickel complexes[122, 123, 124], and the work of Ahmad, Bruce and Knox on complexes which also contain a π-bonded ligand[125]. Publication of the recent papers mentioned above, together with a review by Livingstone[126] and the spectral and magnetic data reported by Bradley and Marsh[127], has shed considerable light on the formation and properties of metal complexes of simple thiols, but has not removed the need for further work on the subject.

In order to study such metal-thiol complexes as may be produced during the course of a kinetic experiment, an apparatus was constructed to enable the formation of such complexes to be studied under controlled conditions. Details of the apparatus, and of the purification of complexes, are given in the following two sections.

2(a) Bubbler vessel

The bubbler vessel is shown schematically in Fig. 5. The vessel consisted of a sperical flask of 150 ml capacity, to which were sealed two glass tubes such that one was above the level of the reactant solution in the flask (generally 50 ml), the other being at

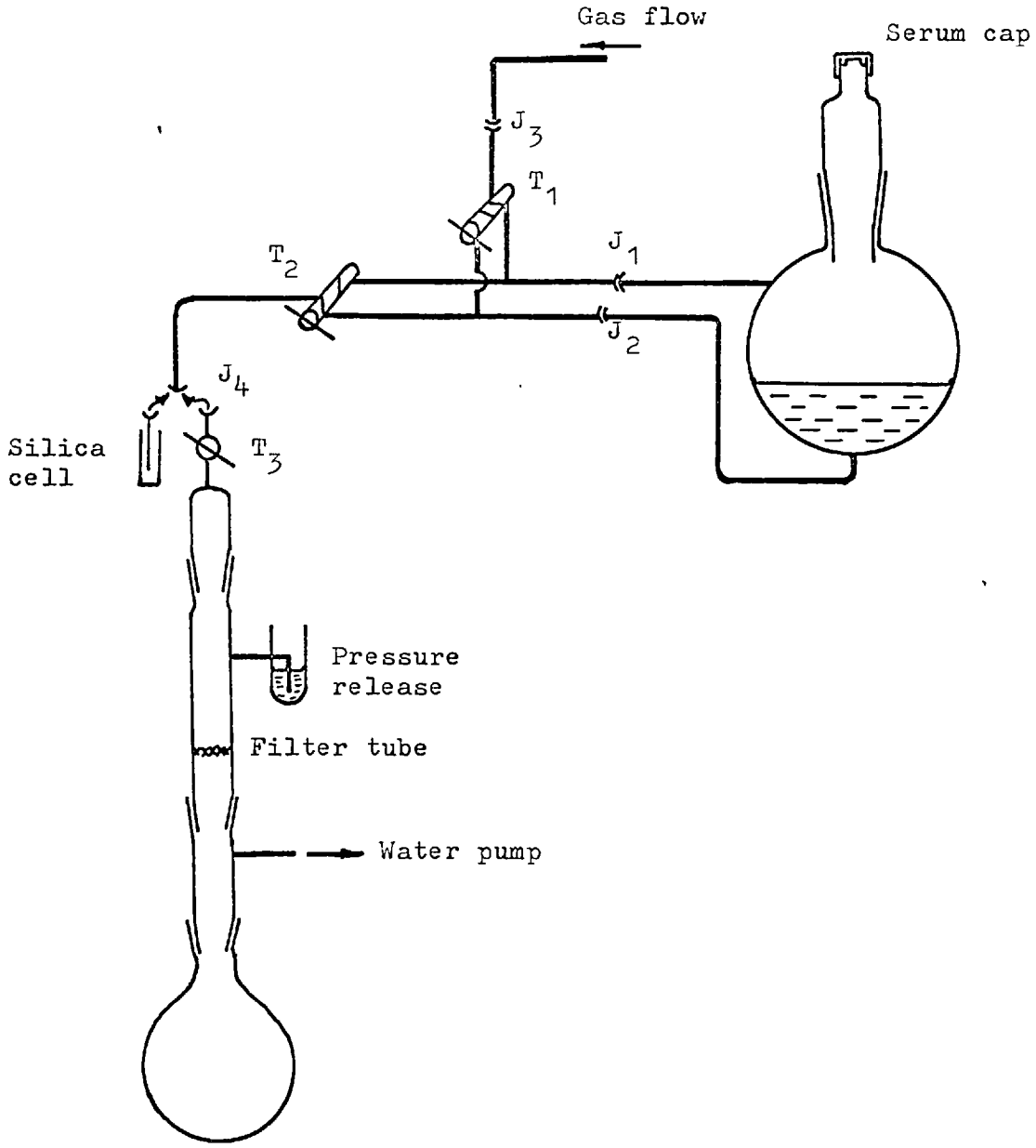


Fig. 5. Bubbler vessel and sample collection apparatus

the bottom of the flask and thus always below the level of the reactant solution. The neck of the flask contained a ground glass joint which was closed by a rubber Suba-seal 30 serum cap.

The two tubes joined to the vessel could be connected by means of the spherical ball and cup joints J_1 and J_2 to a device enabling compressed gas from a cylinder to be admitted to the reactant solution. This device consisted of two double oblique stopcocks T_1 and T_2 such that the direction of gas flow through the system could be reversed. Thus, in order to agitate the reactant solution, the stopcocks T_1 and T_2 were turned such that the gas, which was admitted via the spherical joint J_3, passed through joint J_2 and into the bubbler vessel through the tube sealed into the bottom of the vessel. The solution in the vessel was thus agitated by the passage of the gas, which emerged from the vessel via joint J_1 and stopcock T_2, leaving the system through spherical joint J_4.

By reversal of the direction of the flow of gas through stopcocks T_1 and T_2, the gas could be admitted to the vessel via joint J_1. The pressure of the gas in the vessel could thus be used to expel the reactant solution from the vessel via joint J_2, stopcock T_2 and joint J_4. The emerging solution could either be collected in a spectrophotometric cell, enabling ultraviolet and visible spectral data to be obtained, or the solution could be collected in the sample-collecting device shown in Fig. 5. This consisted of a sintered glass filter tube, equipped with a side arm attached to a small bubble tube to allow the release of the gas being used to blow the sample through into the tube. The reactant solution could be

completely contained within the filter tube, in which any solid residues could be removed for examination by means of the sintered glass filter, the liquid products being sucked through into a receiving flask by means of a water pump.

2(b) Purification apparatus

Solid samples collected in the filter tube described above were dried in a vacuum desiccator, and were in some cases extracted with solvents in a conventional Soxhlet apparatus supplied by Quickfit and Quartz Ltd. Further details of the techniques employed are given in Section G(b).

3. Stopped-flow apparatus

Measurements of the rates of reaction of thiols with certain metal complexes were made with the apparatus shown in Plate 2 and diagramatically in Fig. 6. The apparatus employs the "stopped-flow" technique[128], and has several features in common with published methods of studying rapid reactions[128]. Thermostatted syringes, driven with a variable speed motor, were used to force solutions of the thiol and of metal ions through an eight-jet mixing chamber into a spectrophotometric cell. Changes in the absorbance of the reacting solution were measured as a function of time using a Unicam SP 800 spectrophotometer.

Reactant solutions could be drawn into the syringes at the start of a series of experiments with the aid of a rotary vacuum pump connected to tube B. The reactant solutions, which were admitted to the system through tubes A and A^1, were maintained in flasks in a thermostatted tank supplied by A.Gallenkamp and Co.Ltd.

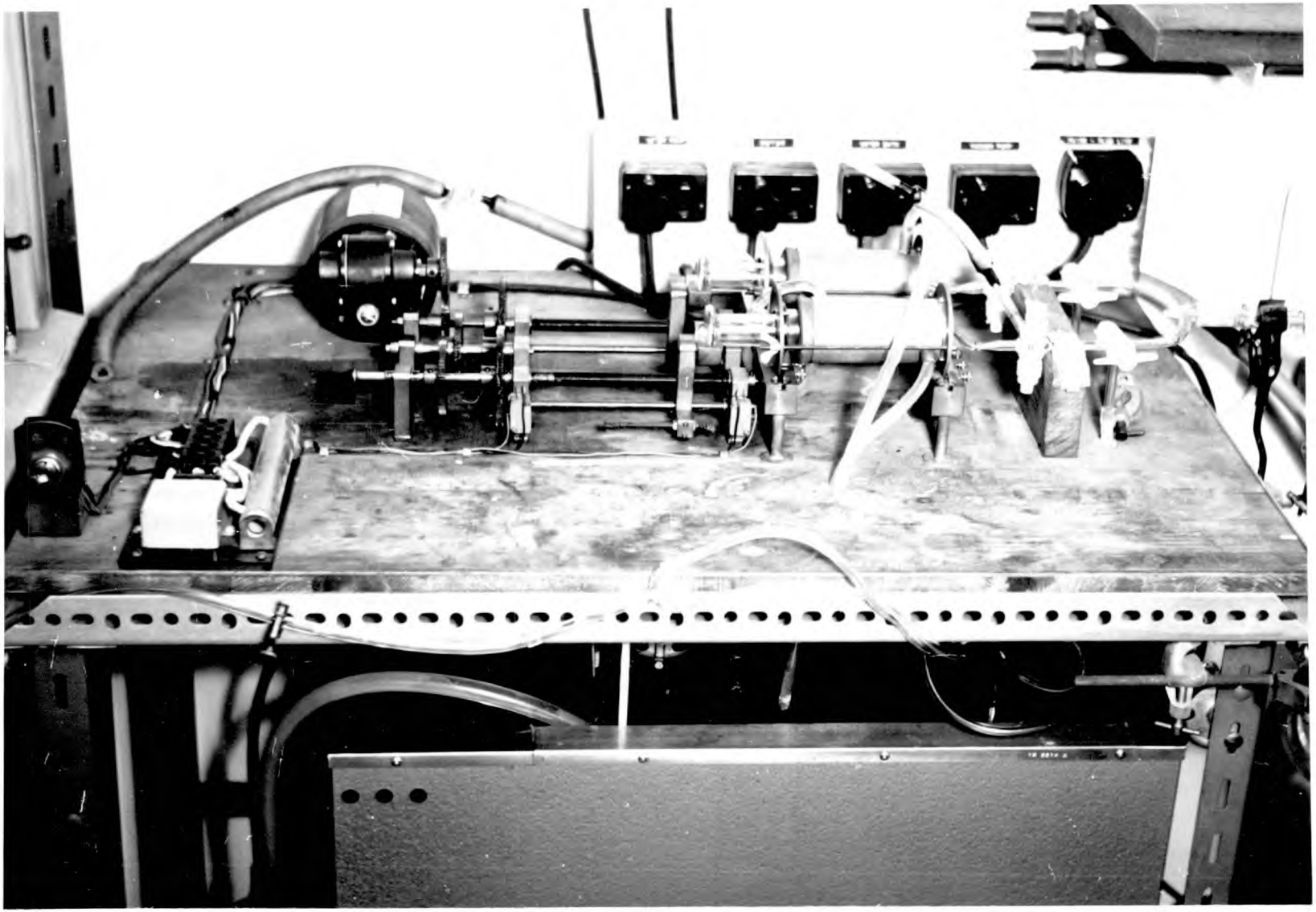


Plate 2 Stopped-flow apparatus

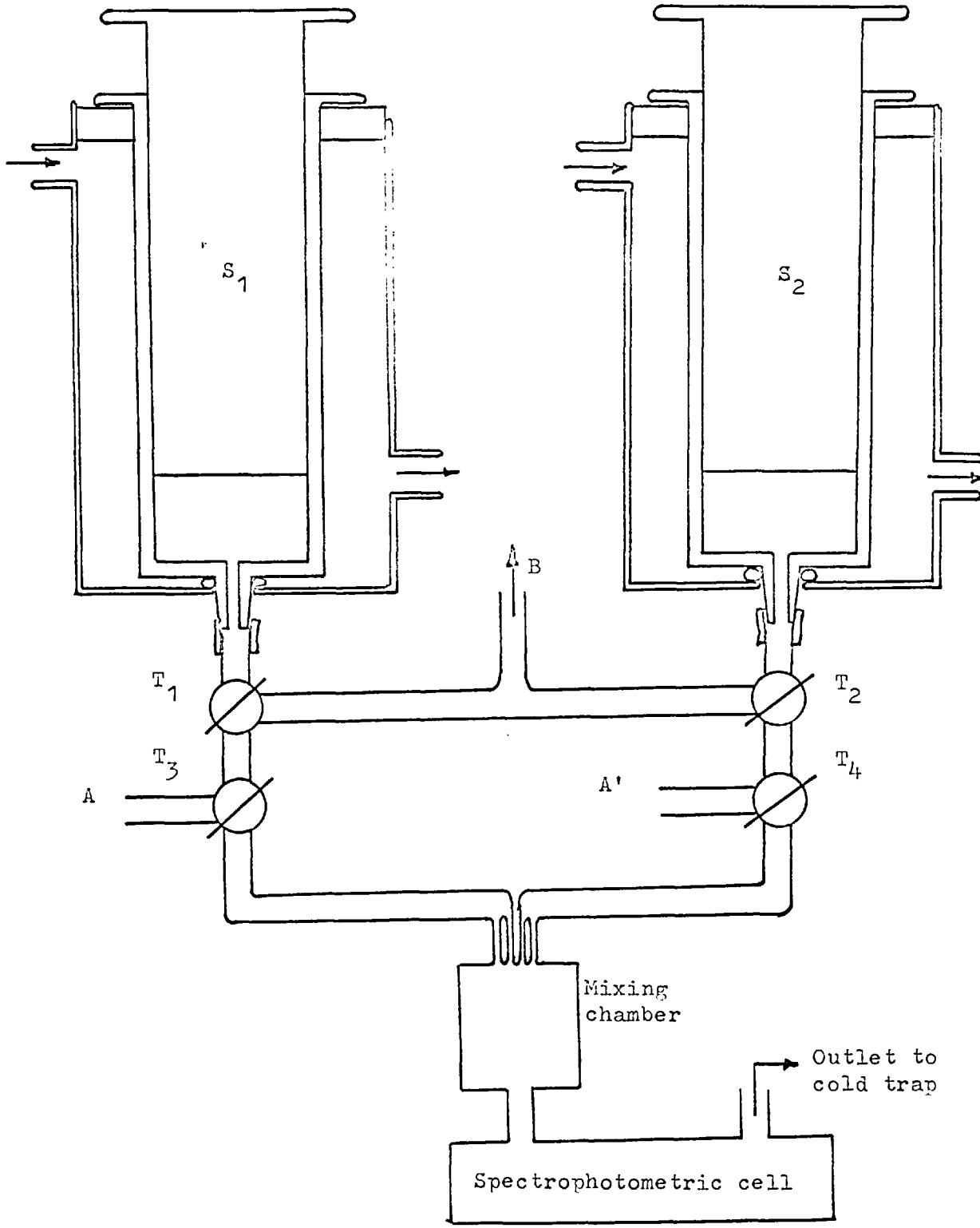


Fig. 6. Stopped-flow apparatus (schematic)

The syringes were all-glass, of 50 ml capacity, (Chance Surgical Equipment Ltd.) and were enclosed in asbestos-lagged brass jackets, which were maintained at a constant temperature by the circulation of water from the thermostatted tank. Water circulation was effected by a small electric water pump (type C15/50, Charles Austen Pumps Ltd.) Using this arrangement, the temperature of the reactant solutions could be controlled to within $\pm 0.2^{\circ}$ C at 25° C. Taps T_1 to T_4 had interchangeable PTFE keys and were obtained from G.Springham and Co.Ltd. These taps can be used satisfactorily in alkaline solutions.

3(a) Drive mechanism

The mechanism for driving the plungers of the syringes is shown in Fig. 7. The syringe operators moved along two lengths of 7/16" BSF screwed mild steel rod, R_1 and R_2. The speed and direction of rotation of these rods was controlled by a Type AB 93 governor controlled variable speed geared reversible motor, supplied by Citenco Ltd. The motor operated through a system of 40 DP steel gears from G. and K.Osborne Ltd. (Bridgwater). The arrangement was such that the ratio of the speeds of the syringe operators on rods R_2 and R_1 could be 1:1 or 2:1. For a 1:1 ratio, gears A(120 teeth), B(60 teeth) and A_1(120 teeth) were in mesh, and gears C and C_1(90 teeth) were out of mesh. For a 2:1 ratio, gears C and C_1 were in mesh, and gear $A_1$was taken out of mesh with gear B, the drive from the motor, through gears D(100 teeth) and D_1(32 teeth) being left in mesh throughout. In order to prevent the syringe operators from over-running, micro-switches S_1 and S_2, operated by the spring-loaded pushers, P_1 and P_2, cut off the current to the motor on the backward

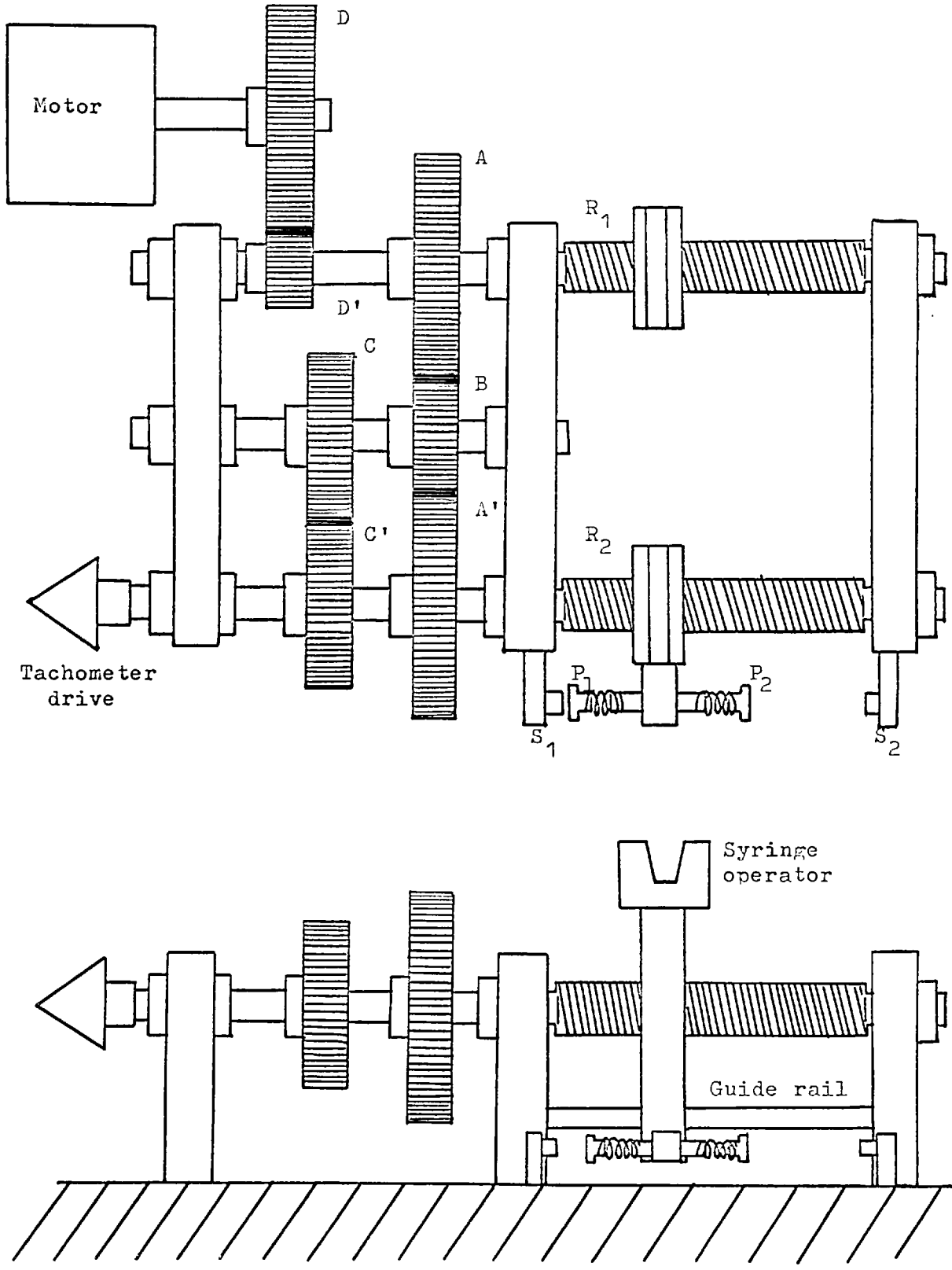


Fig. 7. Stopped-flow gear arrangement

and forward movements respectively. Since the movement of the plungers ceased almost instantaneously when the current to the motor was cut off, the micro-switches were employed as a convenient means of stopping the flow of the reactant solutions.

A tachometer drive was incorporated on the end of rod R_2, to enable accurate values of the speeds of the syringe operators to be obtained. A hand tachometer supplied by Smiths Industries Ltd. was used for this purpose. The tachometer had three speed ranges; 0-400, 0-2,000 and 0-10,000 r.p.m.

3(b) Mixing chamber

The mixing chamber is shown schematically in Fig. 8. The main body of the chamber was constructed from a cylinder of perspex, 1" in diameter and 1.5" long, add this contained eight jets of 0.028" bore which were located in two parallel planes. The jets were arranged around a 0.078" hole in the centre of the chamber; the jets in one plane were arranged clockwise around the hole while the jets in the second plane were arranged anti-clockwise around the hole. The jets were arranged in four pairs, one reactant solution being led to two of the pairs of jets, the other solution being led to the other two pairs. This design of mixing chamber caused the clockwise and anti-clockwise streams of reactants to impinge on one another, and thus gave rise to rapid and efficient mixing of the solutions.

The mixed solutions emerged from the mixing chamber through a silica tube of approximately $\frac{1}{4}$" diameter, which was secured in position by means of an O-ring and a stainless steel plug.

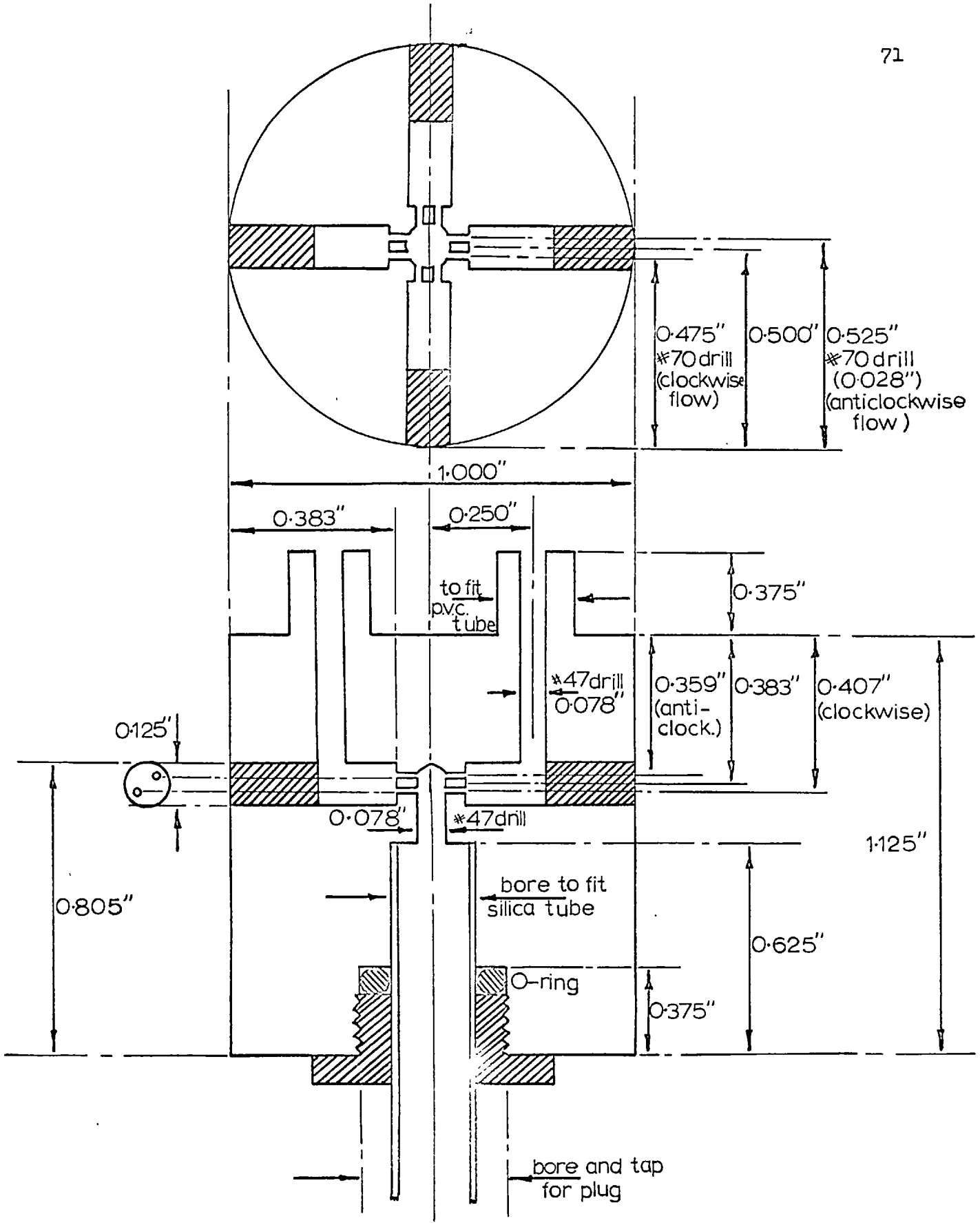


Fig.8. Stopped-flow mixing chamber

The mixing chamber was housed in the thermostatted cell compartment of the spectrophotometer (see Section E.3(d)). Connections between the syringes and the mixing chamber were made with PVC tubing.

3(c) Spectrophotometric cells

All spectrophotometric measurements were made in silica absorption cells. In some experiments 100 mm. cylindrical flow cells, supplied by The Thermal Syndicate Ltd., were used for this purpose, but most of the experimental work was carried out using a 10 mm flow cell from Optica (U.K.) Ltd. The method of cleaning the cells is described in Section E.4.

3(d) Spectrophotometer

All spectral data were obtained using a Unicam SP.800B ultraviolet and visible recording spectrophotometer. The instrument was fitted with the SP.820 constant wavelength scanner, which enabled the absorbance of a solution to be plotted as a function of time. The cell compartment of the spectrophotometer was thermostatted by means of water circulating through a copper coil. By this means, the temperature of the cell compartment could be controlled to within $\pm 0.1^{\circ}$ C at 25° C.

4. The cleaning of glassware

The glassware used in connection with this work was all pyrex. All vessels which came into contact with any of the reagents used in kinetic experiments were cleaned by prolonged treatment with "AnalaR" concentrated nitric acid from Hopkin and Williams Ltd., followed by rinsing with deionised distilled water.

Glassware used for other purposes was cleaned with

chromic acid and rinsed with distilled water. Where necessary, glassware was finally dried with "AnalaR" acetone from Hopkin and Williams Ltd.

Spectrophotometric cells which had been in contact with alkaline solutions were cleaned by boiling in "AnalaR" concentrated nitric acid, followed by rinsing with deionised distilled water and "AnalaR" acetone.

F MATERIALS

(a) Water

All aqueous reagent solutions for use in kinetic experiments were prepared with deionised distilled water. The use of laboratory-distilled water in the reagents gave rise to inconsistent experimental results, this being almost certainly due to the presence of traces of metallic impurities in the water.

The deionised water was prepared by passing distilled water through a "Deeminac" model 32-6 deioniser, from Crystal Research Laboratories, Inc. This deioniser consisted of a polyethylene bottle inverted over a 12 cm cylindrical canister of mixed-bed resin absorbent, through which the water ran slowly under gravity.

The deionised water, and all solutions prepared from it, were stored in screw-capped polyethylene bottles, which were cleaned initially with "AnalaR" nitric acid and deionised water.

(b) Alkali

Most of the experimental work was carried out using "AnalaR" grade sodium hydroxide from Hopkin and Williams Ltd.

A number of experiments were also carried out with "AnalaR" potassium hydroxide, "General Purpose Reagent" grade lithium hydroxide (AnalaR grade being unavailable) and 99.9% caesium hydroxide from Koch-Light Laboratories Ltd.

In order to minimise contamination, the aqueous hydroxide solutions were prepared by weighing the required amounts of deionised water and solid hydroxide directly into polyethylene storage bottles, which were cooled in ice during mixing.

The solutions were standardised against hydrochloric acid which had in turn been standardised against standard sodium hydroxide solution prepared from an ampoule of "Concentrated Volumetric Solutions" sodium hydroxide (British Drug Houses Ltd.) According to the makers' specification these concentrated solutions were accurate to within the factor limits of 0.999 and 1.001. The concentration of the stock solution of alkali prepared in the above manner was usually 5M. When not in use, the storage bottles were sealed by airtight screw caps.

(c) Thiols

All thiols used in this work were obtained from The Eastman Kodak Co., with the exception of 2-butanethiol, which was obtained from Koch-Light Laboratories Ltd., and triphenylmethanethiol, which was obtained from K and K Laboratories, Inc. Most of the thiols were obtained as reagent grade chemicals, but 2-methyl-2-propanethiol was available only as the practical grade material. 1-octanethiol was obtained as practical grade material from The Eastman Kodak Co., and as the reagent grade material from K and K

Laboratories Inc. In view of the extreme sensitivity of thiol autoxidation systems to traces of catalytic impurities, especially metal ions, all samples of thiols were doubly distilled before being used in kinetic experiments.

Distillation of thiols was carried out in an all-Pyrex apparatus, which had been cleaned by the method described in Section E.4. The apparatus, which was built from Quickfit components, had a water-cooled condenser and was completely gas-tight except for an outlet tube which was closed with a calcium chloride drying tube. The apparatus was first purged with a stream of nitrogen and the thiol was then introduced and distilled, the middle fraction being collected, re-distilled and finally collected in the storage vessel shown in Fig. 9, The thiols were stored under one atmosphere of nitrogen in this vessel, which had a capacity of about 100 ml, and incorporated a side-arm of about 5 ml capacity into which the thiol could be tipped for extraction through a Suba-seal 30 serum cap by a hypodermic needle and syringe. The vessel was normally kept immersed to the neck in crushed ice.

In order to keep the thiol nomenclature consistent throughout the following Sections, thiols were named after the corresponding alcohol, the suffix thiol being used in all cases. Thus 1-butanethiol, $CH_3CH_2CH_2CH_2SH$ is named n-butanethiol (abbreviated to Bu^nSH); 2-butanethiol, $CH_3CH_2CH(SH)CH_3$ is named sec-butanethiol (Bu^sSH); 2-methyl-1-propanethiol, $(CH_3)_2CHCH_2SH$ is named iso-butanethiol (Bu^iSH); and 2-methyl-2-propanethiol, $(CH_3)_3CSH$ is named tert-butanethiol (Bu^tSH). α-toluenethiol

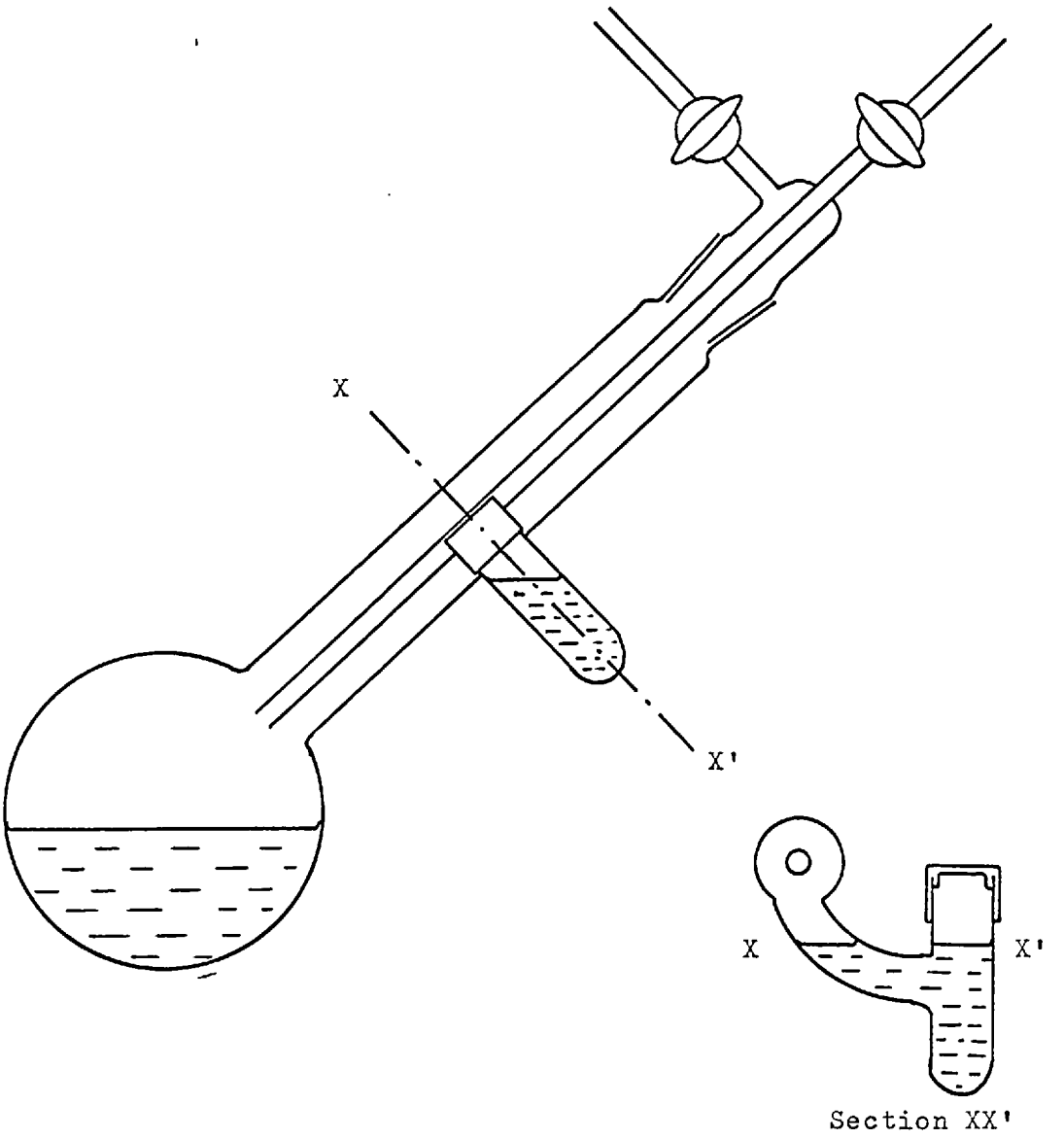


Fig. 9. Thiol storage vessel

(toluene-ω-thiol, benzyl mercaptan, $C_6H_5.CH_2SH$) is named phenylmethanethiol ($PhCH_2SH$).

(d) Metallic salts and complexes

Metal ions were usually added to reagent solutions as measured volumes of standard solutions of the appropriate salts, all of which, with the exception of vanadyl sulphate, platinic chloride and palladous chloride, were "AnalaR" grade reagents from Hopkin and Williams Ltd. Vanadyl sulphate was available only as the "Fine Chemical" grade from Hopkin and Williams Ltd. Platinic chloride and palladous chloride were obtained from Johnson Matthey and Co.Ltd. The metal salts used in the preparation of standard solutions are shown in Table 1. The standard solutions were prepared directly from the dried solids by weighing. The metal contents of the vanadyl sulphate and nickel sulphate were ascertained by standard analytical techniques (see Section G(b)). According to the makers' specifications, these salts were sufficiently pure for the present purpose, and no further purification was undertaken.

Haemin and chlorophyll were obtained from The British Drug Houses Ltd. The haemin was used without further purification, but the chlorophyll, which was obtained as a viscous aqueous solution, was extracted as a waxy solid after evaporation of the water from the solution in vacuo. Vitamin B_{12} (cyanocobalamin), which was obtained from Halewood Chemicals Ltd., and the disodium cobalt ethylenediamine tetra-acetic acid complex, $Na_2CoEDTA$, from Koch-Light Laboratories Ltd., were used without further purification.

Table 1

Metal salts used in the preparation of standard metal solutions

Metal	Salt
Mg	$MgSO_4 \cdot 7H_2O$
Ce	$(NH_4)_2Ce(NO_3)_6$
U	$UO_2(NO_3)_2 \cdot 6H_2O$
V	$VOSO_4$ + aq
Cr	$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$
Mo	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
W	$Na_2WO_4 \cdot 2H_2O$
Mn	$MnSO_4 \cdot 4H_2O$
Fe	$FeSO_4 \cdot 7H_2O$
Co	$CoSO_4 \cdot 7H_2O$
Ni	$NiSO_4$ + aq
Pd	$PdCl_2$
Pt	$PtCl_4$
Cu	$CuSO_4 \cdot 5H_2O$
Ag	$AgNO_3$
Zn	$ZnSO_4 \cdot 7H_2O$
Cd	$3CdSO_4 \cdot 8H_2O$
Hg	$HgCl_2$
Al	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Tl	Tl_2SO_4
Sn	$SnCl_2 \cdot 2H_2O$

Conventional techniques were used for the preparation of the following complexes: tris-ethylenediamine cobalt^{III} chloride, $Co\ en_3Cl_3$[129]; cis- and trans-dichloro-bis-ethylenediamine cobalt^{III} chloride[130]; potassium cobalticyanide[131]; cis-chloroaquotetrammine cobalt^{III} chloride[132]; carbonatopentammine cobalt^{III} nitrate[133], and bis-pyridine cobalt^{II} chloride[134]. Pyrophosphates of iron, cobalt, nickel and copper were prepared by mixing aqueous solutions containing stoichiometric amounts of the appropriate metal sulphate and of tetra-sodium pyrophosphate respectively[109]. Phthalocyanines of copper, cobalt, iron and vanadium were prepared by the method of Linstead et al.[135, 136], using phthalonitrile from Koch-Light Laboratories Ltd. and anhydrous metal chlorides, with the exception of vanadyl phthalocyanine, where vanadium pentoxide, prepared from "AnalaR" ammonium metavanadate, was used instead.

Water-soluble complexes were purified by recrystallisation from deionised distilled water. The pyrophosphate complexes were washed repeatedly with deionised distilled water and were finally dried in vacuo over phosphorus pentoxide. Phthalocyanines were boiled repeatedly in ethanol and water to remove unreacted phthalonitrile and metal halide, and the complexes were then dissolved in 98% sulphuric acid and re-precipitated by pouring the solutions on to crushed ice.

Due to the difficulty of making standard solutions from the pyrophosphates, phthalocyanines and porphyrin compounds, these were normally weighed directly into the reaction vessel at the beginning of each experiment. The water-soluble cobalt complexes

were made up into standard solutions in the same manner as simple salts. These solutions were re-made at regular intervals, and a spectrophotometric check was made at the beginning of each experiment to ensure that decomposition of the complexes had not taken place.

(e) Other additives

The kinetic effects of potassium cyanide, en, EDTA, pyridine, (py), ∝,∝'-dipyridyl, (dipy), and 1,10-phenanthroline, (o-phen) were studied both in the presence and in the absence of added metal catalysts. All of these complexing agents, with the exception of en, were obtained as "AnalaR" grade reagents from Hopkin and Williams Ltd., the EDTA being in the form of the disodium salt. The ethylenediamine was obtained as reagent grade en.2HCl from the Eastman Kodak Co. For comparative purposes, ∝,∝'-dipyridyl was also employed as the Hopkin and Williams "General Purpose Reagent" grade material.

These complexing agents were added to the reactant solution either as standard solutions, or by direct weighing into the reaction vessel. Pyridine was added directly to the reactant solution by means of a micro burette.

In certain experiments, diethyl disulphide was used as an additive. This was obtained from The Eastman Kodak Co., and was purified by distillation in the same manner as were the thiols. The middle fraction was collected and stored in a clean Pyrex bottle.

A number of experiments were conducted using thiocyanato-ethane instead of ethanethiol. This was obtained from The British Drug Houses Ltd., and was also purified by distillation. The

distilled product was stored in a Pyrex bottle which was kept in a refrigerator when not in use.

Diphenylamine was obtained as the "AnalaR" grade material from Hopkin and Williams Ltd., and was used without further purification.

(f) Gases

Oxygen and nitrogen were obtained from cylinders supplied by the British Oxygen Company Ltd. For use in kinetic experiments, oxygen from the cylinder was condensed at just below atmospheric pressure in the trap cooled to -196°C with liquid nitrogen. The condensed gas was then alternately pumped upon and left to stand in equilibrium with its own vapour at this temperature until its vapour pressure was unchanged by further pumping. This was taken as evidence for the complete removal of nitrogen from the condensed oxygen. The Dewar of liquid nitrogen was then removed, the condensed oxygen allowed to boil off, and the middle fraction admitted to the working line or to the storage globe as required. Oxygen for use in non-kinetic experiments was used from the cylinder without further purification.

"Oxygen-free" nitrogen for use in kinetic experiments, was admitted to the storage globe, which served as a pre-mixing vessel, through a trap surrounded by liquid nitrogen to condense any oxygen and less volatile gases. Nitrogen for use in connection with the preparation of complexes was rigourously de-oxygenated by passage through two sintered glass discs immersed in solutions of chromous chloride, prepared in situ by reduction of chromic chloride with

granulated zinc and hydrochloric acid. The nitrogen was finally washed by passage through a third sinter immersed in distilled water which had been de-gassed by means of a rotary vacuum pump.

(g) Reagents for non-kinetic work

Reagents used in volumetric analyses were of "AnalaR" grade from Hopkin and Williams Ltd. Reagents used in colorimetric determinations of metals were of the highest purity available, generally "AnalaR". Solvents used in connection with spectrophotometric measurements were of "AnalaR", or where available, of "Spectrosol" Hopkin and Williams Ltd. grade. All aqueous solutions used in non-kinetic experiments were prepared with distilled water.

G PROCEDURE

In order to decide upon suitable experimental techniques, several requirements had to be taken into account. In particular there was an obvious need to minimise the escape of thiol vapour, since the odour of thiols is considered by most people to be extremely unpleasant. Secondly it was found essential in kinetic experiments to minimise contamination by traces of metals and their salts and complexes, on account of the extreme sensitivity of the kinetics of thiol autoxidation to contamination of this kind.

1. Kinetic experiments

(a) Experimental procedure

Prior to the commencement of a kinetic experiment, the reaction vessel was first cleaned by the methods given in Section E.4, and was finally rinsed with deionised distilled water and its taps refitted. The vessel was then remounted and connected to the working

line, and was pumped upon until dry internally. At the same time the thermostat on the oil bath was set to the temperature required for the experiment.

With tap 4 closed (see Fig. 2), the reaction vessel was brought to atmospheric pressure by opening tap 3, and the serum cap was removed. The appropriate volumes of the reagent solutions were then measured into the reaction vessel with pipettes, the order of admission being: (1) deionised water, (2) standard metal solution, (3) standard solution of additive, (4) any other additive, (5) standard alkali from stock. The final total volume of the aqueous solution was arranged usually to be 50 ml. Separate pipettes were used for the different reagents in order to avoid contamination, the pipettes being left to stand in measuring cylinders filled with "AnalaR" concentrated nitric acid when not in use. Two variations of the above procedure were occasionally adopted; in certain experiments it was found to be more convenient to add the deionised water, standard solution of complexing agent, and standard alkali as one solution, which had previously been prepared. The second variation was adopted in experiments involving metals in a ligand environment where the preparation of standard solutions was not convenient. In these cases the metal complex was added directly to the reaction vessel from a weighing bottle into which the complex had previously been weighed. The weighing bottle was always well rinsed with deionised water after the addition of the complex.

After admission of the reagents, the serum cap was replaced, and the air was displaced from the reaction vessel by a

stream of oxygen. The oxygen was first passed through a bubbler attached to the sampling outlet of the reaction vessel, and containing alkali of the same concentration and at the same temperature as that in the reaction vessel in order to equalise the partial pressure of water vapour and to remove any carbon dioxide. The gas passed through tap 3 into the vessel, sweeping the air out through taps 4 and 11, and through taps 15 and 16 to the atmosphere.

The reaction vessel was then isolated and the rest of the apparatus was pumped out. Oxygen (and nitrogen when required) was introduced into the rest of the working line to the required pressure (see Section F (f)). The reaction vessel was then opened to the working line through tap 4 and the manostat was switched on. Taps 7, 11 and 12 were then closed and tap 6 was turned to connect the electrolytic cell to the rear limb of the burette. The working line was then left to settle down for as long as possible, generally 15 min.

With taps 4 and 5 closed, the reaction vessel was separated from the working line at the ground joint C, and from the shaker, and was transferred to a fume cupboard. The required volume of thiol was then extracted from the storage vessel and injected through the serum cap into the closed reaction vessel which was shaken manually to dissolve the thiol in the alkali. The reaction vessel was re-mounted on the shaker, connected to the working line through the joint C, which with taps 4 and 5 closed was pumped out through tap 11. Tap 11 was then closed, and taps 4 and 5 opened, and the shaker was switched on. Tap 10 was closed to isolate the

standard pressure in the manostat sensing cell, and this was taken as zero time, when readings commenced.

Although the oxidation must have started as soon as the thiol began to dissolve in the alkali, it was convenient to take the end of the starting procedure as zero time. This was generally 1-2 min after injection of the thiol. It was not possible in any event to take useful readings earlier, since the thiol was incompletely dissolved and its vapour pressure not equilibrated.

Gas burette readings were corrected for any deviations from the standard temperature and pressure. The necessary readings were carried out in the order (1) both manometers to give, by difference, the actual working line pressure, the manometer from tap 13 being under vacuum; (2) gas burette; (3) water-tank and oil-bath temperatures (as a check for constancy). These sets of readings were made at regular intervals, as frequently as necessary to follow the gas uptake accurately.

Corrected burette readings were obtained by the method described in Appendix 1. The volume of gas taken up under standard conditions was obtained by subtracting the corrected burette readings from the value at the start of the reaction. The uptake was finally expressed either as the number of moles of oxygen consumed per litre of reagent solution, or as a percentage of the theoretical amount of oxygen required to oxidise all the thiol in the reaction vessel to disulphide according to the equation:

$$RSH + \tfrac{1}{4}O_2 \longrightarrow \tfrac{1}{2}RSSR + \tfrac{1}{2}H_2O \qquad (70)$$

The provisions in the apparatus for sampling the reacting liquid phase are described in Section E.1(a). To carry out liquid sampling, the sampler tube was first evacuated by connecting it at A (Figs. 1 and 2) to the pumping line. Tap 4 was closed, the shaker stopped, and the sampler tube attached to the reaction vessel at B. Taps 2 and 3 were then opened, and tap 3 was closed as soon as all the sample had passed over into the sampler tube, which was then detached. The shaker was then restarted, and tap 4 reopened.

Readings were taken immediately before and after sampling, and the gas-uptake figures corrected, in order to allow for the inevitable loss of a small quantity of gas from the working line.

The sample was rinsed with distilled water from the sampler tube into a bottle containing 20 ml carbon tetrachloride, and the alkali was titrated as soon as possible to minimise further oxidation.

At the end of experiments, tap 4 was closed, and the manostat and thermostat were switched off. The reaction vessel was disconnected at C, and its contents taken for analysis (Section G.1(b)) or carefully poured into nitric acid to destroy any residual thiol.

The reaction vessel was cleaned in the manner described in Section E.4, being left to stand filled with "AnalaR" concentrated nitric acid until required for the next experiment.

1(b) Analytical procedure

The method employed to obtain samples for analysis from oxidising solutions was described in Section G.1(a). When the entire product mixture was to be taken for analysis, it was transferred

from the reaction vessel to a bottle, from which 2 ml samples were pipetted for titration of the alkali, care being taken not to remove any of the floating disulphide. The bulk of the mixture was then acidified and extracted twice with 25 ml carbon tetrachloride. The phases were separated after each extraction and the extracts, which contained the thiol and disulphide, were combined. 2 ml samples of the extract were then analysed by the standard procedure.

The method used for the quantitative estimation of thiols and disulphides was based on standard techniques[137, 138, 139]. Use was made of the fact that, whereas iodine oxidises alkanethiols quantitatively to the corresponding disulphides, bromine oxidises both thiols and disulphides to sulphonic acids:

$$2RSH + I_2 \longrightarrow RSSR + 2HI \qquad (71)$$

$$RSSR + 5Br_2 + 6H_2O \longrightarrow 2RSO_3H + 10HBr \qquad (72)$$

Any monosulphide present is also oxidised by the bromine:

$$R_2S + Br_2 + H_2O \longrightarrow R_2SO + 2HBr \qquad (73)$$

Titrations were carried out with standard solutions of potassium iodate and potassium bromate in the presence of excess iodine or bromide respectively:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + H_2O \qquad (74)$$

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + H_2O \qquad (75)$$

Although it is possible to use bromate throughout these titrations, inconsistent results can occur due to the bromide produced by the reaction:

$$BrO_3^- + 6I^- + 6H^+ \longrightarrow 3I_2 + Br^- + H_2O \qquad (76)$$

reacting further with the bromate to produce bromine, which reacts

with the disulphide produced, resulting in a low disulphide titre.

Analyses for alkali, thiol and disulphide were carried out in three stages on the same sample:

1) Titration with standard hydrochloric acid solution;

2) Titration with standard iodate solution in the presence of acid and excess iodide;

3) Titration with standard bromate solution in the presence of acid and excess bromide.

The details of these stages were as follows:

1) The sample containing alkali, thiol and disulphide was added to 20 ml carbon tetrachloride in a stoppered bottle. The alkali was then titrated with standard acid, thus allowing the determination of the approximate volume of each running sample, or the actual alkali concentration in the case of measured volumes of the liquid product. The indicator used in this analysis was phenolphthalein, since its colour did not interfere with the subsequent stages.

2) The neutralised sample was acidified with 5ml of 4M hydrochloric acid, and 20 ml of 0.5M potassium iodide solution were added together with 20 ml water. The mixture was titrated with approximately 0.025M standard iodate solution until the complete oxidation of the thiol was indicated by a faint iodine colour in the carbon tetrachloride layer.

The two liquid phases were then separated in a funnel, and the aqueous phase was washed with 20 ml carbon tetrachloride. The layers were again separated, and the combined carbon tetrachloride solutions, now containing dissolved disulphide, were placed in a stoppered bottle.

3) To the carbon tetrachloride solution were added 20 ml water, 5 ml of 4M hydrochloric acid, and 20 ml of 4M potassium bromide solution. The mixture was then titrated with approximately 0.025M standard bromate solution until the yellow colour of free bromine persisted in the non-aqueous layer. The bromine-disulphide reaction was rather slow, a single titration requiring 10-20 min. It was found that vigorous shaking to ensure thorough mixing of the phases increased the precision of the titrations. The end point was easily detected in the presence of a small amount of free iodine from stage 2, since this was decolorised by excess bromine with the formation of interhalogen compounds. These analytical techniques were found to give thiol titrations reproducible to within 1%, and disulphide titrations to within 6%. The addition of sufficient water to the sample under investigation to make the total volume of the aqueous phase approximately 50 ml was found to increase the precision of the analyses, since the HBr and HI formed during the titrations tend to reduce the disulphide to thiol[140], giving inaccurate titres.

Early analyses for thiol alone were carried out by titration with standard iodine solution[137], by titration with standard copper oleate solution[141], or spectrophotometrically using bis-(4-nitrophenyl) disulphide[142]. These methods worked satisfactorily, but were discontinued in favour of the more convenient iodate and bromate methods. Similarly, early analyses involving the reduction of disulphides with zinc amalgam[143], together with estimation of the resulting thiol with standard iodine solution, were discontinued on account of the irreproducible results obtained due to

the volatility of the thiols.

2. Non-kinetic experiments

2(a) Preparation of complexes

In addition to complexes formed during kinetic experiments, experiments were undertaken in order specifically to prepare metal-thiol complexes. These experiments were all performed in the bubbler vessel described in Section E.2(a) and shown schematically in Fig. 5.

Prior to the commencement of an experiment, the bubbler vessel was cleaned by the methods described in Section E.4. The ground glass joints and taps were then greased and refitted, and the vessel was clamped to a retort stand and placed under a fume hood. The bubbler vessel was then purged with the gas under which the complexes were to be prepared. For experiments involving complexes prepared under oxygen, the vessel was normally purged with oxygen for $\frac{1}{2}$ hour, whereas prior to the preparation of complexes under de-oxygenated nitrogen, the vessel was purged for 1-1$\frac{1}{2}$ hours. In these experiments, either a spectrophotometric cell, or the sample collecting tube (Fig. 5) was also purged with de-oxygenated nitrogen. Taps T_1 and T_2 were finally turned so that the flow of gas was through joint J_2 to the tube at the bottom of the vessel, and from the tube at the side of the vessel through joint J_1 to joint J_4.

The reactants were then introduced into the bubbler vessel by means of hypodermic syringes, the order of admission being: 1) standard alkali solution, 2) standard metal solution, 3) any other additive, 4) thiol. Alkali and metal solutions were degassed with a rotary vacuum pump before use in experiments carried out under de-

oxygenated nitrogen. A period of 20 min. was normally allowed to elapse between the addition of the solutions of the standard alkali, metal and additive (if any), and the addition of the thiol. This was to ensure that the solutions were fully saturated with the gas under which the experiment was to be conducted. After the addition of the thiol, the reactant mixture was normally agitated by the passage of a stream of gas. The duration of the agitation varied from 5 min. to 2 hr., but was generally approximately 20 min.

The investigation of the contents of the bubbler vessel was normally carried out by means of one or more of the following three methods:

1) By reversal of the direction of the gas-flow through taps T_1 and T_2, a portion of the contents of the vessel was expelled through joint J_2 and tap T_2 to joint J_4, whence it was collected in a spectrophotometric cell.

2) The entire contents of the bubbler vessel, expelled through joint J_4 in the manner described above, were filtered through the sinter disc of the sample collecting tube (Fig, 5), leaving any solid material on the sinter disc. Solid complexes isolated in this manner were washed with de-gassed distilled water and de-gassed ethanol, and were dried over phosphorus pentoxide. In the case of complexes prepared under nitrogen, the washing procedure was carried out under de-oxygenated nitrogen.

3) In order to investigate complexes spectrophotometrically in the absence of aqueous reagents, 25 ml chloroform was injected into the bubbler vessel through the serum cap, and the contents of the vessel

were agitated by means of the stream of gas. The gas-flow was then stopped, and the phases allowed to separate. By reversal of the direction of the gas flow through taps T_1 and T_2, a portion of the chloroform extract was then expelled into a spectrophotometric cell in the manner described in method 1.

2(b) Analysis of complexes

Spectrophotometric investigations on complexes were performed with the Unicam SP 800 spectrophotometer (see Section E.3(d)) Silica absorption cells were used in all investigations. The solvents used were all of "AnalaR" or where available, of "Spectrosol" grade.

Magnetic measurements were made with a conventional Gouey balance, using a permanent magnet of field strength 6,450 gauss. Whenever diamagnetic samples were investigated, a correction was made for the diamagnetism of the air contained in the empty Gouey tube.

Samples of the metal complexes were subjected to microanalysis for carbon, hydrogen, oxygen and sulphur, (Imperial College microanalytical laboratories) and the results obtained were found to be reproducible to within $\pm 2\%$. In some earlier experiments, rapid and moderately accurate sulphur determinations were performed by oxidation of the sulphur in the sample to sulphate. The sample was subjected to a Lassaigne fusion, using a large excess of sodium, and the resulting solution was boiled, filtered and treated with hydrogen peroxide to oxidise the sodium sulphide to sodium sulphate. Excess hydrogen peroxide was destroyed by boiling, and the resulting solution was passed through a 15cm column containing Amberlite IR 120H cation exchange resin in order to remove interfering cations.

The effluent solution was adjusted to pH7 with hydrochloric acid, then to pH4 with potassium hydrogen phthalate, and the sulphate content was determined spectrophotometrically using barium chloranilate[144].

Metals were determined by the following standard methods: nickel - colorimetric determination of the dimethylglyoxime complex[145]; cobalt - colorimetric determination of the nitroso-R salt complex[146]; copper - colorimetric determination of the complex formed with sodium diethyldithiocarbamate[147]; thallium - volumetric determination by oxidation with potassium iodate[148]; palladium - gravimetric determination of the dimethylglyoxime complex[148]. Solutions containing known amounts of these metals were analysed in the absence and presence of alkali and thiol, and results accurate to within ±2% were obtained in all cases.

3 Stopped-flow experiments

The stopped-flow apparatus was used to investigate the reaction of thiols with specific metal complexes in solution. In order to minimise turbidity on mixing the reactant solutions, these were arranged to contain the same concentration of alkali. The two reactant solutions normally consisted of an alkaline solution of the thiol under investigation, and an alkaline solution of the metal complex. In certain experiments these solutions were made up in 50% aqueous ethanol in order to prevent turbulence as disulphide is formed.

The solutions were maintained in 1 litre volumetric flasks immersed to their necks in the water contained in the thermostatted bath. The necks of the flasks were sealed with rubber stoppers which each contained a glass tube to enable the solutions to be drawn up into

the syringes, and two small glass tubes to enable the solutions to be purged with gas from a cylinder.

With taps T_1 to T_4 opened in the appropriate directions (Fig.6), solutions from the volumetric flasks were drawn as far as taps T_1 and T_2 by means of careful suction from the tube B. Taps T_1 and T_2 were then turned to connect the syringes to tube B, and by means of a rotary vacuum pump attached to tube B, the syringes were evacuated. Taps T_1 and T_2 were then turned so as to admit the solutions to the appropriate syringes.

At this point the apparatus was ready to be used to obtain experimental results. The plungers of the syringes were then drawn back by means of the syringe drive mechanism, powered by the electric motor. The gears were arranged to give the ratio required for the experiment in hand, (see Section 3(a)), and the taps T_3 and T_4 were turned to enable the solutions to be expelled through the mixing chamber. This was carried out by reversal of the direction of rotation of the motor. When the rotation of the motor was stopped by the microswitch S_2 being tripped by the spring loaded pusher P_2 (Fig.7), taps T_3 and T_4 were turned to re-admit reagent solutions to the syringes, which were re-filled by reversal of the direction of the motor as described above.

The above procedure was repeated two or three times, to ensure that all the air in the mixing chamber and the spectrophotometric cell had been replaced by reagent solutions. The procedure was then repeated with the spectrophotometer in operation, using the SP 820 constant wavelength scanner, which had previously been set to

take adsorbance readings at a specific wavelength. The procedure was repeated three or four times as a check for consistency.

At the end of an experiment, the syringes and mixing chamber were cleaned with 2M nitric acid to destroy all traces of remaining alkali, and were washed repeatedly with deionised water and finally dried by rinsing with A.R. methanol. The spectrophotometric cell was cleaned by the methods described in Section E.4.

Reagent solutions were made up freshly before the commencement of each experiment, and solutions of thiols were always maintained under nitrogen to prevent autoxidation.

The maximum distance between the mixing chamber and the spectrophotometric cell was 10cm, and this allowed the mixed solutions to reach the cell approximately 0.1 sec after mixing. This was found to be adequate, since the reactions studied all had times of half reaction of $\geq$ 6sec., thus rendering the results accurate to $\pm$1.7%. The exact speed of the syringe operators was checked during each experiment with the hand tachometer, as described in Section E.3(a).

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RESULTS

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H KINETIC OXYGEN-UPTAKE EXPERIMENTS

1. The method of presentation of results

(a) The reagent concentrations given in the Figures and Tables are initial values unless otherwise stated. Values of the oxygen pressure given in the captions of figures are mean values for the particular series of experiments. Slight differences occurred from run to run due to the difficulty of adjusting the pressure exactly to the required value, but the actual pressures were within 1 cm of the mean. Unless otherwise stated, reactions described in the text were performed with the following reagent concentrations: [thiol] = 0.5M, [NaOH] = 2.0M, [Metal] (if any) = 10^{-3}M, under a constant oxygen pressure of 75 cm.Hg; volume of solution = 50 ml, temperature = 30°C. These conditions are referred to in the text as "standard conditions".

(b) The rates of reaction in the nominal absence of catalysts were reproducible only within fairly wide limits (see Section H.2(a)); the rates in the presence of catalysts were more reproducible, but small inconsistencies exist in some cases. Wherever possible, reactions in a given series were carried out under the most nearly comparable conditions, generally with samples from the same batches of reagents.

(c) Rates of reaction are normally expressed as rates of consumption of oxygen per unit volume of solution, viz. mole O_2 litre^{-1} sec^{-1}, and the term "rate" used without qualification refers to this.

2. The oxidation of thiols in the absence of added metallic catalysts

2(a) Ethanethiol

A number of early experiments were carried out on the uncatalysed oxidation of ethanethiol in order to establish the conditions necessary to obtain reproducible results. Subsequent uncatalysed reactions were performed to ensure that minimum impurity levels were maintained.

Initially a series of ten uncatalysed reactions was investigated whilst refinements were progressively made in the experimental procedure. These reactions proceeded with a mean initial rate of 1.72×10^{-6} mole l^{-1} sec^{-1}, (standard deviation 19%). A subsequent series of ten uncatalysed experiments was performed when the experimental techniques had been established. The mean initial rate of these reactions was 1.50×10^{-6} mole l^{-1} sec^{-1}, with a standard deviation of 9%. The following results were obtained after the rate of the uncatalysed oxidation had been reduced to the lower level above.

i) Stoichiometry

A number of uncatalysed oxidations were followed to completion in order to check the validity of the overall equation:

$$4EtSH + O_2 \longrightarrow 2EtSSEt + 2H_2O \qquad (78)$$

and to test the accuracy of the analytical methods used for the estimation of thiol and disulphide. Reactions were assumed to have reached completion when there was no significant further uptake of oxygen over a 15 min. period. Analyses for thiol and disulphide

were performed on samples withdrawn from oxidising solutions, and on solutions in which the oxidation had gone to completion. Values of oxygen uptake, consumption of thiol, and production of disulphide are expressed as the percentage of the theoretical uptake, consumption, or yield for oxidation of thiol to disulphide according to Equation (78). The results of these investigations are reported in Fig.10 and Table 2.

These experiments show that the stoichiometry of Equation (78) is closely followed at all stages of the reaction. However, in the presence of more concentrated alkali, a deficiency of disulphide appeared in the reaction products, together with a slight decrease in the alkali concentration. Correlation between this decrease and the disulphide deficiency was uncertain, especially in view of the tolerance of the disulphide determination, but the results suggest the formation of sulphur containing acids as minor oxidation products.

ii) Comparison of samples of thiol from different sources

During the initial series of experiments on the oxidation of ethanethiol described above, samples of ethanethiol from different sources were compared. Four samples of thiol were oxidised under standard conditions in the absence of added metal catalysts, and the lowest rates of oxidation were taken as indicating a sample of thiol of the highest purity. Samples of ethanethiol from The Eastman Kodak Company gave a mean rate of oxidation of 1.50×10^{-6} mole l^{-1} sec^{-1}, whereas the samples of thiol from the other three sources had

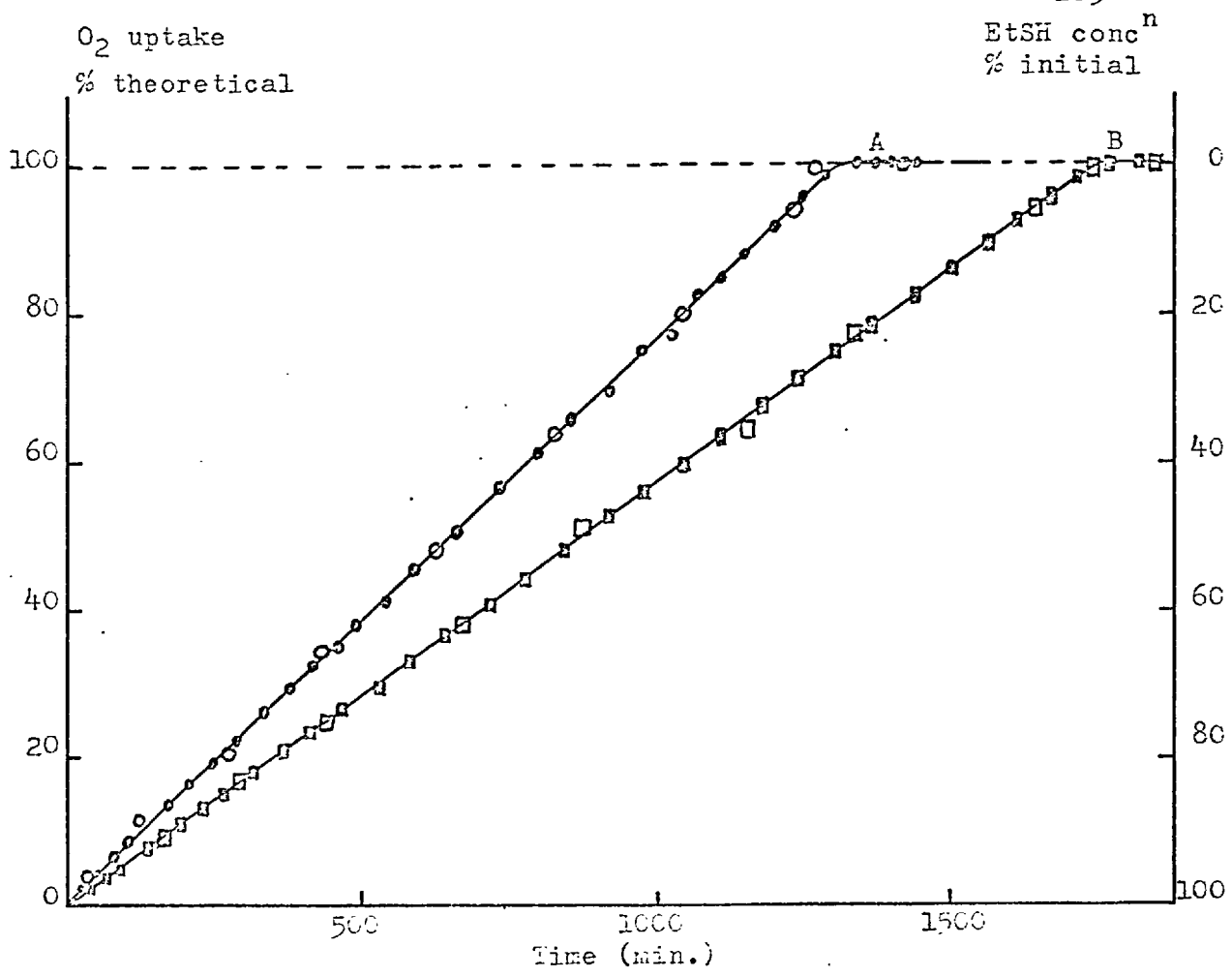


Fig.10 The oxidation of ethanethiol: the stoichiometric relationship between decrease in thiol concentration and oxygen uptake, 75 cm.O_2, 30° C.

A - 0.5 M EtSH, 2.0 M NaOH

B - 0.4 M EtSH, 1.0 M NaOH

● ■ Oxygen uptake

○ □ EtSH concentration

Table 2

The oxidation of ethanethiol; results of sample analyses for thiol, disulphide and alkali

Conditions	Time (min)	Sample volume (ml)	O_2 uptake % theor.*	EtSH consumed % init.	EtSSEt produced % theor.*	Decrease in NaOH % init.
	0	1.06	0	0	0	0
	30	0.58	3	3.5	4	0
	120	1.01	10	11	9	1
0.5M EtSH	270	0.96	21	20	15	1
2.0M NaOH	420	0.91	33	34	24	2
75 cm.O_2	620	1.24	43	43	36	4
30°C	825	0.88	63	63	48	4
	1050	1.11	80	80	63	5
	1230	1.23	94	94	75	6
	1260	1.37	97	100	86	7
	1420	(a)	101	100	87	7

(a) Remaining product mixture taken for analysis

* Based on equation (78)

Table 2 continued

Conditions	Time (min)	Sample volume (ml)	O_2 uptake % theor.*	EtSH consumed % init.	EtSSEt produced % theor.*	Decrease in NaOH % init.
	0	1.54	0	0	0	0
	60	0.62	4	4	3	0
	160	1.47	9	9	9	0
	280	0.71	16	17	19	0
0.4M EtSH	425	0.98	25	25	24	0.5
1.0M NaOH	675	0.86	38	38	36	0.5
75 cm. O_2	875	1.63	50	51	47	0.5
30°C	1145	1.38	66	65	59	0.7
	1350	1.47	77	78	81	0.7
	1630	1.57	94	95	92	0.8
	1740	0.51	99	100	96	0.8
	1860	(a)	100	100	97	0.8

(a) Remaining product mixture taken for analysis

* Based on equation (78)

a mean rate of oxidation of 2.56×10^{-6} mole l^{-1} sec^{-1}. In subsequent experiments on the oxidation of ethanethiol, all samples of thiol were obtained from The Eastman Kodak Company.

iii) Effect of oxygen pressure

In a number of early experiments to determine the effect of oxygen pressure on the oxidation of ethanethiol, the total pressure was ballasted to a constant value with nitrogen, which was admitted to the working line after the oxygen. Difficulties were experienced in flushing the reaction vessel with gas of the same composition as that in the working line. Experiments were carried out using oxygen and nitrogen which had been pre-mixed in the gas storage globe, and for comparison, an experiment was performed where the line and reaction vessel were flushed with air from a cylinder. The results of these experiments are shown in Fig.11 and in Table 3.

Table 3

The oxidation of ethanethiol; effect of ballasted oxygen pressure on the rate of oxidation

Total pressure (cm)	Oxygen pressure (cm)	Rate of oxidation (mole l^{-1} sec^{-1})
76.00	76.00	1.54×10^{-6}
76.08	54.84	1.10×10^{-6}
75.96	42.04	0.84×10^{-6}
76.02	27.66	0.55×10^{-6}
75.98*	16.00	0.31×10^{-6}

* air used in place of O_2/N_2 mixture.

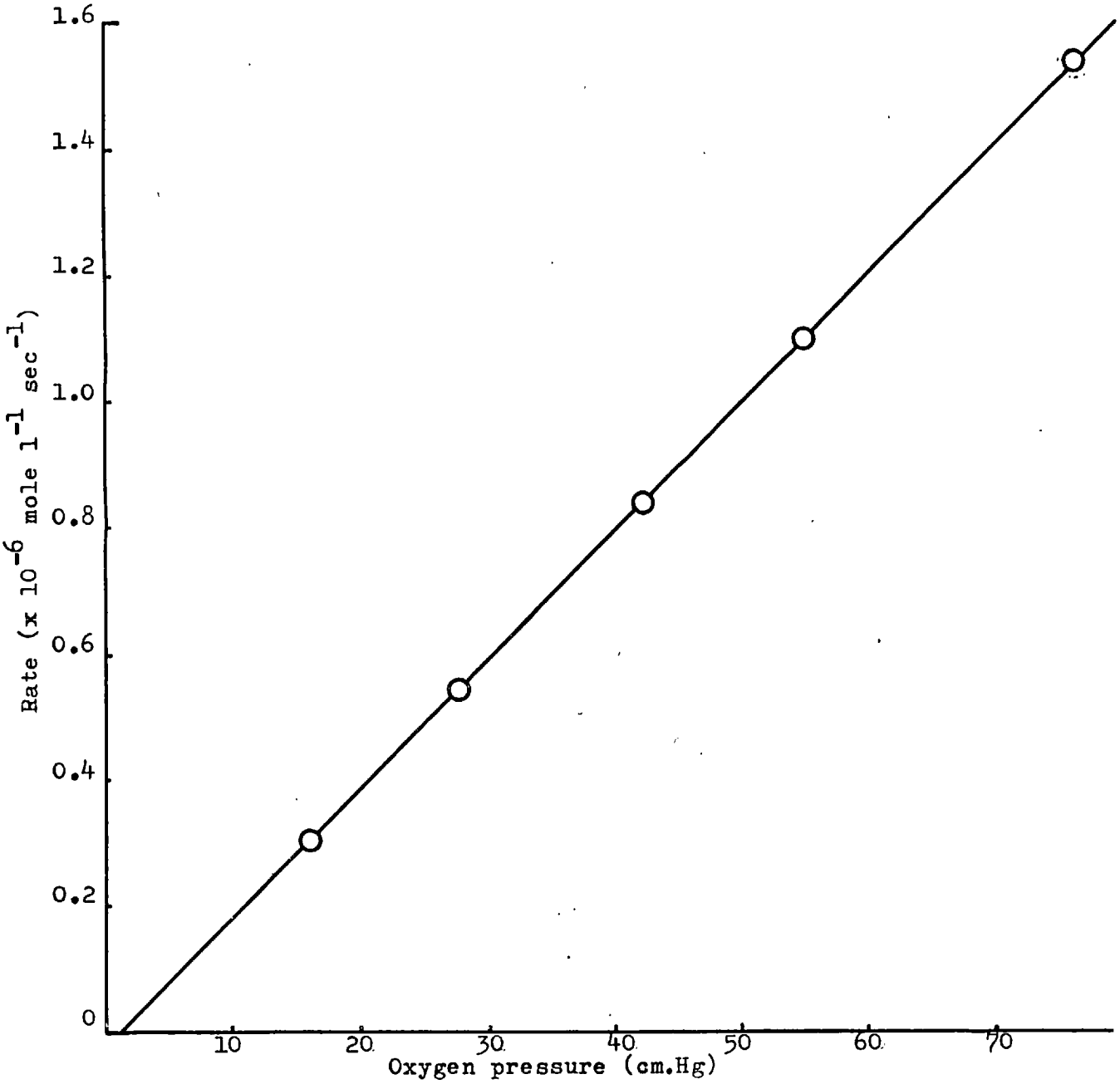


Fig.11 The oxidation of ethanethiol. Effect of oxygen pressure on the rate of reaction.

The rate of oxidation increases linearly with oxygen pressure. The graph of rate of oxidation versus oxygen pressure (Fig.11) does not pass through the origin, and a rate of zero corresponds to about 1.5cm on the oxygen pressure axis. The rate of oxidation is first-order with respect to the oxygen pressure.

iv) Effect of alkali concentration

The effect of the concentration of sodium hydroxide on the oxidation of ethanethiol was investigated using alkali concentrations of 1.0 M and 2.0 M. The results are reported in Table 4, and with the exception of the alkali concentration, the reactions were carried out under standard conditions. The rate of oxidation is seen to be higher in the experiments with 2.0 M alkali, and this increase is made more pronounced by consideration of the Bunsen coefficients (α) for the solubility of oxygen in the alkaline solutions. Values of these coefficients are given in Appendix A3.

Table 4

The oxidation of ethanethiol, effect of alkali concentration

Alkali concentration (M)	Rate Mole l^{-1} sec^{-1}	Rate/α mole l^{-1} sec^{-1}
1.0	1.78×10^{-6}	1.04×10^{-4}
2.0	2.08×10^{-6}	1.87×10^{-4}

The effect of the alkali concentration in the presence of metal-ion catalysts will be discussed in section H.3.

v) Effect of cyanide

A number of experiments were conducted to investigate the effect of potassium cyanide on the rate of oxidation. The cyanide concentration during these experiments was 0.25 M, and the results are reported in Table 5. A marked decrease in the rate of oxidation was observed in the presence of cyanide, and for comparison the table includes a reaction carried out under standard conditions in the absence of cyanide.

Table 5

The oxidation of ethanethiol, effect of potassium cyanide on the rate of oxidation

[EtSH] M	[NaOH] M	[KCN] M	Rate mole $l^{-1}sec^{-1}$	Time of final reading hr.	Oxygen uptake % theor*	Disulphide produced % theor*
0.5	2.0	0	2.08×10^{-6}	5	30	29
0.5	2.0	0.25	1.10×10^{-6}	220	300	0
0.5	1.0	0	1.78×10^{-6}	3	15	14
0.5	1.0	0.25	0.98×10^{-6}	5	13	0

* Based on equation (78).

The experiment with 2 M alkali and 0.25 M cyanide was allowed to proceed for 220 hr. At this time, the oxygen consumption was 300% of the theoretical value for oxidation of thiol to disulphide and the reaction was still proceeding. No disulphide could be detected amongst the reaction products, and the alkali strength was

found to have decreased to 68% of its original value. This decrease in alkali strength suggests the formation of sulphinic and sulphonic acids as oxidation products; analytical tests for these acids were attempted, but positive results could not be obtained either with these solutions or with solutions containing known amounts of acids, in the presence of cyanide. The reaction in the presence of 2 M alkali and 0.25 M cyanide is compared in Fig.12 with a normal uncatalysed reaction (curve A) which was followed to completion. Using a time interval of 100 hours, the reaction in the presence of cyanide was investigated by Guggenheim's method[149]. The resulting plot (Fig.13) of log (C'-C) versus time, where C represents the oxygen uptake at some time t, and C' represents that at time t + 100 hours, shows two distinct slopes, whose intersection corresponds to a time of 20 hours. The gradient of the slope for the first 20 hours is 4.93×10^{-3} hour^{-1}, and that for the remaining time is 2.69×10^{-3} hour^{-1}.

In an extension of the investigations of the effect of cyanide on the oxidation of ethanethiol, an experiment was conducted in which 0.5 M thiocyanatoethane was substituted for ethanethiol. No oxygen uptake occurred during this experiment, but after five hours the solution in the reaction vessel possessed a strong odour of diethyl disulphide. Titration of this solution showed that the disulphide had been formed in 100% yield by hydrolysis of the thiocyanatoethane.

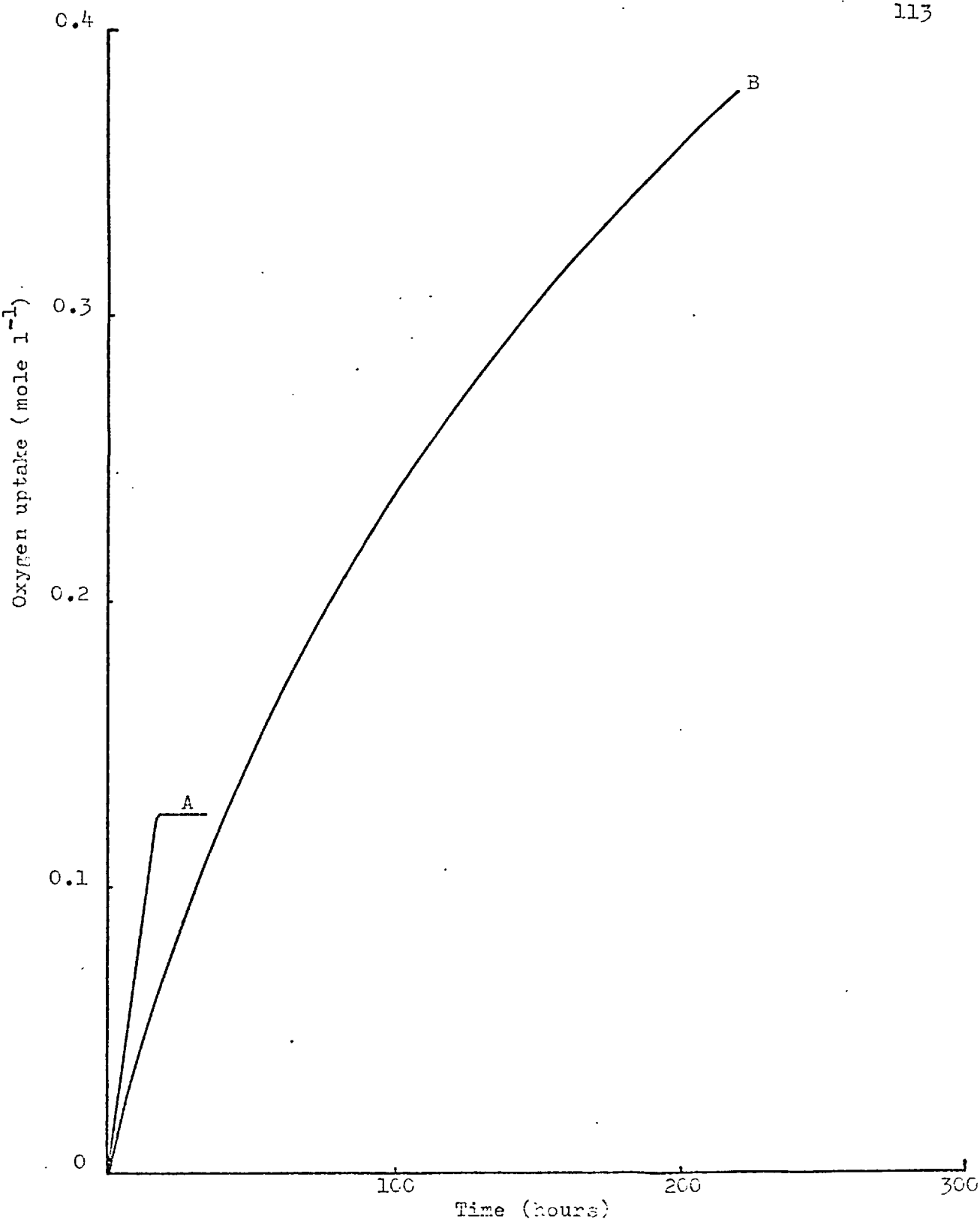


Fig.12 The oxidation of ethanethiol, effect of 0.25 M potassium cyanide on the rate of oxidation.

A - 0.5 M EtSH, No KCN: B - 0.5 M EtSH, 0.25 M KCN

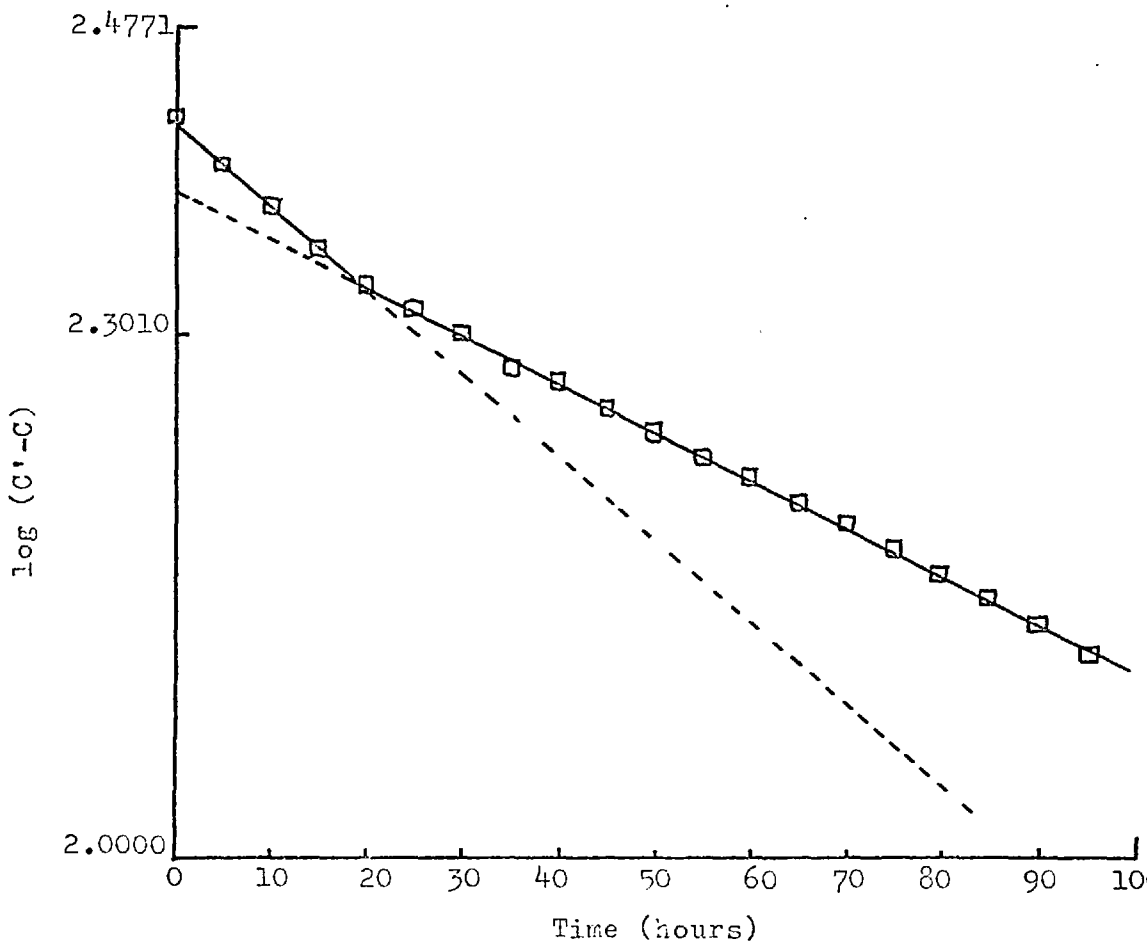


Fig.13 The oxidation of ethanethiol; Guggenheim plot showing the effect of 0.25 M potassium cyanide on the rate of oxidation.

vi) Effect of added diethyl disulphide

In order to investigate the reported catalytic effect of diethyl disulphide[66], the effect of 0.5 M added diethyl disulphide was studied both in the absence and in the presence of potassium cyanide. If the reported catalytic effect of the disulphide is due to the presence of metallic impurities, a noticeable decrease in the rate of reaction should be evident in the presence of cyanide, since such metallic impurities should be fully complexed by the cyanide and prevented from taking part in catalysis. A normal uncatalysed experiment was therefore compared with one in the presence of 0.5 M diethyl disulphide both in the absence and in the presence of 0.25 M potassium cyanide. The results are reported in Table 6, from which it can be seen that an appreciable decrease in the rate of oxidation occurs in the presence of cyanide.

Table 6

The oxidation of ethanethiol, effect of added diethyl disulphide.

[EtSH] M	[EtSSEt] M	[KCN] M	Rate mole l^{-1} sec^{-1}
0.5	0	0	1.78×10^{-6}
0.5	0.5	0	2.58×10^{-6}
0.5	0.5	0.25	1.04×10^{-6}
0.5	0	0.25	1.10×10^{-6}

vii) Comparison of different alkalies

The uncatalysed oxidation of ethanethiol has been studied in solutions of four different alkali metal hydroxides. The experiments were carried out under standard conditions with the exception of the alkali concentration, which was 1.0 M throughout the investigation. The results are compared in Table 7 and Fig.14 with similar experiments performed in the presence of 0.25 M potassium cyanide.

Table 7

The oxidation of ethanethiol, effect of various alkaline solutions

Alkali	Rate of oxidation mole l^{-1} sec^{-1}		First ionization potential[150]	Ionic Radius[150]
	No KCN	0.25 M KCN	eV	Å
LiOH	2.76×10^{-6}	0.90×10^{-6}	5.39	0.68
NaOH	1.78×10^{-6}	0.98×10^{-6}	5.14	0.97
KOH	3.72×10^{-6}	1.22×10^{-6}	4.34	1.33
CsOH	3.58×10^{-6}	1.68×10^{-6}	3.89	1.67
	6.78×10^{-6}*			

*Apparently impure sample of caesium hydroxide.

Although no correlation of rates with the physical properties of the system is apparent in the absence of cyanide, the rates in the presence of cyanide apparently bear some relationship to the first ionization potentials of the alkali metals, although

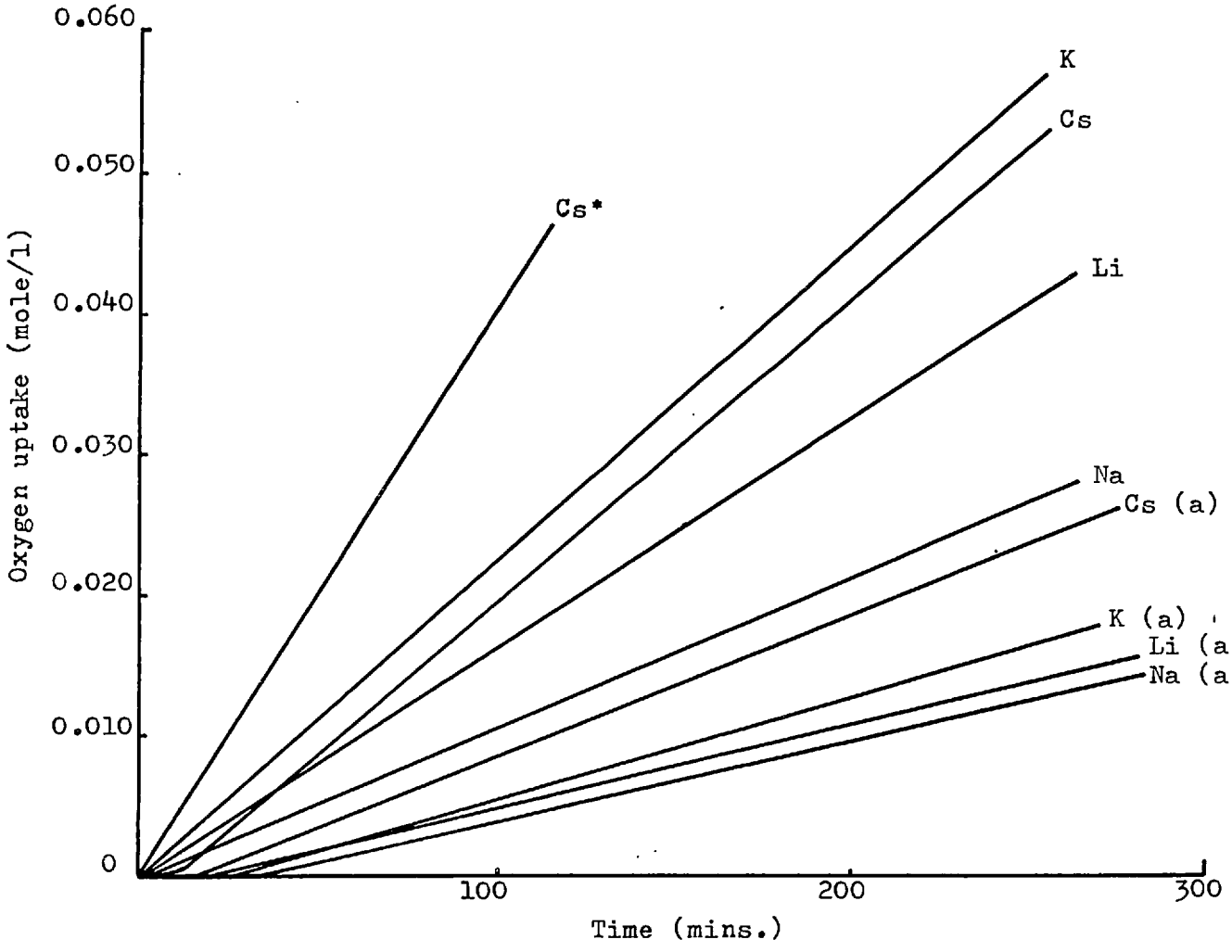


Fig.14 The oxidation of ethanethiol. Comparison of different alkali metal hydroxides in the absence and in the presence of potassium cyanide.

* Apparently impure sample of caesium hydroxide.

(a) Reaction in the presence of 0.25 M KCN.

the rate for caesium hydroxide is somewhat high in this respect. Noticeable induction periods occurred in the presence of cyanide.

viii) Effect of diphenylamine

The effect of 0.1 M diphenylamine on the oxidation of ethanethiol is shown in Fig.15 and Table 8. In addition to an increase in the rate of oxidation over a normal uncatalysed experiment there is no evidence of an induction period in the presence of diphenylamine.

ix) Effect of pyridine

The presence of 0.1 M pyridine (py) in reactant solutions is seen from Fig.15 and Table 8 to cause an increase in the rate of oxidation of ethanethiol, presumably due to the introduction to the solution of catalytic metal compounds in the pyridine.

x) Effect of α,α'-dipyridyl

The addition of 0.1 M α-α'-dipyridyl (dipy) to reactant solutions caused a large increase in the rate of oxidation. The α,α'-dipyridyl, which was of "AnalaR" quality was therefore replaced by material which was of "General Purpose Reagent" grade. The subsequent decrease in the rate of oxidation suggests that of the two grades of α,α'-dipyridyl, the "AnalaR" grade was the less pure at least with respect to metal ion impurities. Experimental results are shown in Fig.15 and Table 8.

xi) Effect of 1,10-phenanthroline

The effect of 0.1 M 1,10-phenanthroline (o-phen) on the rate of oxidation of ethanethiol was not great in the absence of

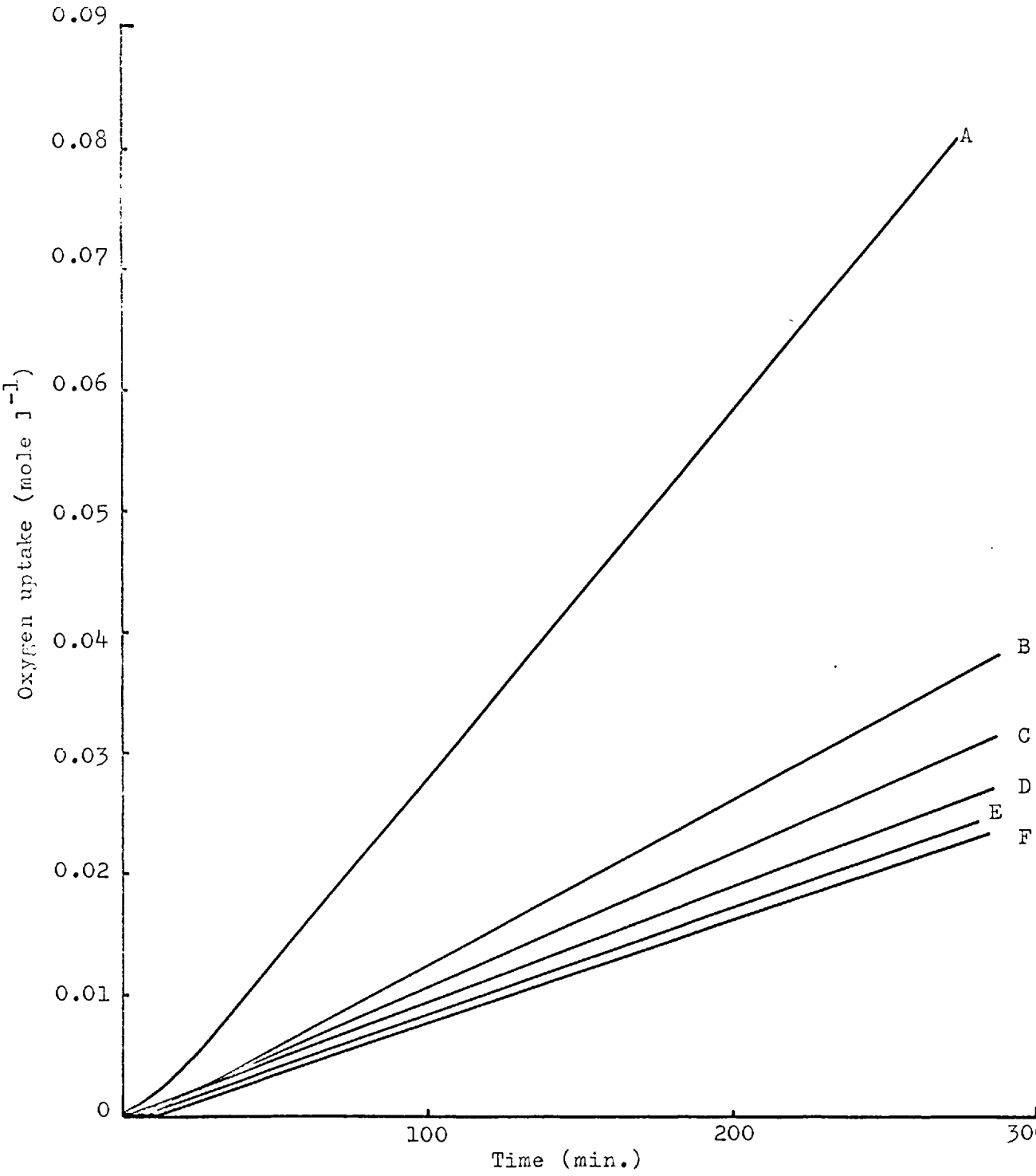


Fig.15 The oxidation of ethanethiol, effect of diphenylamine, pyridine, α,α'-dipyridyl and 1,10-phenanthroline on the rate of oxidation. Additive concentration 0.1 M.

A - dipy (AnalaR), B - py, C - dipy (G.P.R.), D - Ph_2NH, E -o-phen F - no ligands.

added metal catalysts. Experimental results are shown in Fig.15 and Table 8. The effect of 1,10-phenanthroline on the oxidation of ethanethiol in the presence of metal catalysts will be compared with the effects of pyridine and α,α'-dipyridyl in Section H.3.

Table 8

The oxidation of ethanethiol, effect of diphenylamine, pyridine, α,α'-dipyridyl and 1,10-phenanthroline on the rate of oxidation

Additive	Additive conc^{n}. M	Rate of oxidation mole l^{-1} sec^{-1}
-	-	1.42×10^{-6}
diphenylamine	0.1	1.94×10^{-6}
py	0.1	2.32×10^{-6}
dipy (a)	0.1	5.08×10^{-6}
dipy (b)	0.1	1.88×10^{-6}
o-phen	0.1	1.42×10^{-6}

(a) "AnalaR" grade

(b) "General Purpose Reagent" grade

2(b) Other thiols

In addition to the work on ethanethiol described above, experiments have been carried out on the oxidation of certain other thiols in the absence of added metal catalysts. The investigations with sec- and iso-butanethiol are compared with corresponding experiments involving n- and tert-butanethiols which have been

reported previously[66].

i) iso-Butanethiol

The uncatalysed oxidation of iso-butanethiol, unlike that of n-butanethiol, proceeded without any noticeable induction period. The increase in oxygen uptake with time is shown together with the other butanethiols in Fig.16, and the initial (steady) rates of oxidation are shown in Table 9.

ii) sec-Butanethiol

Whereas the rate of oxidation of n- and iso-butanethiol was approximately constant over the entire period throughout which the reactions were followed, that of sec-butanethiol can be seen from Fig.16 to decrease slightly as the oxidation proceeded, suggesting a dependence of the rate of oxidation on the thiol concentration. The rate of oxidation reported in Table 9 is the initial rate of oxidation after the induction period.

iii) n-Octanethiol

The uncatalysed oxidation of n-octanethiol was investigated under standard conditions and the results are shown in Table 10. The rate of oxidation of a sample of re-distilled thiol from the Eastman Kodak Company is shown as experiment A, and the rate is seen to be of the order of 30 times faster than a comparable experiment using ethanethiol. Experiment B was performed using n-octanethiol which had been thoroughly washed twice with 1 M KCN, followed by three successive washings with de-ionised distilled water. The rate is seen to be unchanged after this treatment.

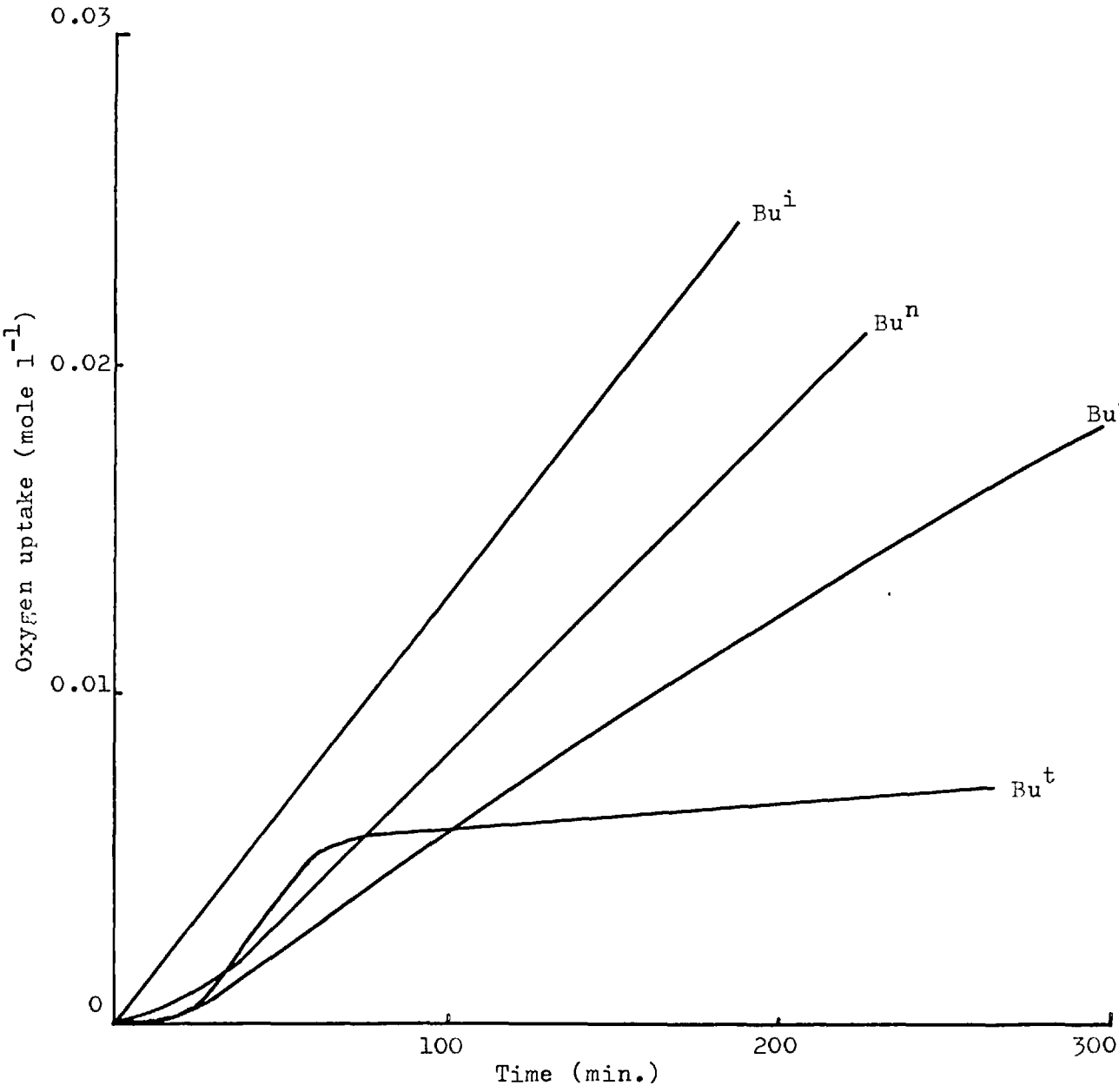


Fig.16 The uncatalysed oxidation of iso-butanethiol and sec-butanethiol; comparison with n- and tert-butanethiol.

Table 9

The uncatalysed oxidation of iso- and sec-butanethiol; comparison with n- and tert-butanethiol; standard conditions

Thiol	Initial rate of oxidation mole l^{-1} sec^{-1}
Bu^nSH	1.70×10^{-6}
Bu^iSH	2.38×10^{-6}
Bu^sSH	1.04×10^{-6}
Bu^tSH	2.33×10^{-6} (a)
	0.13×10^{-6} (b)

(a) Rate for 30 min. after induction period

(b) Final steady rate

Table 10

The uncatalysed oxidation of n-octanethiol. The conditions corresponding to the experiment letters are described in the text

Experiment	Rate of oxidation mole l^{-1} sec^{-1}
A	59.6×10^{-6}
B	59.6×10^{-6}
C	38.4×10^{-6}
D	32.8×10^{-6}
E	0.74×10^{-6} (a)

(a) Rate after 2 hour induction period

Experiment D was performed using the original re-distilled thiol which had been subjected to a second re-distillation, and the rate is seen to be reduced substantially by this procedure.

Experiment E was carried out using the original re-distilled thiol in the presence of 0.25 M KCN, whereupon the reaction proceeded, after a 2 hour induction period, at a very low rate. For comparison, a sample of thiol from K and K Laboratories, Inc. was re-distilled, and the rate of oxidation of this sample of thiol (experiment C) is seen to be comparable with that of the doubly re-distilled sample of the original n-octanethiol. In view of the high levels of impurity which were evidently present in the n-octanethiol samples, metal-catalysed experiments were not performed on n-octanethiol.

3. The oxidation of ethanethiol in the presence of metallic catalysts

3(a) Comparison of different metals

The effect on the rate of oxidation of ethanethiol of a series of metal salts has been investigated. The metals were all added to the reactant solutions as simple salts, such that the concentration of the metal in the solution was 10^{-3} M. The results of the series of experiments are given in Fig.17 and Table 11, from which it is evident that copper, cobalt and nickel are by far the best catalysts. The rate of oxidation decreased as the reaction proceeded in the case of cobalt and nickel catalysis, whereas with all other catalysts the rate was constant throughout the reaction. In order to avoid confusion in Fig.17, the majority of the less catalytic

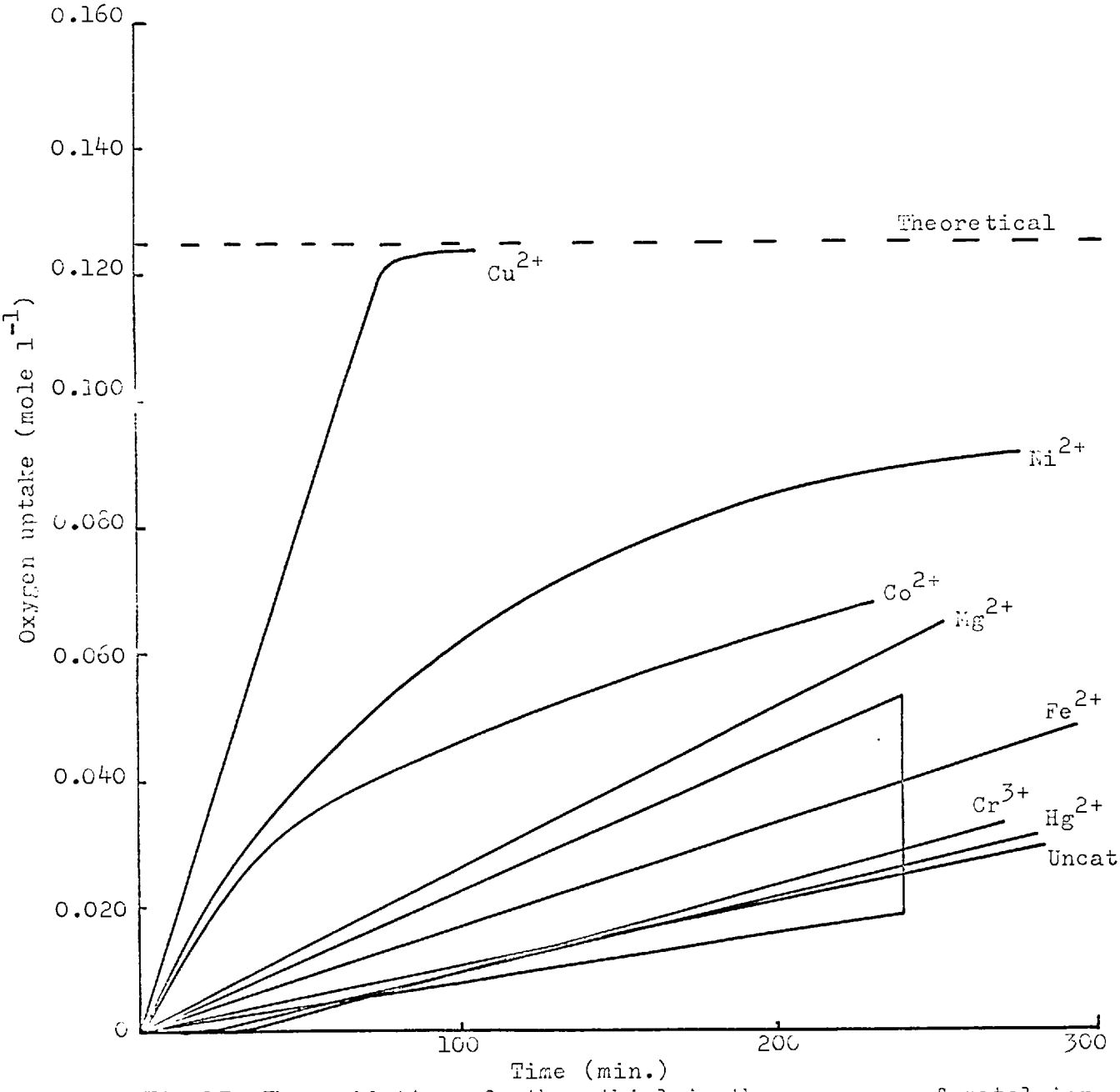


Fig.17 The oxidation of ethanethiol in the presence of metal-ion catalysts. Comparison of different metals. Solutions all 10^{-3} M in metal. Metal-ions are given alongside the corresponding curves, with the exception of the wedge shaped area which comprises Zn^{2+}, Mn^{2+}, WO_4^{2-}, Ce^{4+}, UO_2^{2+}, VO^{2+}, Cd^{2+}, Tl^{+}, $Mo_7O_{24}^{6-}$, Pt^{4+}, Sn^{2+}, Al^{3+}, Ag^{+}, Pd^{2+}.

Table 11

The oxidation of ethanethiol catalysed by metal ions

Metal	Added as	% conversion after 1.5 hours	Rate of oxidation mole l^{-1} sec^{-1}	Notes
-	-	7.1	1.87×10^{-6}	
Ce^{4+}	$(NH_4)_2Ce(NO_3)_6$	12.8	3.08×10^{-6}	
UO_2^{2+}	$UO_2(NO_3)_2.6H_2O$	11.8	2.90×10^{-6}	
VO^{2+}	$VOSO_4$ + aq.	11.5	2.60×10^{-6}	
Cr^{3+}	$Cr_2(SO_4)_3.K_2SO_4.24H_2O$	6.4	2.10×10^{-6}	
$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}.4H_2O$	13.9	3.15×10^{-6}	
WO_4^{2-}	$Na_2WO_4.2H_2O$	14.3	3.42×10^{-6}	
Mn^{2+}	$MnSO_4.4H_2O$	11.4	4.60×10^{-6}	Brown ppt. in Et_2S_2 layer
Fe^{2+}	$FeSO_4.7H_2O$	11.4	3.60×10^{-6}	Brown ppt. in Et_2S_2 layer
Co^{2+}	$CoSO_4.7H_2O$	35.7	12.80×10^{-6}	Red ppt. in Et_2S_2 layer
Ni^{2+}	$NiSO_4$ + aq.	45.7	15.16×10^{-6}	Brown ppt. in Et_2S_2 layer
Pd^{2+}	$PdCl_2$	4.8	1.45×10^{-6}	Orange ppt.

Table 11 continued

Metal	Added as	% conversion after 1.5 hours	Rate of oxidation mole l^{-1} sec^{-1}	Notes
Pt^{4+}	$PtCl_4$	12.2	2.62×10^{-6}	
Cu^{2+}	$CuSO_4.5H_2O$	96.7	26.75×10^{-6}	
Ag^{+}	$AgNO_3$	5.7	1.67×10^{-6}	Ppt. of Ag_2O dissolved on add^{n}. of EtSH
Zn^{2+}	$ZnSO_4.7H_2O$	17.5	3.85×10^{-6}	
Cd^{2+}	$3CdSO_4.8H_2O$	13.9	3.15×10^{-6}	Ppt. of $Cd(OH)_2$ dissolved on add^{n}. of EtSH
Hg^{2+}	$HgCl_2$	6.1	1.97×10^{-6}	
Al^{3+}	$Al_2(SO_4)_3.K_2SO_4.24H_2O$	11.8	2.92×10^{-6}	
Tl^{+}	Tl_2SO_4	10.3	2.37×10^{-6}	Yellow ppt.
Sn^{2+}	$SnCl_2.2H_2O$	15.4	2.22×10^{-6}	
Mg^{2+}	$MgSO_4.7H_2O$	19.0	4.32×10^{-6}	

metal ions are included within a wedge shaped area, individual rates of oxidation being given in Table 11.

One feature of oxidations carried out in the presence of metal ions was the formation, in some cases, of brightly coloured voluminous precipitates. In the case of thallium and palladium, these precipitates formed immediately on injection of the thiol into the reaction vessel, whilst in the case of iron, manganese, cobalt and nickel, these precipitates formed only after the reaction had been proceeding for 10-15 min. In the case of silver and cadmium, whilst no evidence for the formation of such precipitates was obtained, the precipitates of the hydrated metal oxides and hydroxides respectively dissolved on addition of the thiol.

From Table 11 it can be seen that the rate of oxidation in the presence of palladium and silver was less than the rate obtained in the absence of added metal-ion catalysts, and whilst the rates in the presence of chromium and mercury are higher than the uncatalysed rate, the conversion after 1.5 hours was less in the case of these two metals, since induction periods of 20 min. and 30 min. respectively were observed. The oxygen uptake curves for these metals are shown separately in Fig.17.

The oxidation of ethanethiol in the presence of the three most efficient catalysts, viz. copper, cobalt and nickel, will be described for each metal individually in the following Sections.

3(b) Effect of nickel sulphate

i) Effect of nickel concentration

The effect of nickel sulphate on the oxidation of ethanethiol was measured over the concentration range 10^{-3} M to 10^{-7} M nickel; the results are shown in Fig.18 and in Table 12. The rate increased with nickel concentration, and even at a nickel concentration of 10^{-7} M, the rate was appreciably greater than that observed in an uncatalysed experiment performed under the same conditions. The reaction mixtures from all experiments contained varying amounts of the brown precipitate noted in Table 11. No noticeable induction periods were observed during these experiments, and at all values of the nickel concentration the rate was observed to decrease as the oxidation proceeded.

ii) Effect of ethanethiol concentration

The effect on the rate of oxidation of variations in the initial ethanethiol concentration is shown in Fig.19 and Table 12. The rate was unaffected by the thiol concentration at values above 0.5 M. If log (rate) is plotted versus log ([EtSH]), (Fig.20) the rate is seen to have a first-order dependence on the thiol concentration for $[EtSH] < 0.5$ M, and a zero-order dependence for $[EtSH] \gg 0.5$ M. Values of the rate used in Fig.20 were expressed in mole sec^{-1}.

iii) Effect of oxygen pressure

The influence on the rate of oxidation of the oxygen pressure is shown in Table 12 and Fig.21. The rate was observed

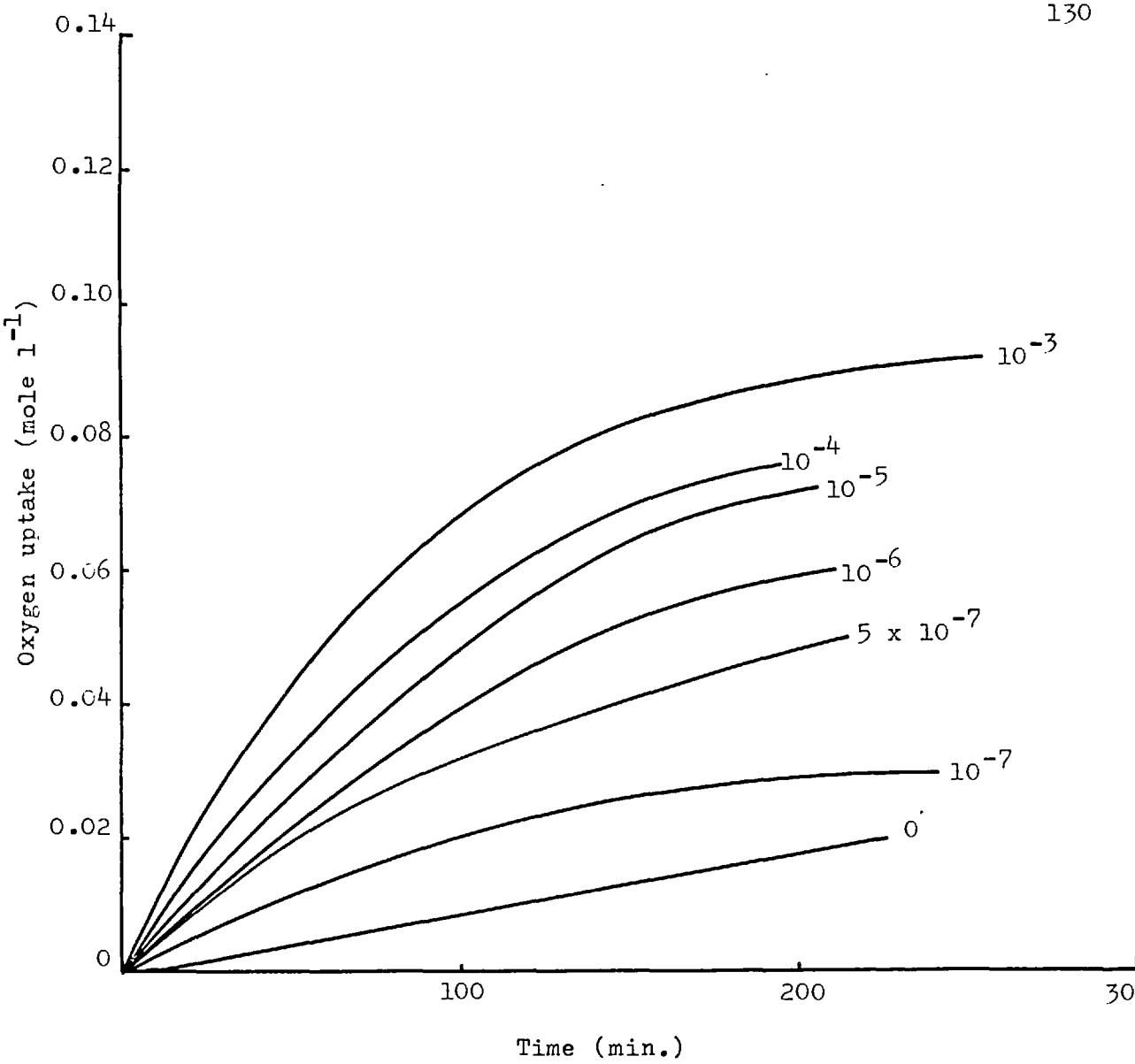


Fig.18 The oxidation of ethanethiol, effect of nickel sulphate. Nickel concentrations (M) are given against curves.

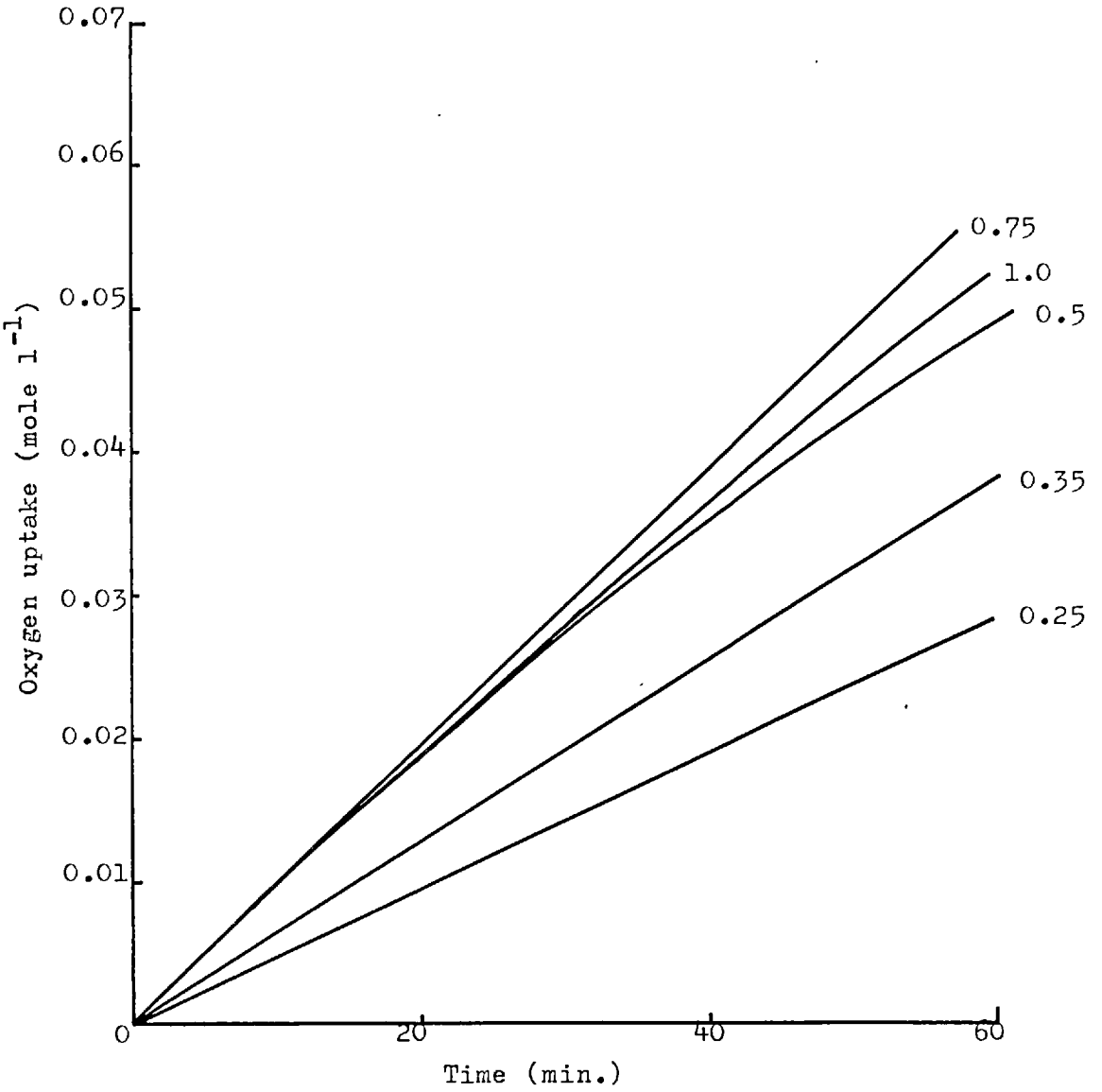


Fig. 19 The oxidation of ethanethiol, in the presence of nickel sulphate. Effect of initial thiol concentration on rate of oxidation. Thiol concentrations (M) are shown against curves.

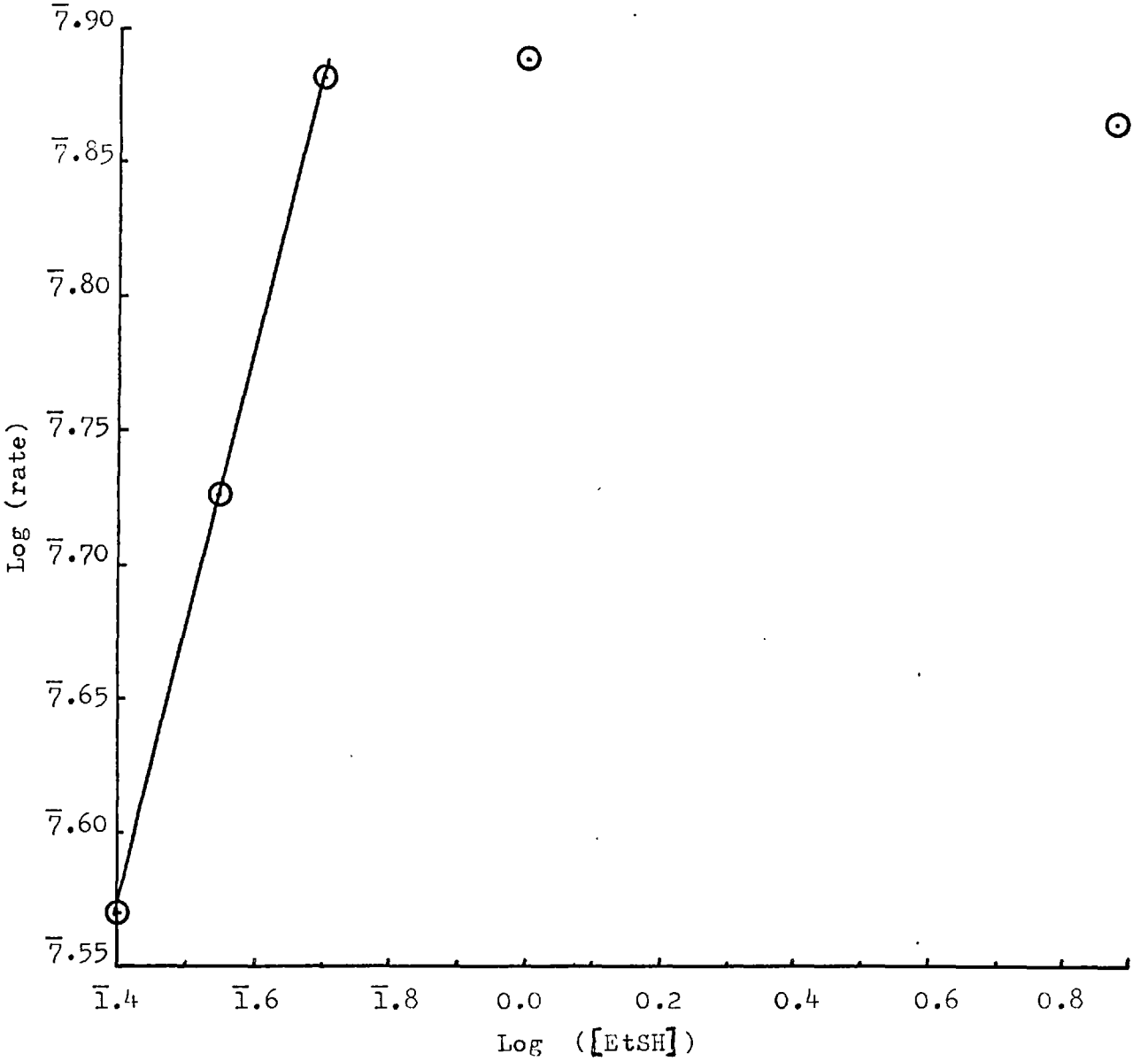


Fig.20 The oxidation of ethanethiol in the presence of 10^{-3} M nickel sulphate. Effect of initial ethanethiol concentration.

to increase linearly with increasing oxygen pressure, but the line did not extrapolate to the intercept of the axes. Fig.22 shows two plots of log (rate) versus log (oxygen pressure), where the oxygen pressure is taken respectively as the actual oxygen pressure (P), and the actual pressure minus the value of the intercept (P-Po). Both plots show that the rate has first-order dependence on the pressure of oxygen.

iv) Effect of alkali concentration

The effect of a decrease in the alkali concentration from 2.0 M to 1.0 M is seen from Table 12 to cause a considerable increase in the rate of oxidation. However, the values of the rate corrected for the solubility of oxygen in the alkali are found to be very close to each other, the rate for the 2 M alkali being slightly higher than that for the 1 M alkali.

v) Effect of cyanide

In the presence of 0.25 M potassium cyanide, the rate of oxidation of ethanethiol, catalysed by 10^{-3} M nickel sulphate, was reduced to around 10% of the value in the absence of cyanide. Furthermore, an induction period of 40 min. was observed, and no brown precipitate or coloration was evident after 5 hours. The results are shown in Fig.22 and in Table 13, which also includes for comparison, the effect of other ligands. Diethyl disulphide could not be detected amongst the products in the presence of cyanide.

vi) Effect of added diethyl disulphide

The presence of 0.5 M diethyl disulphide in addition to

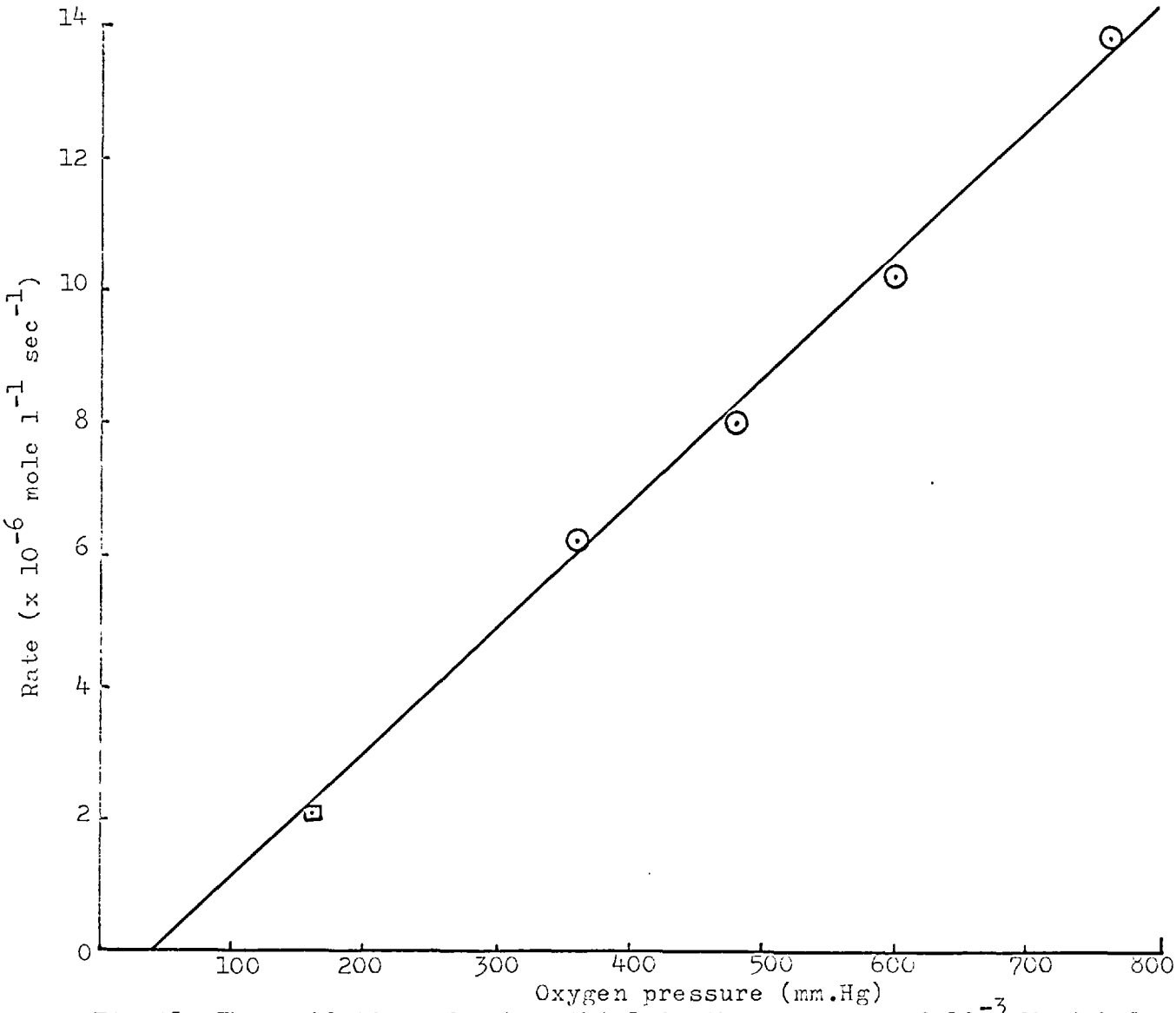


Fig.21 The oxidation of ethanethiol in the presence of 10^{-3} M nickel sulphate. Effect of oxygen pressure on the rate of oxidation.

⊙ Unballasted pressure.

⊡ Pressure balanced to 750 mm.Hg with nitrogen.

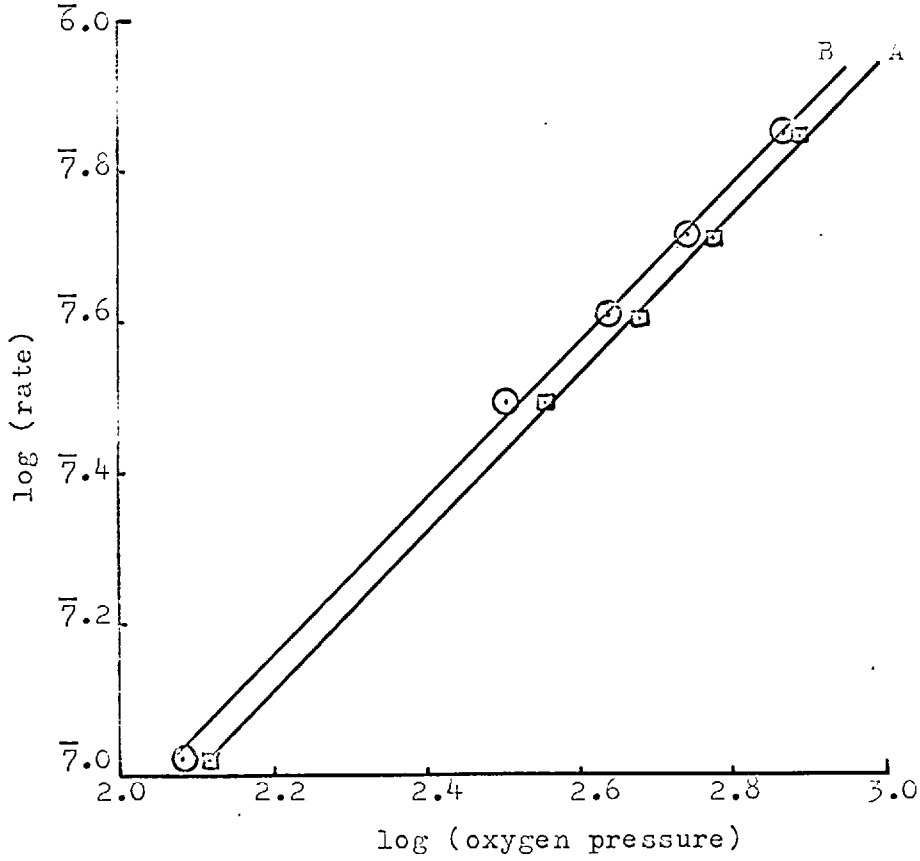


Fig.22 The oxidation of ethanethiol in the presence of 10^{-3} M nickel sulphate. Effect of oxygen pressure on rate of reaction.

Line A - pressure is the actual oxygen pressure

Line B - pressure is the actual oxygen pressure minus the value of the intercept from Fig.21 (55 mm).

Table 12

The oxidation of ethanethiol, effect of reagent concentrations on the nickel-catalysed reaction

[Ni] M	[EtSH] M	[NaOH] M	Oxygen pressure mm. Hg	Rate mole l^{-1} sec^{-1}	Rate/α* mole l^{-1} sec^{-1}
10^{-3}	0.5	2.0	750.0	15.16×10^{-6}	-
10^{-4}	0.5	2.0	750.0	11.92×10^{-6}	-
10^{-5}	0.5	2.0	750.0	8.50×10^{-6}	-
10^{-6}	0.5	2.0	750.0	7.44×10^{-6}	-
5×10^{-7}	0.5	2.0	750.0	7.40×10^{-6}	-
10^{-7}	0.5	2.0	750.0	4.02×10^{-6}	-
10^{-3}	0.25	2.0	750.0	7.44×10^{-6}	-
10^{-3}	0.35	2.0	750.0	10.58×10^{-6}	-
10^{-3}	0.75	2.0	750.0	15.50×10^{-6}	-
10^{-3}	1.0	2.0	750.0	14.60×10^{-6}	-
10^{-3}	0.5	1.0	750.0	19.40×10^{-6}	1.14×10^{-3}
10^{-3}	0.5	2.0	750.0	11.92×10^{-6}	1.08×10^{-3}
10^{-3}	0.5	2.0	761.6 (a)	13.88×10^{-6}	-
10^{-3}	0.5	2.0	597.8 (a)	10.28×10^{-6}	-
10^{-3}	0.5	2.0	479.1 (a)	8.04×10^{-6}	-
10^{-3}	0.5	2.0	358.2 (a)	6.24×10^{-6}	-
10^{-3}	0.5	2.0	160.8 (b)	2.08×10^{-6}	-
0	0.5	2.0	750.0	1.68×10^{-6}	-

(a) No nitrogen ballast

(b) Nitrogen ballast to 750.0 mm. Hg total pressure

* α is the Bunsen coefficient (Appendix 3)

the normal amount of thiol had a negligible effect on the rate of oxidation in the presence of 10^{-3} M nickel sulphate. The results obtained are presented in Table 13. The usual amount of brown precipitate was present in the product mixtures from these experiments.

vii) Effect of ethylenediamine

A series of experiments was performed to investigate the effect of ethylenediamine (en) on the nickel-catalysed oxidation of ethanethiol. At a concentration of 10^{-1} M, en had a pronounced inhibiting effect on the oxidation, and no brown precipitate or coloration was observed. A small amount of brown precipitate was formed in the presence of 10^{-2} M en, and a substantial amount was formed when the en concentration was 10^{-3} M. Kinetic results are presented in Fig.23 and Table 13.

viii) Effect of ethylenediamine tetra-acetic acid (EDTA)

The influence of EDTA on the nickel-catalysed oxidation of ethanethiol was similar to that of en, although the inhibiting effect of EDTA was generally slightly less than that of en. Similar amounts of brown precipitate were formed in the presence of similar concentrations of EDTA and en. The results obtained are given in Fig.23 and Table 13. The nature of the brown precipitate formed under certain conditions in nickel-catalysed experiments is described in Section I.

ix) Effect of temperature

A series of experiments was carried out to investigate the effect of temperature on the rate of oxidation of ethanethiol, in the

Table 13

The oxidation of ethanethiol; effect of 10^{-3} M nickel sulphate in the presence of EtSSEt, en, EDTA and KCN

Ligand	Ligand concentration M	Rate mole l^{-1} sec^{-1}	Notes
EtSSEt	0.5	15.20×10^{-6}	Brown ppt. formed
en	10^{-1}	2.50×10^{-6}	Brown ppt. not formed
en	10^{-2}	6.67×10^{-6}	Brown ppt. formed, but in reduced amount
en	10^{-3}	11.83×10^{-6}	Brown ppt. formed
EDTA	10^{-1}	3.00×10^{-6}	Brown ppt. not formed
EDTA	10^{-2}	9.00×10^{-6}	Brown ppt. formed, but in reduced amount
EDTA	10^{-3}	13.32×10^{-6}	Brown ppt. formed
KCN	0.25	1.25×10^{-6}	Brown ppt. not formed; 40 min induction period
None	-	15.20×10^{-6}	Brown ppt. formed

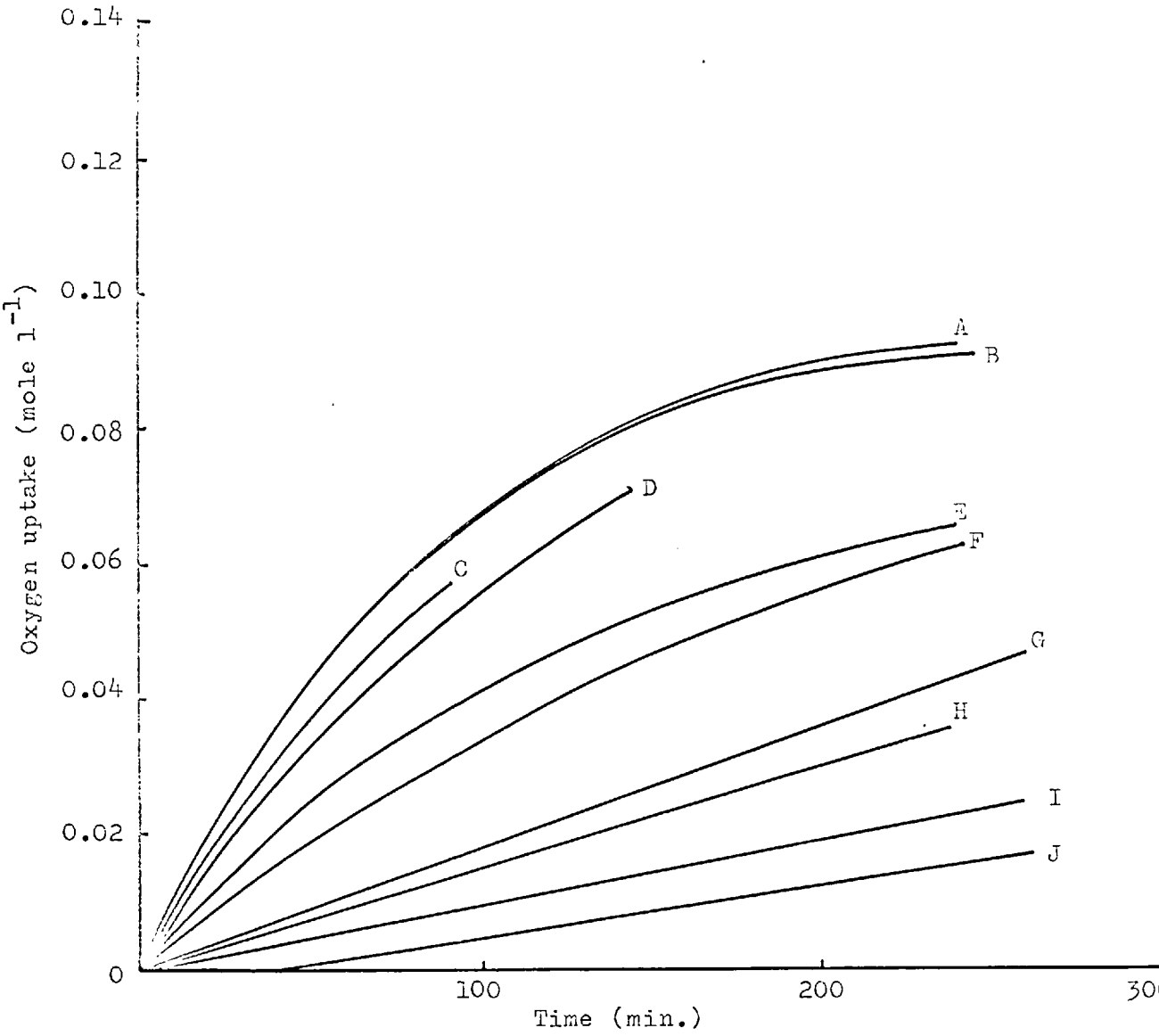


Fig.23 The oxidation of ethanethiol, effect of EtSSEt, en, EDTA and KCN in the presence of 10^{-3} M nickel sulphate. Ligands corresponding to the curves are as follows:

A - 0.5 M EtSSEt, B - No ligands, C - 10^{-3} M EDTA,

D - 10^{-3} M en, E - 10^{-2} M EDTA, F - 10^{-2} M en,

G - 10^{-1} M EDTA, H - 10^{-1} M en, I - Uncatalysed, no ligands,

J - 0.25 M KCN.

presence of 10^{-3} M nickel sulphate. Rates obtained in the temperature range 20 to 40° C were corrected for oxygen-solubility and values of rate/α are given in Table 14. An Arrhenius plot of log (rate/α) versus 1/T was constructed (Fig.24) from which a value of 8.0 K.cal $mole^{-1}$ was obtained for the activation energy.

Table 14

The oxidation of ethanethiol, effect of temperature on the reaction in the presence of 10^{-3} M nickel sulphate

Temperature °C	Temperature (T) °K	Rate mole sec^{-1}	Rate/α mole sec^{-1}
20	293	5.81×10^{-7}	4.42×10^{-5}
25	298	6.84×10^{-7}	5.60×10^{-5}
30	303	7.58×10^{-7}	6.82×10^{-5}
35	308	8.94×10^{-7}	8.55×10^{-5}
40	313	10.20×10^{-7}	10.50×10^{-5}

x) Effect of pyridine

In an extension of the investigation into the inhibition of the oxidation of ethanethiol by en, EDTA and KCN, the effect of 0.1 M pyridine on the rate of oxidation was studied. The results are given in Fig.25 and Table 15, from which the rate is seen to be very slightly higher in the presence of pyridine than in the absence of added ligands.

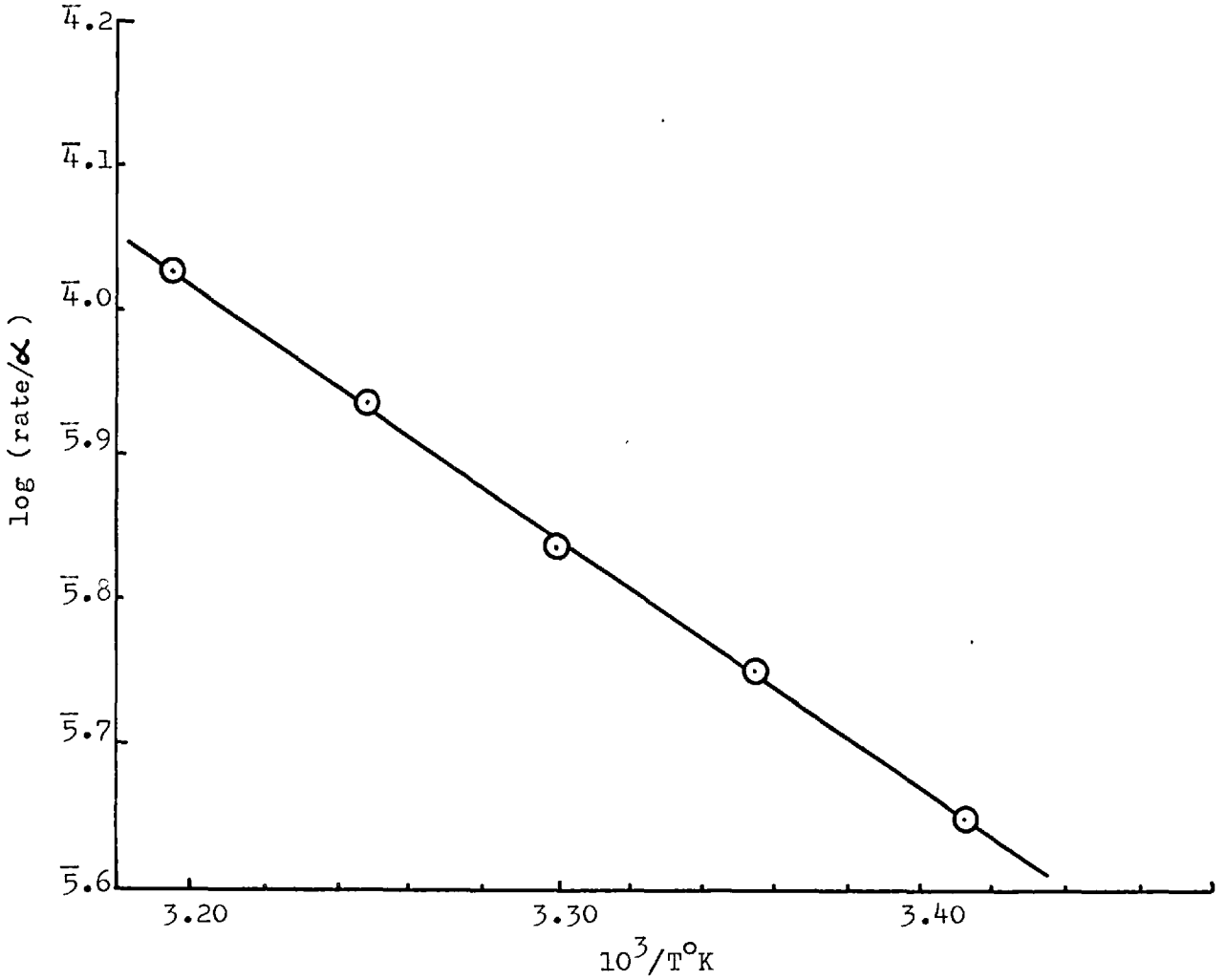


Fig.24 The oxidation of ethanethiol, effect of temperature in the presence of 10^{-3} M nickel sulphate.

xi) Effect of α,α'-dipyridyl (dipy)

Unlike the experiments with pyridine, the presence of 0.1 M dipy had a profound effect on the rate of oxidation of ethanethiol. The product mixtures from experiments in the presence of dipy contained a certain amount of brown precipitate, although this amount appeared to be smaller than that obtained in the absence of added ligands. The results obtained are summarized in Fig.25 and Table 15.

Table 15

The oxidation of ethanethiol, effect of py, dipy and o-phen on the reaction in the presence of 10^{-3} M nickel sulphate

Ligand	Ligand concentration M	Rate mole l^{-1} sec^{-1}
None	-	10.44×10^{-6}
py	0.1	10.70×10^{-6}
dipy	0.1	2.68×10^{-6}
o-phen	0.1	2.68×10^{-6}

xii) Effect of 1,10-phenanthroline (o-phen)

The influence of o-phen was found to be similar to that of dipy, and rates obtained in the presence of these two ligands were identical. The amounts of brown precipitate produced in the presence of these two ligands were also similar. The results of experiments in the presence of o-phen are included in Fig.25 and Table 15.

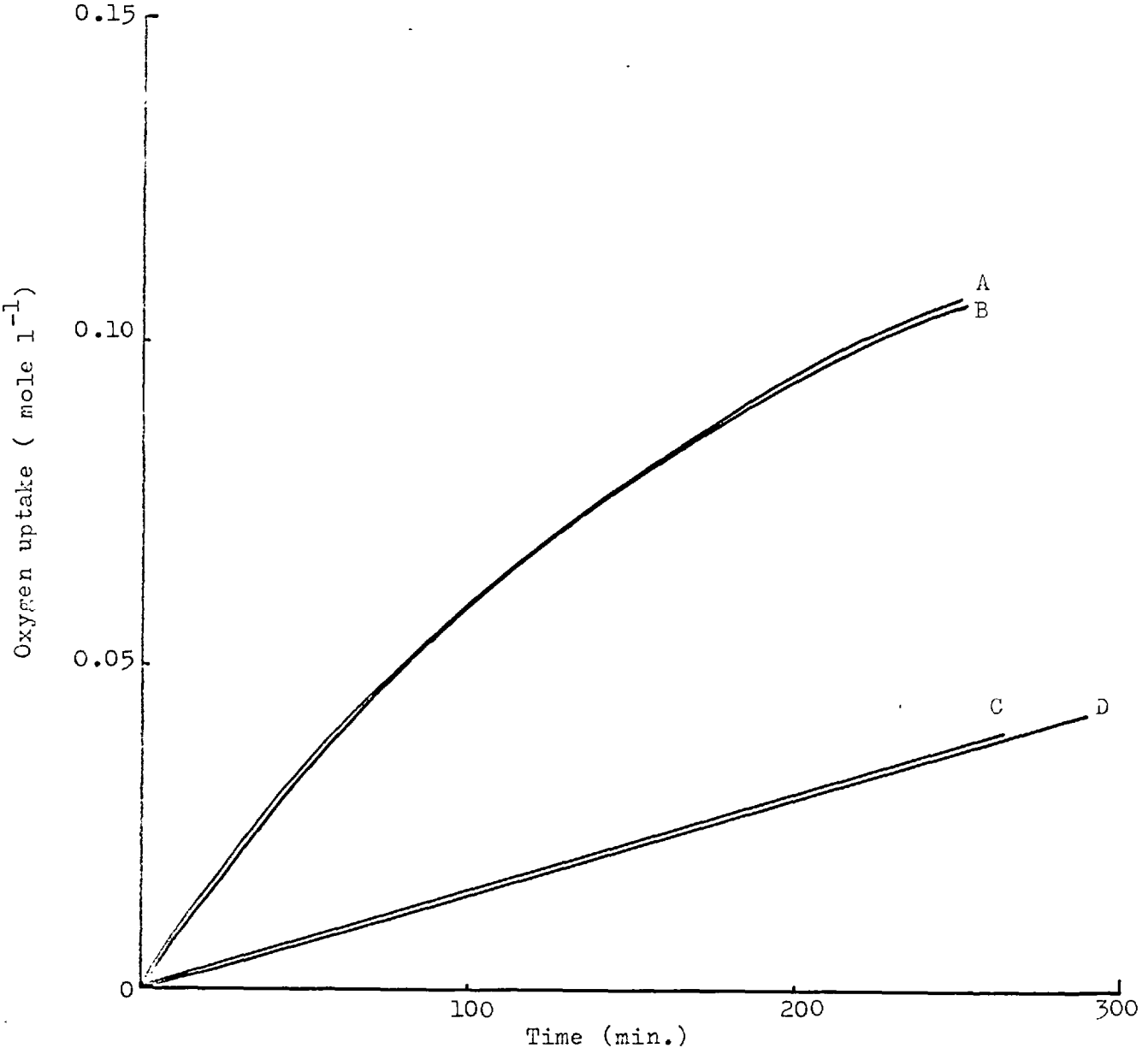


Fig.25 The oxidation of ethanethiol, effect of py, dipy and o-phen on the reaction in the presence of 10^{-3} M nickel sulphate. Letters against curves refer to the following ligands

A - no ligands, B - 0.1 M py, C - 0.1 M dipy, D - 0.1 M o-phen

3(c) Effect of copper sulphate

The oxidation of ethanethiol was studied in the presence of copper sulphate at concentrations of 10^{-3} M and 10^{-5} M. At the former concentration, the rate of oxidation was controlled by the rate of diffusion of oxygen into the reactant solution[66]. Experiments involving this concentration of copper were carried out under carefully controlled conditions, and in particular, the rate of shaking of the reaction vessel (250 c.p.m) was checked during each experiment.

i) Effect of thiol concentration

In a series of experiments in the presence of both 10^{-3} M and 10^{-5} M copper sulphate, the effect of variations in the initial thiol concentration was studied. The rates of oxidation at both values of the copper concentration were found to be virtually unaltered by the initial thiol concentration (Fig.26 and Table 16.) In a number of experiments the rate was observed to increase slightly as the oxidation proceeded, and this is noticeable in several of the curves in Fig.26.

ii) Effect of oxygen pressure

The influence on the rate of oxidation of ethanethiol of the oxygen pressure, ballasted with nitrogen to a total pressure of 75 cm.Hg, was investigated in the presence of 10^{-5} M copper sulphate. Fig.27 shows the dependence of rate upon the partial pressure of oxygen, and a rate of zero corresponded to an oxygen pressure of 6.0 cm.Hg. A plot of log (rate) versus log (oxygen pressure minus

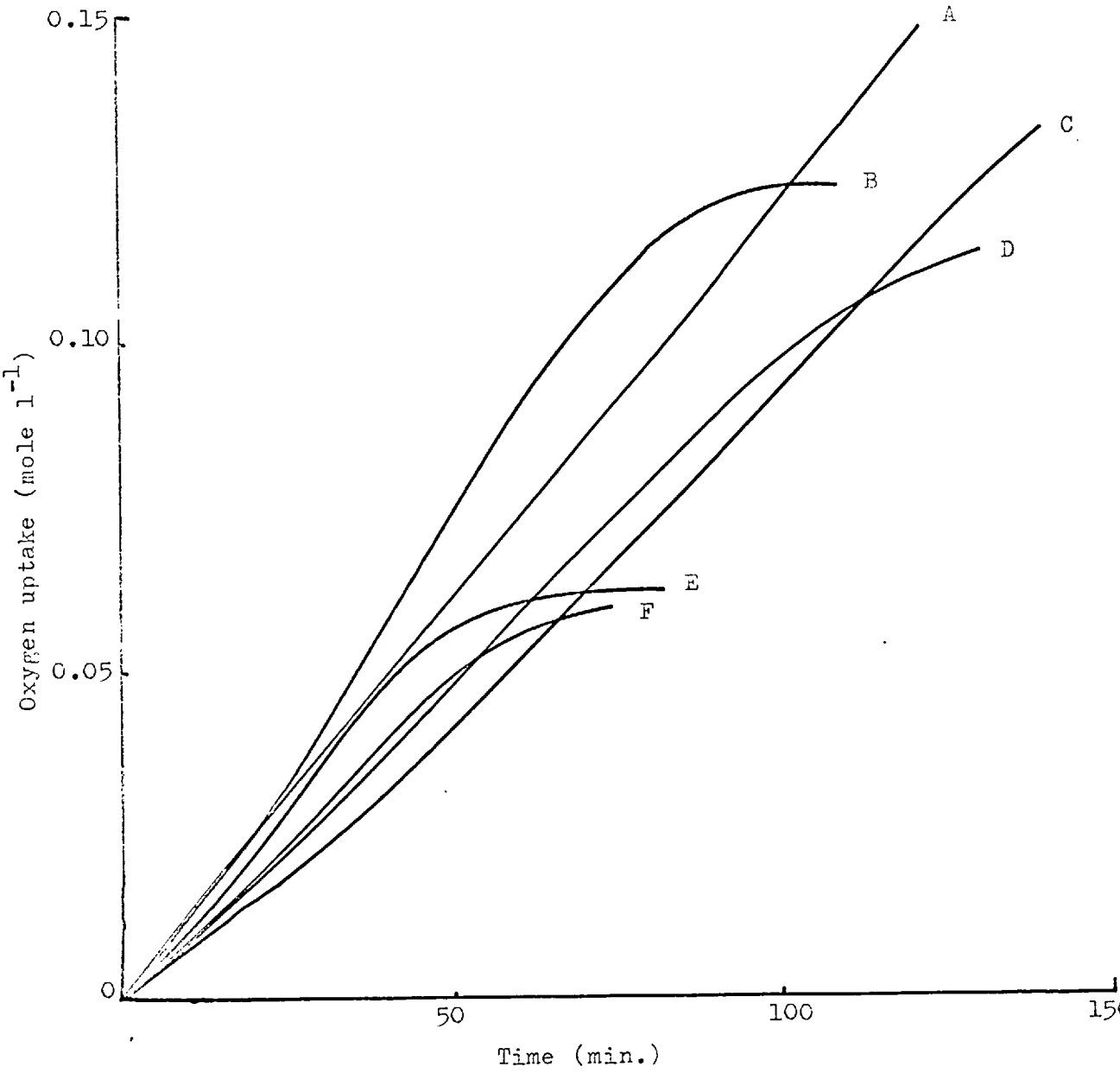


Fig. 26 The oxidation of ethanethiol, effect of initial thiol concentration in the presence of copper sulphate.

A - 10^{-3} M Cu, 1.0 M EtSH, B - 10^{-3} M Cu, 0.5 M EtSH,

C - 10^{-5} M Cu, 1.0 M EtSH, D - 10^{-5} M Cu, 0.5 M EtSH,

E - 10^{-3} M Cu, 0.25 M EtSH, F - 10^{-5} M Cu, 0.25 M EtSH.

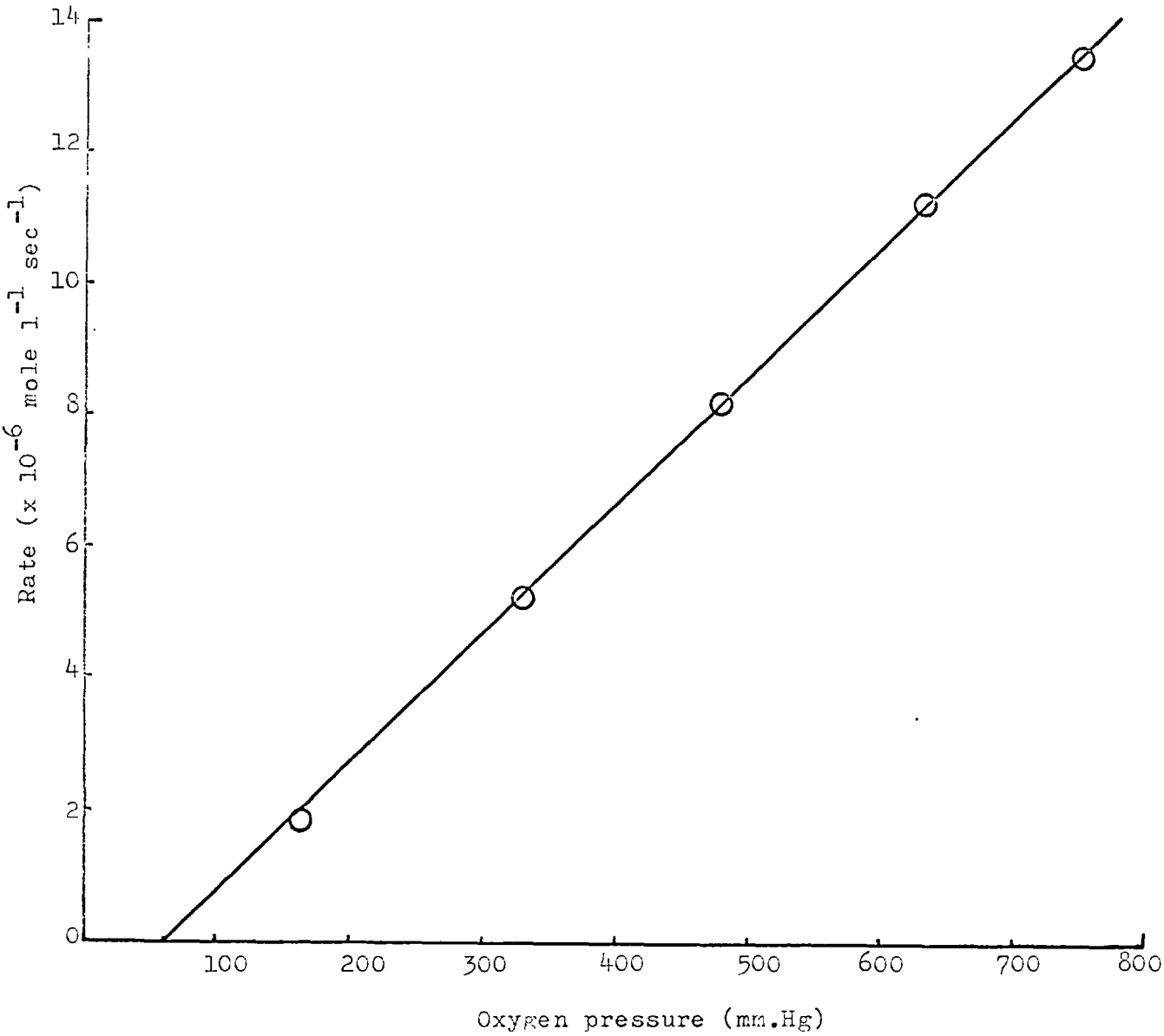


Fig.27 The oxidation of ethanethiol, effect of nitrogen-ballasted oxygen pressure in the presence of 10^{-5} M copper sulphate.

intercept) (P-Po) was constructed (Fig.28), and the rate was thus found to have a first-order dependence upon the oxygen pressure.

Table 16

The oxidation of ethanethiol, effect of initial thiol concentration on the rate in the presence of copper sulphate

Copper concentration M	Thiol concentration M	Initial Rate mole l^{-1} sec^{-1}
10^{-3}	0.25	18.80×10^{-6}
10^{-3}	0.5	20.24×10^{-6}
10^{-3}	1.0	20.24×10^{-6}
10^{-5}	0.25	13.10×10^{-6}
10^{-5}	0.5	13.40×10^{-6}
10^{-5}	1.0	12.22×10^{-6}

Table 17

The oxidation of ethanethiol, effect of alkali concentration in the presence of 10^{-3} M copper sulphate

Alkali concentration M	Rate mole l^{-1} sec^{-1}	Rate/α mole l^{-1} sec^{-1}
1.0	32.20×10^{-6}	18.24×10^{-4}
2.0	20.24×10^{-6}	18.86×10^{-4}
3.0	11.02×10^{-6}	22.97×10^{-4}

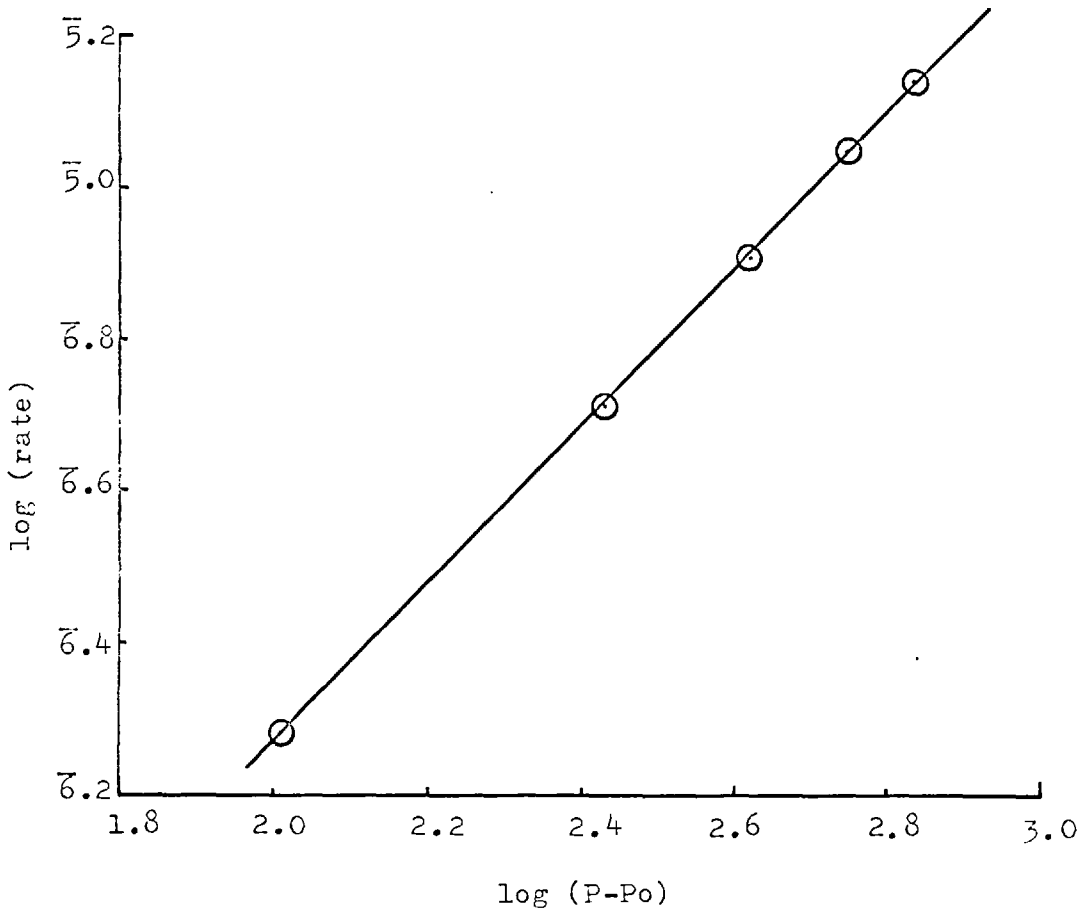


Fig. 28 The oxidation of ethanethiol, effect of oxygen pressure in the presence of 10^{-5} M copper sulphate.

iii) Effect of alkali concentration

In a series of experiments on the oxidation of ethanethiol in the presence of 10^{-3} M copper sulphate, the rates of oxidation were observed to decrease with increasing alkali concentration (Table 17). However, when results are adjusted for the solubility of oxygen in the alkaline solutions, the rates become very similar to one another.

iv) Effect of temperature

A series of experiments was carried out to investigate the effect of temperature on the oxidation of ethanethiol in the presence of copper sulphate at concentrations of 10^{-3} and 10^{-5} M respectively. Individual experiments, were carried out at a particular temperature (Table 18). Values of the activation energy, Ea, are calculated using values of the rate corrected for the solubility of oxygen in the alkaline solution at the appropriate temperature.

v) Effect of pyridine

The presence of 0.1 M pyridine in reactant solutions containing 10^{-5} M copper sulphate had virtually no effect on the rate of oxidation. The results are compared in Table 19 and Fig.29 with an experiment in which no ligands were added.

vi) Effect of α,α'-dipyridyl

The effect of dipy on the rate of oxidation of ethanethiol in the presence of 10^{-5} M copper sulphate was again negligible, unlike the effect of dipy on the nickel-catalysed reaction (see Section H.3(a)xi)). The results are given in Table 19 and Fig.29.

Table 18

The oxidation of ethanethiol; effect of temperature on the reaction in the presence of copper sulphate

Copper concentration M	Temperature °C	Rate mole l^{-1} sec^{-1}	E_a kcal $mole^{-1}$
10^{-3}	20	20.80×10^{-6}	7.6
10^{-3}	30	27.56×10^{-6}	
10^{-3}	40	34.20×10^{-6}	
10^{-5}	30	17.40×10^{-6}	3.3
10^{-5}	40	17.90×10^{-6}	

vii) Effect of 1,10-phenanthroline

Solutions of ethanethiol containing 10^{-5} M copper sulphate were oxidised at approximately the same rate in the presence and in the absence of o-phen. This is again in contrast to the results obtained with nickel sulphate. The results of experiments in the presence of o-phen are compared with those obtained in the presence of dipy and pyridine in Table 19 and Fig.29.

Table 19

The oxidation of ethanethiol in the presence of 10^{-5} M copper sulphate, effect of py, dipy and o-phen on the rate of oxidation

Ligand	Ligand concentration M	Rate mole l^{-1} sec^{-1}
none	-	13.50×10^{-6}
py	0.1	13.40×10^{-6}
dipy	0.1	12.50×10^{-6}
o-phen	0.1	11.30×10^{-6}

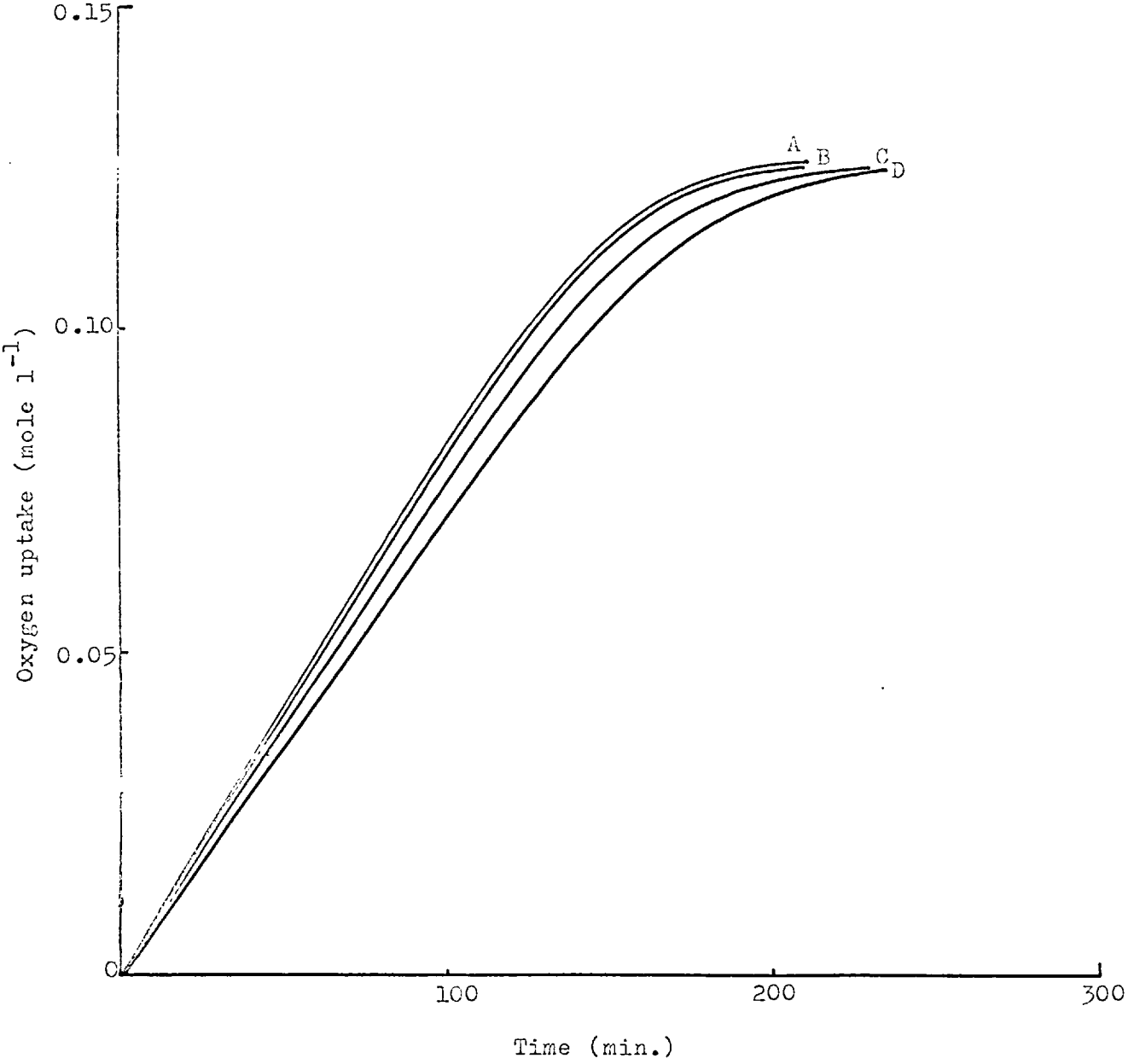


Fig.29 The oxidation of ethanethiol in the presence of 10^{-5} M copper sulphate, effect of py, dipy and o-phen.

A - No ligands, B - 0.1 M py, C - 0.1 M dipy D - 0.1 M o-phen.

3(d) Effect of cobalt sulphate

The effects of a number of parameters on the oxidation of ethanethiol were studied in the presence of 10^{-3} M cobalt sulphate, and the results obtained are presented in the following Sections.

i) Effect of thiol concentration

Experiments were carried out on the oxidation of ethanethiol in which the initial thiol concentration varied between 0.25 M and 1.0 M. All experiments resulted in the production of a voluminous red precipitate, which separated from the aqueous phase into the disulphide phase when shaking had ceased. Further experiments involving the precipitates from cobalt catalysed reactions are described in subsequent Sections. The results of experiments involving different initial thiol concentrations are presented in Table 20 and Fig.30.

Using values of the reaction rate after one hour, a plot of log (rate) versus log (initial thiol concentration) was constructed (Fig.31). Thus the rate of oxidation, which appears to have a zero-order dependence on the initial thiol concentration at the start of an experiment, has a first-order dependence after one hour. This period was chosen since the rates, which decreased sharply after approximately 30 min., were subsequently more steady. The change in rate is particularly evident in the curves with initial thiol concentrations of 0.5 M and 0.25 M.

ii) Effect of oxygen pressure

The effect of oxygen pressure on the rate of oxidation of ethanethiol in the presence of cobalt sulphate was measured at

Table 20

The oxidation of ethanethiol in the presence of 10^{-3} M cobalt sulphate, effect of initial thiol concentration

Thiol concentration M	Initial rate mole l^{-1} sec^{-1}	Rate after 1 hour mole l^{-1} sec^{-1}
0.25	12.40×10^{-6}	2.72×10^{-6}
0.50	12.80×10^{-6}	4.90×10^{-6}
1.00	14.20×10^{-6}	9.84×10^{-6}

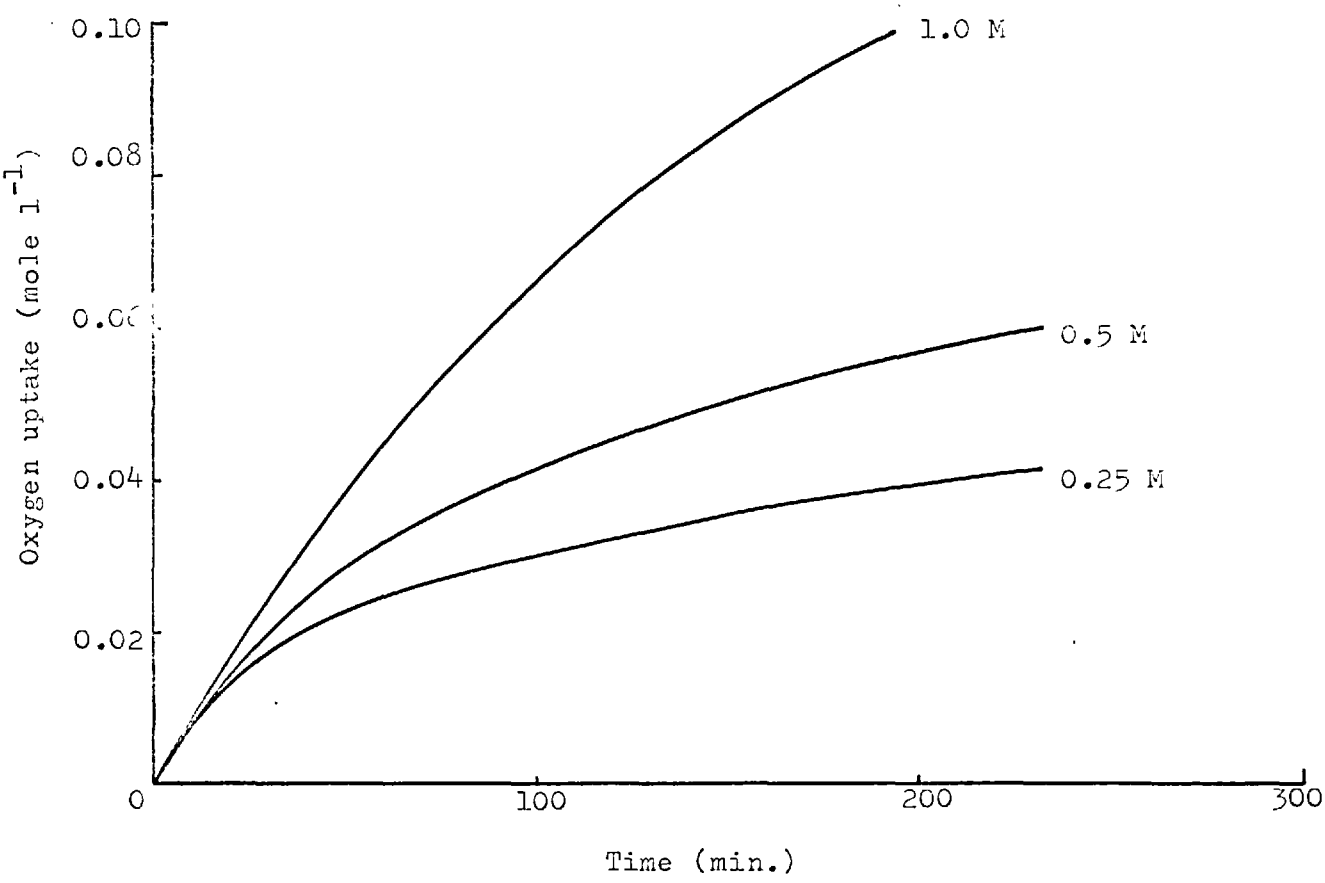


Fig. 30 The oxidation of ethanethiol in the presence of 10^{-3} M cobalt sulphate, effect of initial thiol concentration, values of [RSH] are given against curves.

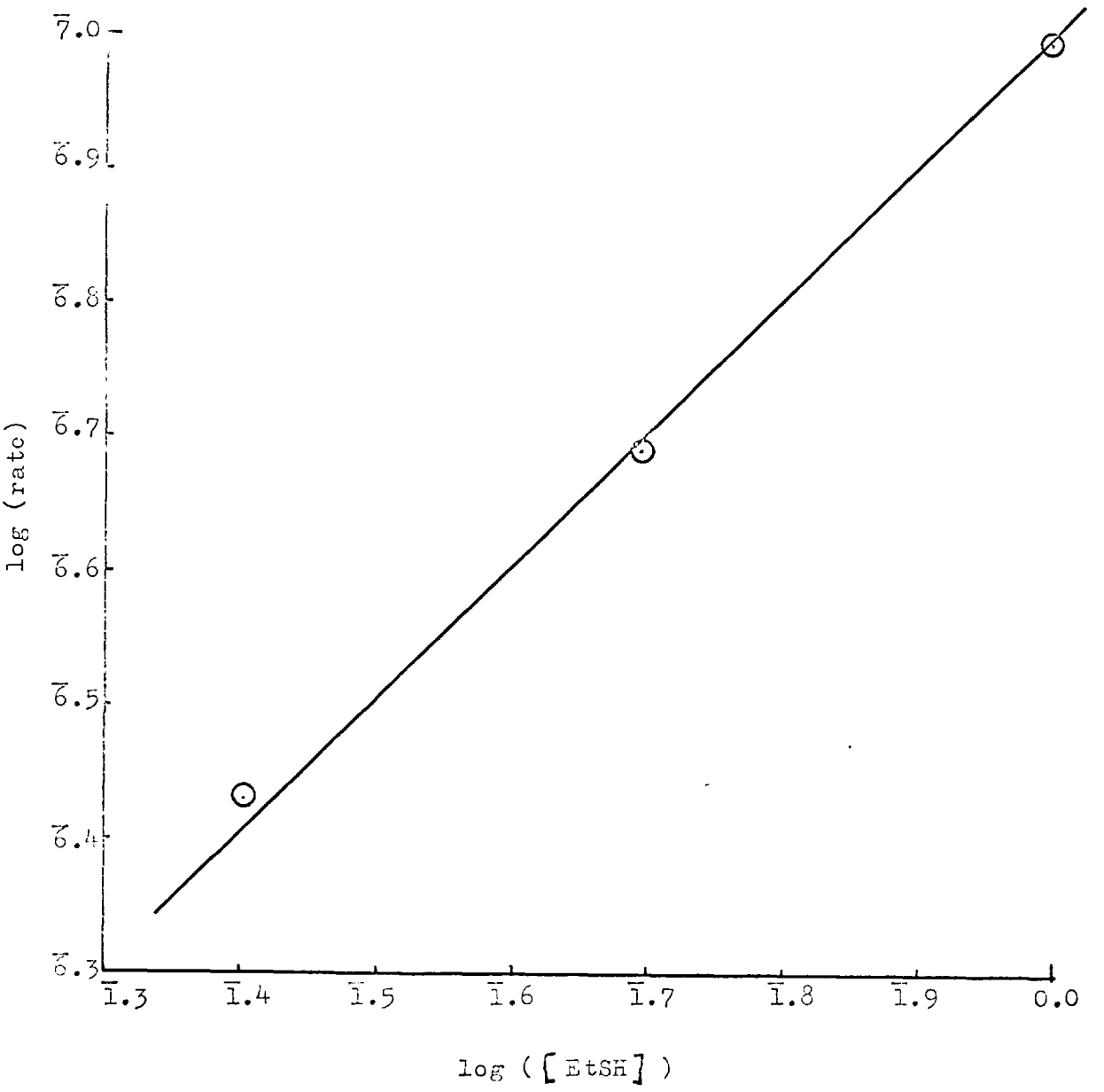


Fig.31 The oxidation of ethanethiol in the presence of 10^{-3} M cobalt sulphate, effect of initial thiol concentration.

four values of the oxygen pressure. One series of measurements was carried out using an atmosphere of oxygen, and the others using lower oxygen pressures ballasted to 75 cm.Hg with nitrogen. The results are given in Fig.32 and Table 21, and a rate of zero is observed to correspond to an oxygen pressure of 22 mm.Hg. The rate of oxidation was found to have a first-order dependence on the oxygen pressure.

Table 21

The oxidation of ethanethiol in the presence of 10^{-3} M cobalt sulphate, effect of oxygen pressure

Oxygen Pressure (P) mm.Hg	P-Po mm.Hg	Rate mole l^{-1} sec^{-1}
161.0	139.0	2.24×10^{-6}
295.0	273.0	4.32×10^{-6}
485.5	463.5	7.48×10^{-6}
751.0	729.0	11.76×10^{-6}

iii) Effect of alkali concentration

The rate of oxidation of ethanethiol in the presence of 10^{-3} M cobalt sulphate was found to decrease as the alkali concentration increased. However, on correction by the appropriate Bunsen coefficients for the solubility of oxygen in the alkaline solutions, the rate is found to increase with increasing alkali concentration. The results of experiments performed are given in Table 22.

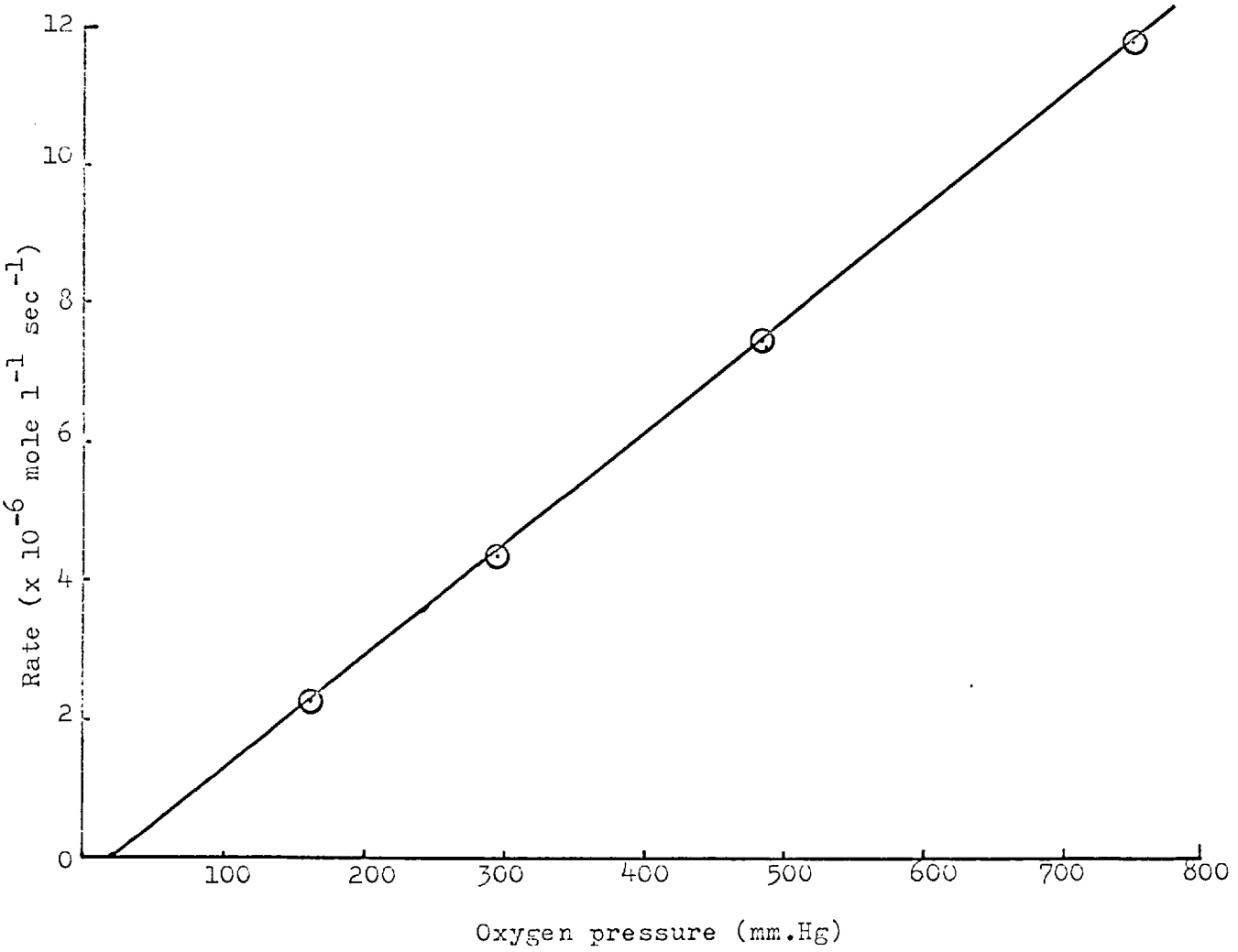


Fig.32 The oxidation of ethanethiol in the presence of 10^{-3} M cobalt sulphate, effect of nitrogen-ballasted oxygen pressure.

Table 22

The oxidation of ethanethiol in the presence of 10^{-3} M cobalt sulphate, effect of alkali concentration

Alkali concentration M	Rate mole l^{-1} sec^{-1}	Rate/α mole l^{-1} sec^{-1}
1.0	15.80×10^{-6}	9.26×10^{-4}
2.0	12.80×10^{-6}	11.50×10^{-4}
3.0	8.62×10^{-6}	17.90×10^{-4}

Table 23

The oxidation of ethanethiol in the presence of 10^{-3} M cobalt sulphate, effect of temperature

Temperature ^{o}C	Rate mole l^{-1} sec^{-1}	Rate/α mole l^{-1} sec^{-1}
21	9.90×10^{-6}	7.60×10^{-4}
25	11.90×10^{-6}	9.74×10^{-4}
31	13.50×10^{-6}	12.10×10^{-4}
37	15.60×10^{-6}	15.40×10^{-4}

iv) Effect of temperature

The effect of temperature on the rate of oxidation of ethanethiol in the presence of 10^{-3} M cobalt sulphate was studied in the range 20 - 40°C, and the results are presented in Table 23. An Arrhenius plot was constructed, using values of the rates which had been corrected for oxygen-solubility, and a value of 7.5 kcal $mole^{-1}$ was obtained for the activation energy.

v) Effect of pyridine

The presence of 0.1 M pyridine in solutions of ethanethiol caused an increase in the rate of oxidation in the presence of 10^{-3} M cobalt sulphate, but no significant change in shape of the kinetic curve. The effect of 10^{-3} M bis-pyridine $cobalt^{II}$ chloride on the rate of oxidation is included for comparison in Fig.33 and Table 24, although the effect of this complex is discussed more fully in Section H.3(e). Prior to addition to the reactant solution, a standard solution of this complex was prepared in acetone, from which 1 ml aliquots were taken, such as to provide a concentration of 10^{-3} M Co in the reactant solution.

vi) Effect of α,α'-dipyridyl

The presence of 0.1 M dipy in solutions of ethanethiol containing 10^{-3} M cobalt sulphate had a profound effect on the rate of oxidation and on the shape of the oxygen-uptake versus time curve. In contrast to experiments in the absence of added ligands, the rate of oxidation increased as the oxidation proceeded, and subsequently decreased slightly. The pronounced increase in rate occurred after the reaction had proceeded for 100 min. The results are given in

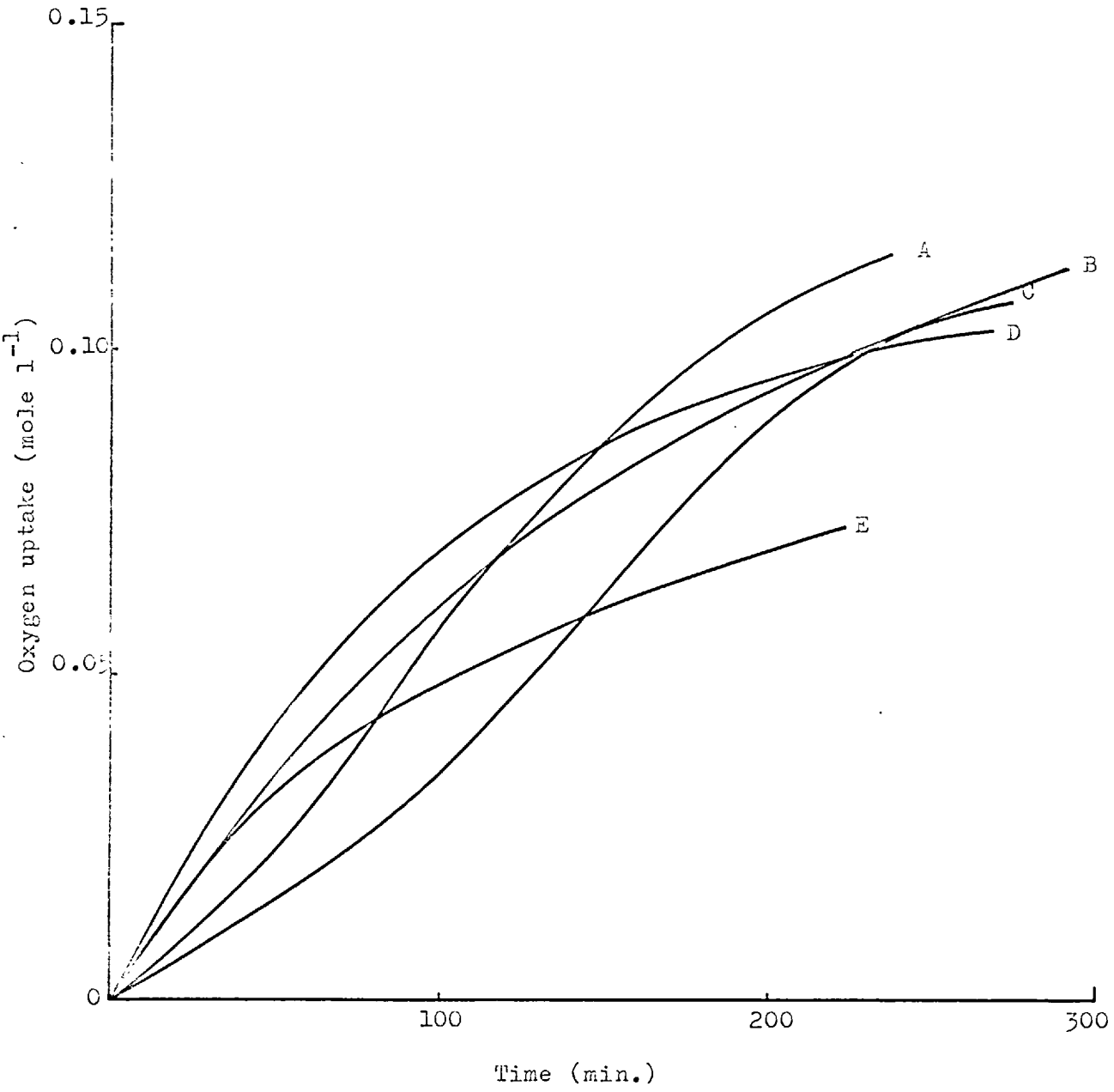


Fig.33 The oxidation of ethanethiol in the presence of 10^{-3} M cobalt sulphate, effect of ligands.

A - 0.1 M o-phen, B - 0.1 M dipy, C - No $CoSO_4.7H_2O$, 10^{-3} M $Copy_2Cl_2$, D - 0.1 M py, E - No ligands.

Fig.33 and Table 24.

vii) Effect of 1,10-phenanthroline

The effect of o-phen on the rate of oxidation of ethanethiol was similar to that of dipy, in so far as a pronounced increase in rate occurred as the reaction proceeded, and the rate of oxidation was lower than that in the absence of added ligands. The sharp increase in rate occurred earlier than in the case of dipy, viz. after approximately 50 min. In all of the reactions in the presence of py, dipy and o-phen, the amount of red complex produced during the oxidation was comparable with that produced in the absence of added ligands.

Table 24

The oxidation of ethanethiol in the presence of 10^{-3} M cobalt sulphate, effect of py, dipy and o-phen on the rate of oxidation

Ligand	Ligand concentration M	Rate mole l^{-1} sec^{-1}
None	-	11.90×10^{-6}
py	0.1	13.70×10^{-6}
py	10^{-3}*	11.90×10^{-6}
dipy	0.1	5.36×10^{-6}
o-phen	0.1	7.14×10^{-6}

* added as $Copy_2Cl_2$

3(e) Effect of cobalt complexes

Experiments were carried out in which the cobalt was added to the reactant solutions as various cobalt complexes, in order to investigate the effect on the rate of oxidation of the ligand environment of the cobalt. The concentration of cobalt in all experiments was 10^{-3} M, and the results are given in Fig.34 and Table 25. Thus the initial rate of oxidation in the presence of bis-pyridine cobalt^{II} chloride was similar to that with cobalt sulphate, although the rate with cobalt sulphate became less as the oxidation proceeded. A similar trend was observed in the presence of carbonatopentammine cobalt^{III} nitrate and cis-chloroaquotetrammine cobalt^{III} chloride. Since trans-$[Coen_2Cl_2]Cl$ formed the cis-isomer immediately on contact with the alkaline solution, the rates for these two isomers are identical. In the presence of all of the above complexes, the red precipitate common to reactions in the presence of cobalt sulphate was produced, details of which are given in Section I.2. In the presence of tris-ethylenediamine cobalt^{III} chloride, an induction period of approximately 5 min. was observed, and the amount of red precipitate formed during the oxidation was substantially less than with the previous complexes.

The presence of cobalt as potassium cobalticyanide resulted in the rate of oxidation being considerably lower, and an induction period of 10 min. was observed. No red precipitate was formed during experiments involving this complex. The disodium cobalt^{II} salt of EDTA resulted in a rate of oxidation similar to that found with cis$[Coen_2Cl_2]Cl$, and this is consistent with the results

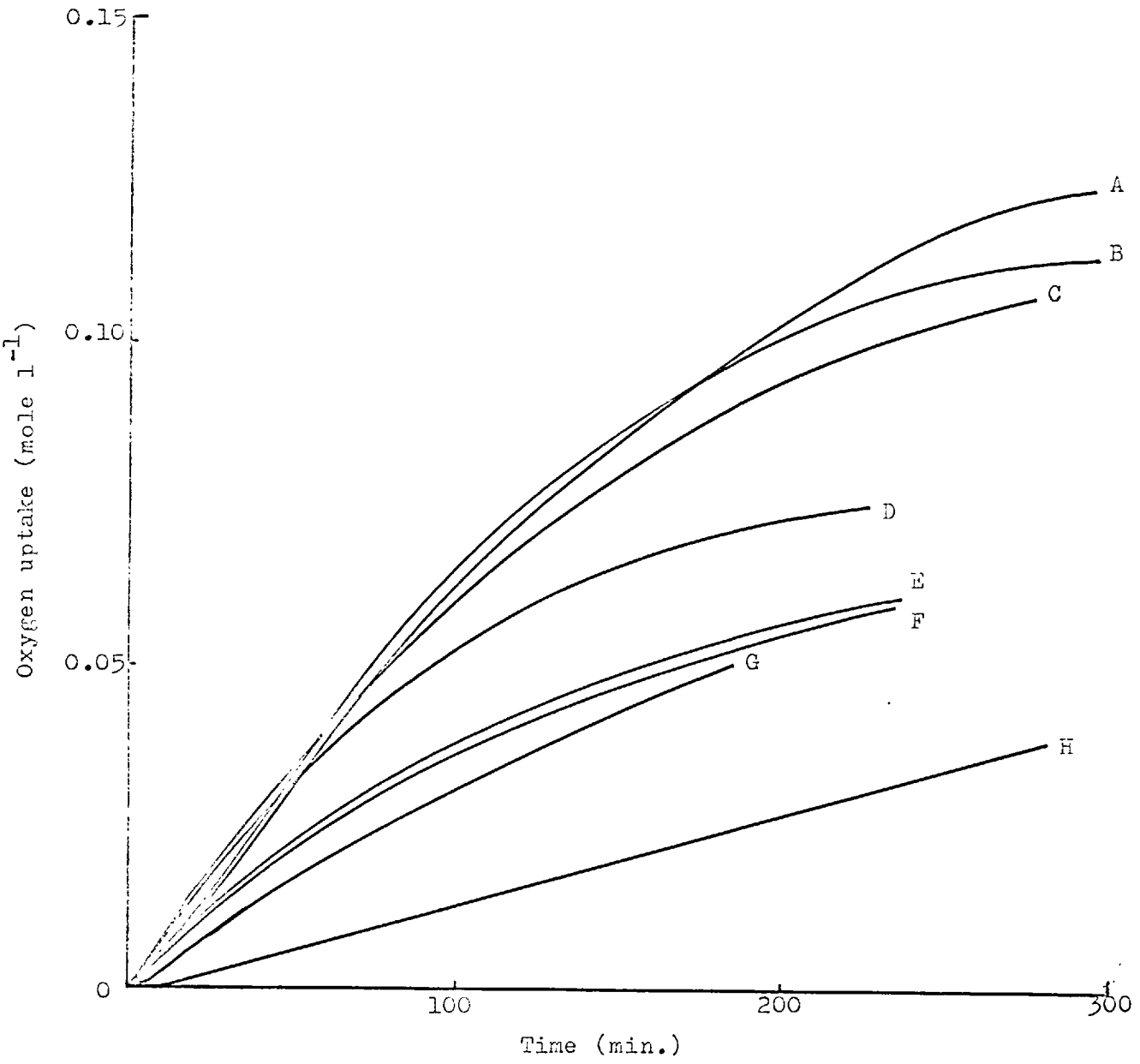


Fig.34 The oxidation of ethanethiol in the presence of cobalt complexes. Cobalt concentration = 10^{-3} M. Letters against curves correspond to the following complexes.

A - $[Co(NH_3)_5CO_3]NO_3$, B - cis-$[Co(NH_3)_4(H_2O)Cl]Cl_2$, C - $Copy_2Cl_2$, D - $CoSO_4.7H_2O$, E - $Na_2Co(EDTA)$, F - cis- and trans-$[Coen_2Cl_2]Cl$, G - $Coen_3Cl_3.3H_2O$, H - $K_3Co(CN)_6$.

obtained in Section H.3(b) for the oxidation of ethanethiol in the presence of 10^{-3} M nickel sulphate, and en and EDTA respectively.

Table 25

The oxidation of ethanethiol, effect of cobalt complexes

Complex (10^{-3} M Co)	Rate mole l^{-1} sec^{-1}
$CoSO_4.7H_2O$	11.90×10^{-6}
$Copy_2Cl_2$	11.90×10^{-6}
$[Co(NH_3)_5CO_3]NO_3$	9.80×10^{-6}
cis-$[Co(NH_3)_4(H_2O)Cl]Cl_2$	10.72×10^{-6}
cis-$[Coen_2Cl_2]Cl$	8.04×10^{-6}
trans-$[Coen_2Cl_2]Cl$	8.04×10^{-6}
$Na_2Co(EDTA)$	8.20×10^{-6}
$Coen_3Cl_3.3H_2O$	6.24×10^{-6}
$K_3Co(CN)_6$	2.14×10^{-6}

The results of experiments on the formation of coloured precipitates in the presence of these complexes are described in Section I.2(a).

3(f) Effect of metal-thiol complexes

The coloured precipitates which were a feature of oxidations carried out in the presence of cobalt and nickel, and which are shown in Section I to be metal-thiol complexes, were added to reactant solutions in order to compare their catalytic ability with that of the parent metal sulphate. The complexes were added

in two series, firstly the actual complex formed during experiments in the presence of 10^{-3} M metal sulphate were removed from the product mixture by filtration, washed successively with 2N sodium hydroxide and with deionised distilled water and used immediately as the catalyst for a subsequent experiment. Thus the amount of metal present in the subsequent experiment was $\leq 10^{-3}$ M, depending upon the extent to which the metal-thiol complex was formed from the metal sulphate in the previous experiment.

In the second series of experiments, samples of complexes which had been specially prepared and purified were used. These samples, which had previously been analysed, were added to the reactant solutions as dry solids, the amount of which was adjusted so that the concentration of metal in the solutions was 10^{-3} M. The results of these experiments are given in the following Sections.

i.) Cobalt complex with ethanethiol

Addition of the red cobalt complex with ethanethiol to solutions of ethanethiol resulted in approximately the same rate of oxidation as was observed in the presence of cobalt sulphate. The results are given in Fig.35 and Table 26, which contain for comparison the results of experiments involving cobalt sulphate. One feature of the curves in Fig.35 is that the rate of oxidation in the presence of the complexes was approximately constant throughout the oxidation, whereas in the presence of cobalt sulphate the rate decreased as the reaction proceeded. In the former case, however, the rate did change slightly, becoming lower, after approximately 20 min, but theoretical conversion of thiol to disulphide was,

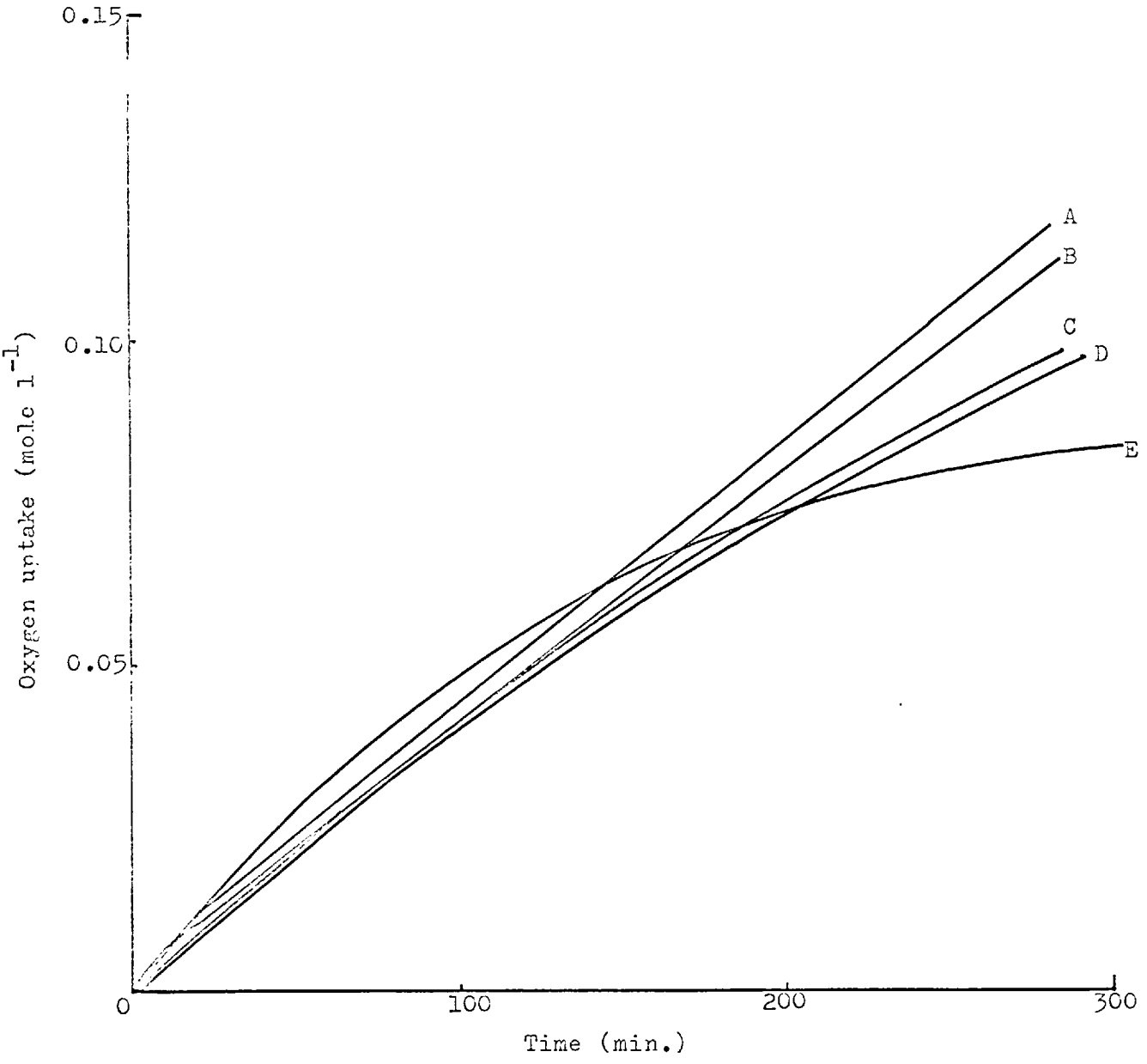


Fig.35 The oxidation of ethanethiol in the presence of cobalt-thiol complexes. Letters against curves refer to the following complexes.

A - Co-EtSH complex[(a)], B - Co-EtSH complex[(b)], C - Co-Hex^{n}SH complex (a), D - Co-Hex^{n}SH complex[(b)], E - $CoSO_4.7H_2O$.

(a) added as dry analysed complex to give 10^{-3} M Co.

(b) complex obtained from experiment with $CoSO_4.7H_2O$.

however, reached earlier than in the case of cobalt sulphate. No significant difference was observed between cobalt-thiol complexes which were used immediately after their formation, and those which had been purified, dried, and added to the reactant solutions to give a cobalt concentration of 10^{-3} M.

ii) Cobalt complex with n-hexanethiol

The effect on the rate of oxidation of ethanethiol of the red cobalt complex formed from an alkaline mixture of cobalt sulphate and n-hexanethiol is shown in Fig.35 and Table 26. Both the rate and the shape of the kinetic curve were basically similar to those observed in the presence of the cobalt complex of ethanethiol, although the rate did tend to decrease slightly as the reaction proceeded.

iii) Soluble nickel complex with ethanethiol

The brown complex formed during experiments involving nickel sulphate can be separated into a soluble portion and an insoluble portion (Section I). In the experiments described below, both complexes were added separately as dry analysed solids so as to make the reactant solution 10^{-3} M in nickel. The results, which are given in Fig.36 and Table 27, are compared with an experiment where the complex was added as a precipitate obtained during a reaction in the presence of 10^{-3} M nickel sulphate. This latter complex contains both the soluble and insoluble portions.

Experiments in the presence of the soluble nickel complex with ethanethiol gave initial rates slightly lower than corresponding experiments in the presence of nickel sulphate, but the decrease in

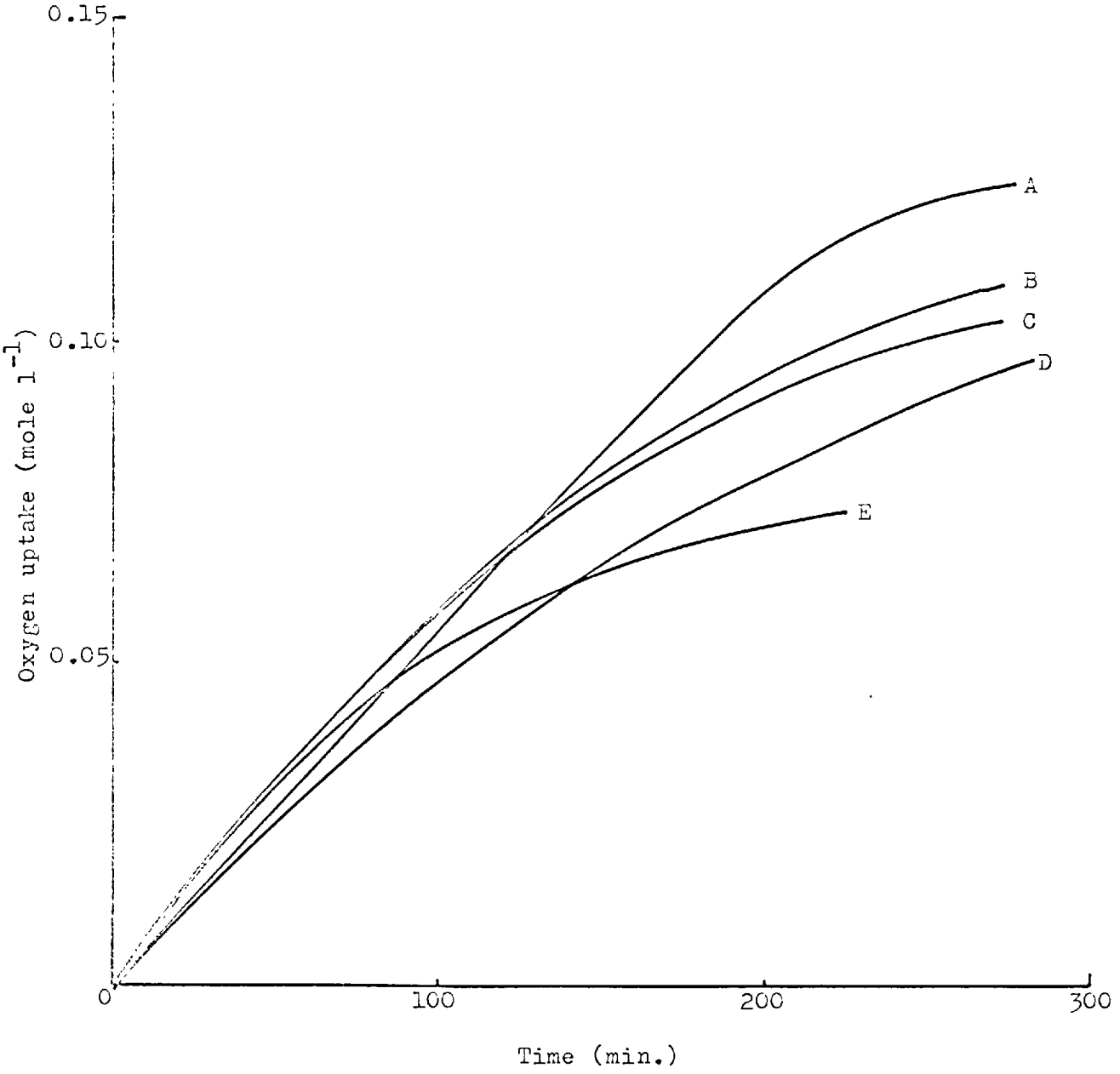


Fig.36 The oxidation of ethanethiol in the presence of nickel-thiol complexes. Letters against curves refer to following complexes.

A - Black insoluble complex, B - soluble complex,

C - mixed complex[(a)], D - insoluble brown complex,

E - nickel sulphate.

(a) product of reaction in the presence of 10^{-3} M nickel sulphate.

Table 26

The oxidation of ethanethiol, effect of cobalt-thiol complexes

Complex	Cobalt concentration M	Rate mole l^{-1} sec^{-1}
$CoSO_4.7H_2O$	10^{-3}	9.62×10^{-6}
Co-EtSH complex	10^{-3} (a)	9.62×10^{-6}
Co-EtSH complex	$\leqslant 10^{-3}$ (b)	9.56×10^{-6}
Co-Hex^{n}SH complex	10^{-3} (a)	8.83×10^{-6}
Co-Hex^{n}SH complex	$\leqslant 10^{-3}$ (b)	8.79×10^{-6}

(a) Added as dry analysed complex to give 10^{-3} M Co

(b) Complex obtained from experiment with 10^{-3} M $CoSO_4.7H_2O$

Table 27

The oxidation of ethanethiol, effect of nickel-thiol complexes

Complex	Nickel concentration M	Rate mole l^{-1} sec^{-1}
$NiSO_4$ + aq.	10^{-3}	11.30×10^{-6}
soluble	10^{-3}	9.82×10^{-6}
insoluble (a)	10^{-3}	9.84×10^{-6}
insoluble (b)	$\geqslant 10^{-3}$	9.20×10^{-6}
mixed (c)	$\leqslant 10^{-3}$	10.01×10^{-6}

(a) True insoluble brown complex

(b) Black insoluble complex

(c) Mixed complex obtained from reaction with nickel sulphate

rate as the oxidation proceeded was not so pronounced as in the latter case.

iv) Insoluble nickel complex with ethanethiol

Addition of the insoluble brown complex of nickel with ethanethiol to reactant solutions again resulted in similar rates and similar kinetic curves to those obtained with nickel sulphate. The decrease in rate as the oxidation proceeded was not as great as that observed with nickel sulphate. Investigations were also made on another sample of the insoluble complex, which was black in colour, and this complex gave a kinetic curve which resembled closely those obtained with cobalt complexes, i.e. the rate of oxidation remained constant throughout the oxidation. Analysis of this sample, however, showed that the insoluble (brown) nickel complex was present to the extent of only ca. 10% of the total, the remainder being hydrated nickel oxide, (see Section I). The results of these experiments are given in Fig.36 and Table 27.

3(g) Effect of macrocyclic tetrapyrrolic complexes

In all of the experiments described in the previous sections, with the exception of those carried out in the presence of cyanide or cyanide ligands, the initial reaction on addition of the metal salt solution to the reactants was the formation of metal hydroxides or hydrated oxides. Experiments were therefore performed in which the metal was added to the solutions in the form of an alkali-soluble complex. A convenient example was provided by macrocyclic tetrapyrrolic complexes, and in particular, haemin, vitamin B_{12} and chlorophyll were used in the present investigations,

the results of which are described below.

i) Haemin

The effect of haemin on the rate of oxidation of ethanethiol is given in Figs.37 and 38 and in Table 28. Comparison is made with the effects of vitamin B_{12} and chlorophyll in Table 29. The rate of oxidation was increased by a factor of approximately 4 in the presence of haemin compared with the rate in the presence of ferrous sulphate. The brown precipitate common to oxidations in the presence of ferrous sulphate (Table 11) was not present in haemin-catalysed experiments. In a series of experiments in which the haemin concentration was varied, the rate of oxidation was observed to increase with increasing haemin concentration. The shape of the kinetic curves varied during these experiments, the rate being approximately constant at the two lower concentrations, whereas at the highest concentration (1.5×10^{-3} M) the rate decreased as the reaction proceeded. The results of these experiments are given in Fig.37 and Table 28.

a Effect of thiol concentration

The influence of the initial thiol concentration on the rate of oxidation of ethanethiol in the presence of haemin is shown in Table 28. The fact that the rates of oxidation are identical at thiol concentrations of 0.5 M and 1.0 M may be due to the rate of reaction being controlled by the rate of diffusion of oxygen into the reactant solution, since the rate at a thiol concentration of 0.25 M was substantially lower. Taking values of log(rate) and log ($[EtSH]$) for thiol concentrations of 0.5 and 0.25 M, the reaction is

approximately first-order with respect to thiol in the range $[EtSH] \leqslant 0.5$ M.

Table 28

The oxidation of ethanethiol in the presence of haemin

Haemin concentration M	Thiol concentration M	Oxygen pressure mm.Hg	Rate mole l^{-1} sec^{-1}
0.6×10^{-3}	0.5	750.0	11.90×10^{-6}
1.0×10^{-3}	0.5	750.0	17.10×10^{-6}
1.5×10^{-3}	0.5	750.0	26.50×10^{-6}
1.0×10^{-3}	1.0	750.0	17.10×10^{-6}
1.0×10^{-3}	0.25	750.0	8.92×10^{-6}
1.0×10^{-3}	0.5	761.6	25.20×10^{-6} (a) 15.00×10^{-6} (b)
1.0×10^{-3}	0.5	161.6	2.22×10^{-6}

(a) Rate after 25 min.

(b) Rate for first 25 min.

b Effect of cyanide

In all the experiments previously described, potassium cyanide has had a marked retarding effect on the rate of oxidation. However, in experiments carried out in the presence of haemin, the rates were observed to increase in the presence of cyanide. Furthermore, substantially quantitative amounts of disulphide were present at the end of the oxidation. The results are given in Fig.38

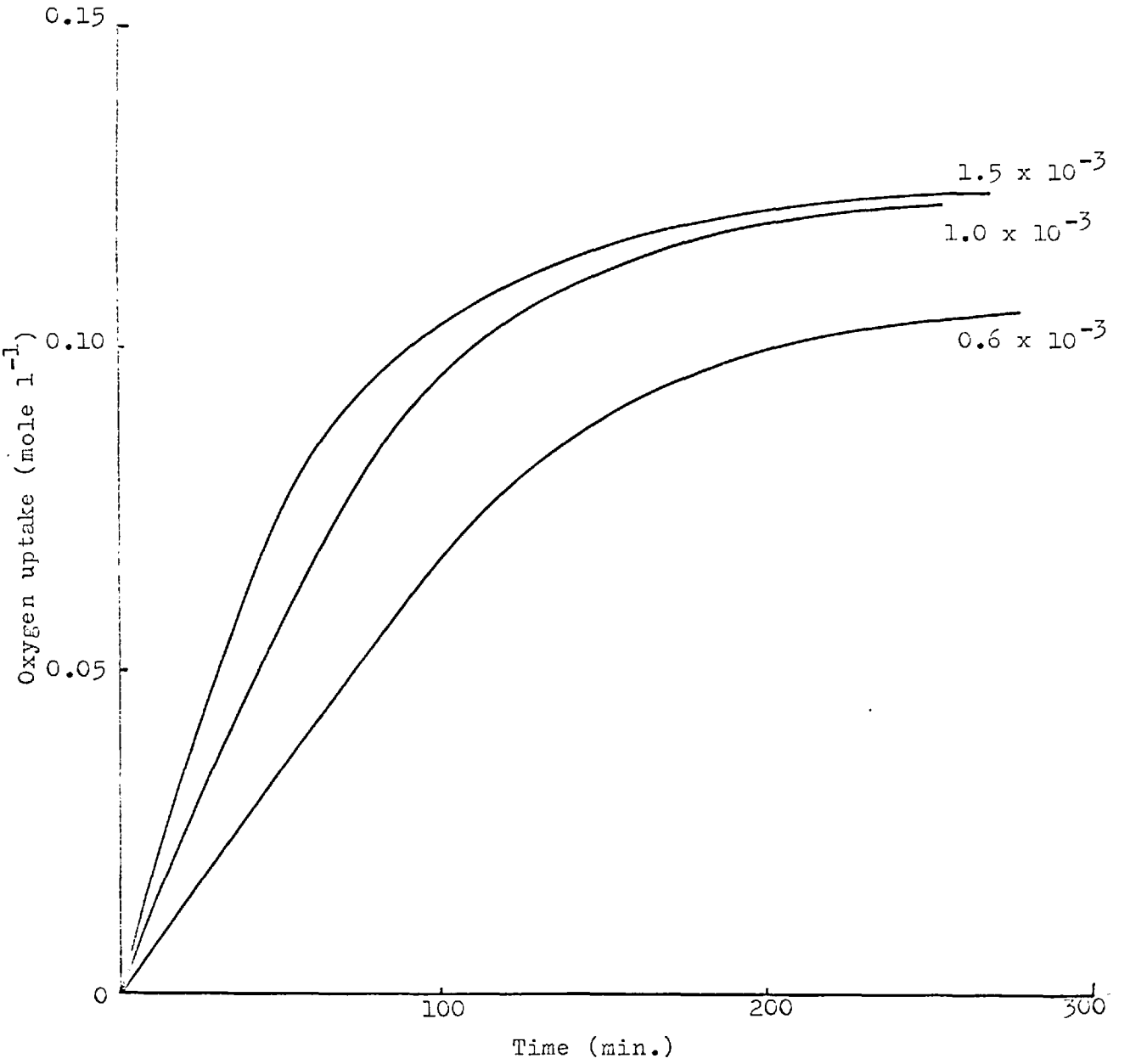


Fig.37 The oxidation of ethanethiol in the presence of haemin. Haemin concentrations are shown against curves.

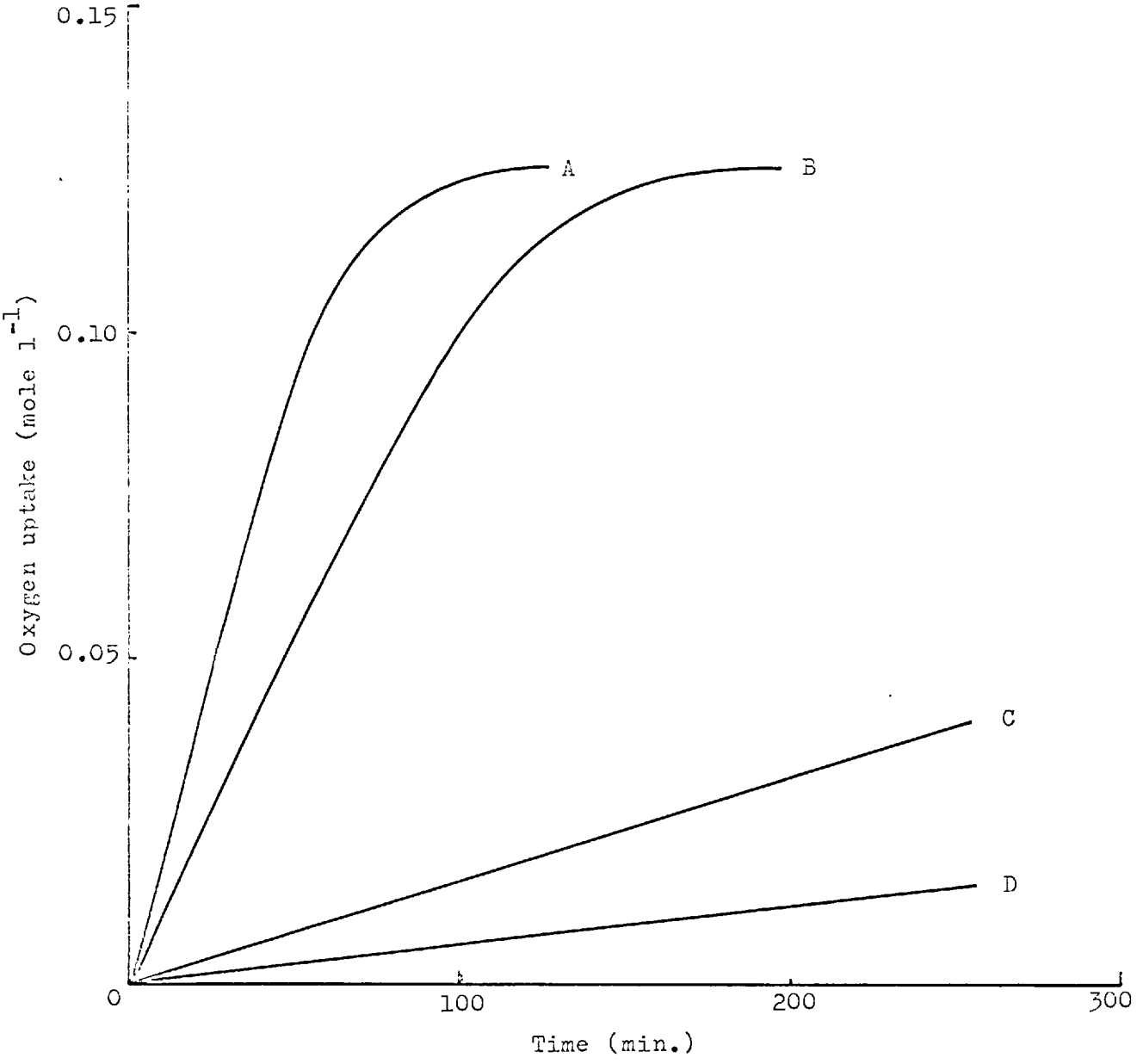


Fig.38 The oxidation of ethanethiol in the presence of haemin.

Letters against curves refer to the following conditions.

A - 10^{-3} M Haemin, 0.25 M KCN, B - 10^{-3} M Haemin,

C - 10^{-3} M $FeSO_4.7H_2O$, D - Uncatalysed.

and in Table 29.

c Effect of oxygen pressure

The oxidation of ethanethiol in the presence of haemin was investigated with oxygen at atmospheric pressure, and with a sub-atmospheric pressure of oxygen ballasted to 75 cm.Hg with nitrogen. The results are given in Table 28. An interesting feature of the experiment carried out under one atmosphere pressure of oxygen was that the rate changed abruptly after 25 min; this was not observed in other experiments in the presence of haemin. Extrapolation of the rate obtained gives zero-rate intercepts of 57 mm.Hg and 104 mm.Hg respectively, using the initial rate and the rate after 25 min. Thus by comparison of values of log (rate) and log (P-Po) for the two values of the oxygen pressure, where Po is the value of the intercept, the rate is found to have a first-order dependence on the oxygen pressure.

ii) Vitamin B_{12}

The effect of vitamin B_{12} on the rate of oxidation of ethanethiol is shown in Fig.39 and Table 29. The rate of oxidation was increased by a factor of approximately seven compared with that found in the presence of cobalt sulphate, and there was no evidence of the red precipitate associated with experiments in the presence of cobalt sulphate.

a Effect of cyanide

Unlike experiments with haemin, the rate of oxidation in the presence of 0.25 M potassium cyanide was extremely low, and no disulphide could be detected amongst the products of the oxidation.

Table 29

The oxidation of ethanethiol, effect of haemin, vitamin B_{12} and chlorophyll

Metal	Added as	Rate mole l^{-1} sec^{-1}		% conversion in 1 hour*		Final percentage of disulphide formed	
		No KCN	0.25 M KCN	No KCN	0.25 M KCN	No KCN	0.25 M KCN
None	-	1.08×10^{-6}	0.25×10^{-6}	3	3	100	0
Fe	$FeSO_4.7H_2O$	3.60×10^{-6}	1.11×10^{-6}	10	6	101	0
Fe	Haemin	17.10×10^{-6}	29.44×10^{-6}	100	100	100	101
Co	$CoSO_4.7H_2O$	12.34×10^{-6}	1.10×10^{-6}	32	3.5	100	0
Co	Vitamin B_{12}	80.40×10^{-6}	1.34×10^{-6}	100	5	101	0
Mg	$MgSO_4.7H_2O$	4.32×10^{-6}	0.60×10^{-6}	12.5	3	102	0
Mg	Chlorophyll	9.00×10^{-6}	0.98×10^{-6}	26	3	101	0

* Based on theoretical conversion of thiol to disulphide

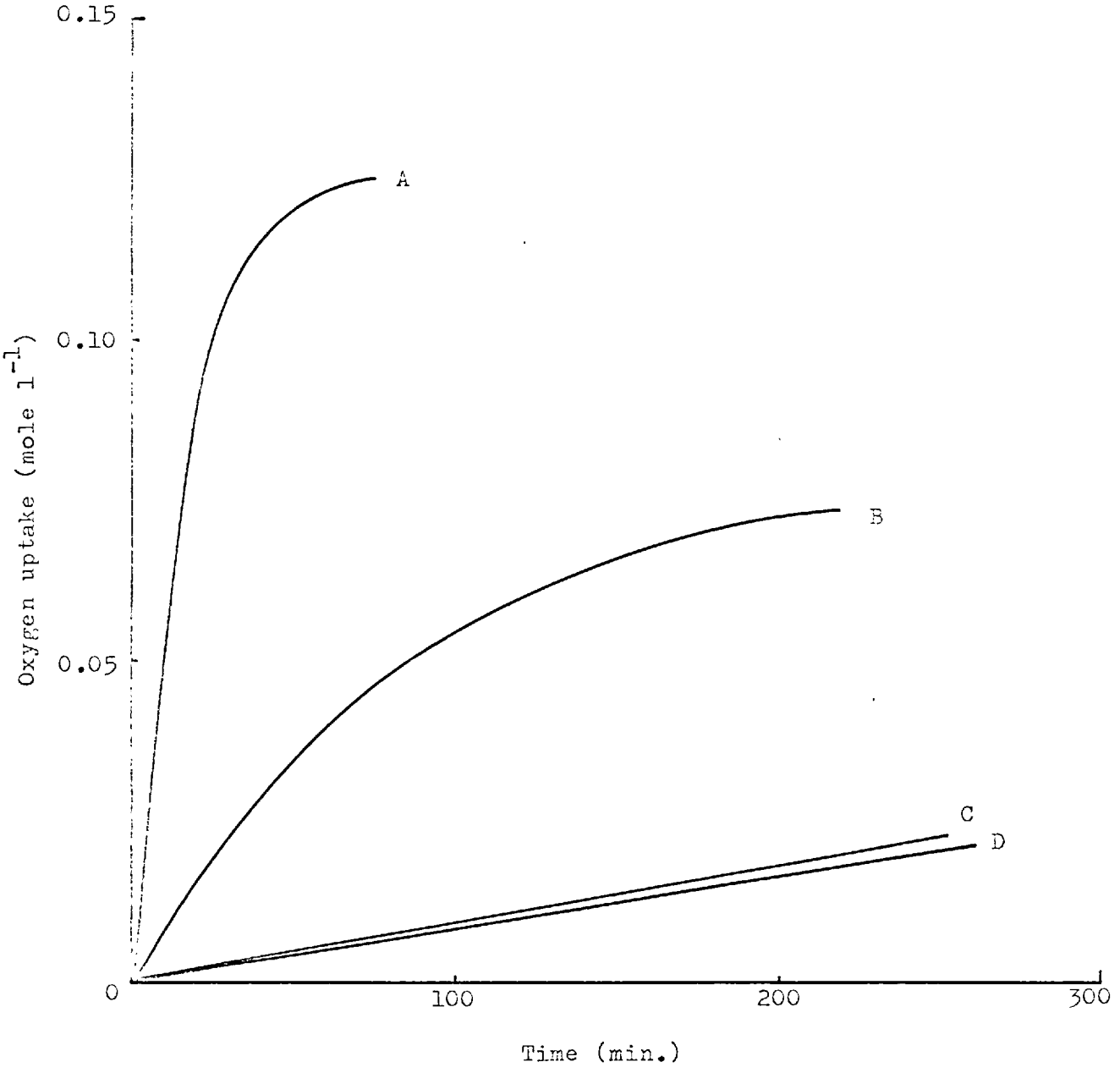


Fig.39 The oxidation of ethanethiol in the presence of vitamin B_{12}. Letters against curves refer to the following conditions.

A - 10^{-3} M vitamin B_{12}, B - 10^{-3} M $CoSO_4$, C - Uncatalysed,

D - 10^{-3} M vitamin B_{12}, 0.25 M KCN.

No evidence of the formation of the red cobalt-thiol complex was observed.

iii) Chlorophyll

The presence of 10^{-3} M chlorophyll in solutions of ethanethiol gave a rate of oxidation which was approximately twice as high as that observed in the presence of 10^{-3} M magnesium sulphate. This rate was, however, considerably lower than those obtained in the presence of haemin and vitamin B_{12}. The results of experiments are given in Fig.40 and Table 29.

a Effect of cyanide

The rate of oxidation observed in the presence of chlorophyll was markedly reduced by the presence of 0.25 M potassium cyanide in the reactant solutions. In agreement with the results obtained with vitamin B_{12}, the presence of diethyl disulphide could not be detected amongst the reaction products.

3(h) Effect of phthalocyanines

The phthalocyanine structure is not dissimilar to the porphyrin structure present in the naturally-occurring complexes described above, (see Appendix A.4), and transition metal phthalocyanines are used in commercial petroleum sweetening methods[21]. The following experiments were carried out to investigate the influence of structure and solubility on the activity of metal-containing-catalysts for the oxidation of thiols. The phthalocyanines were all added to the reactant solutions as solids, of which 100 mg were used in each experiment. Thus the metal concentration in all phthalocyanine-catalysed experiments was 3.5×10^{-3} M, in contrast

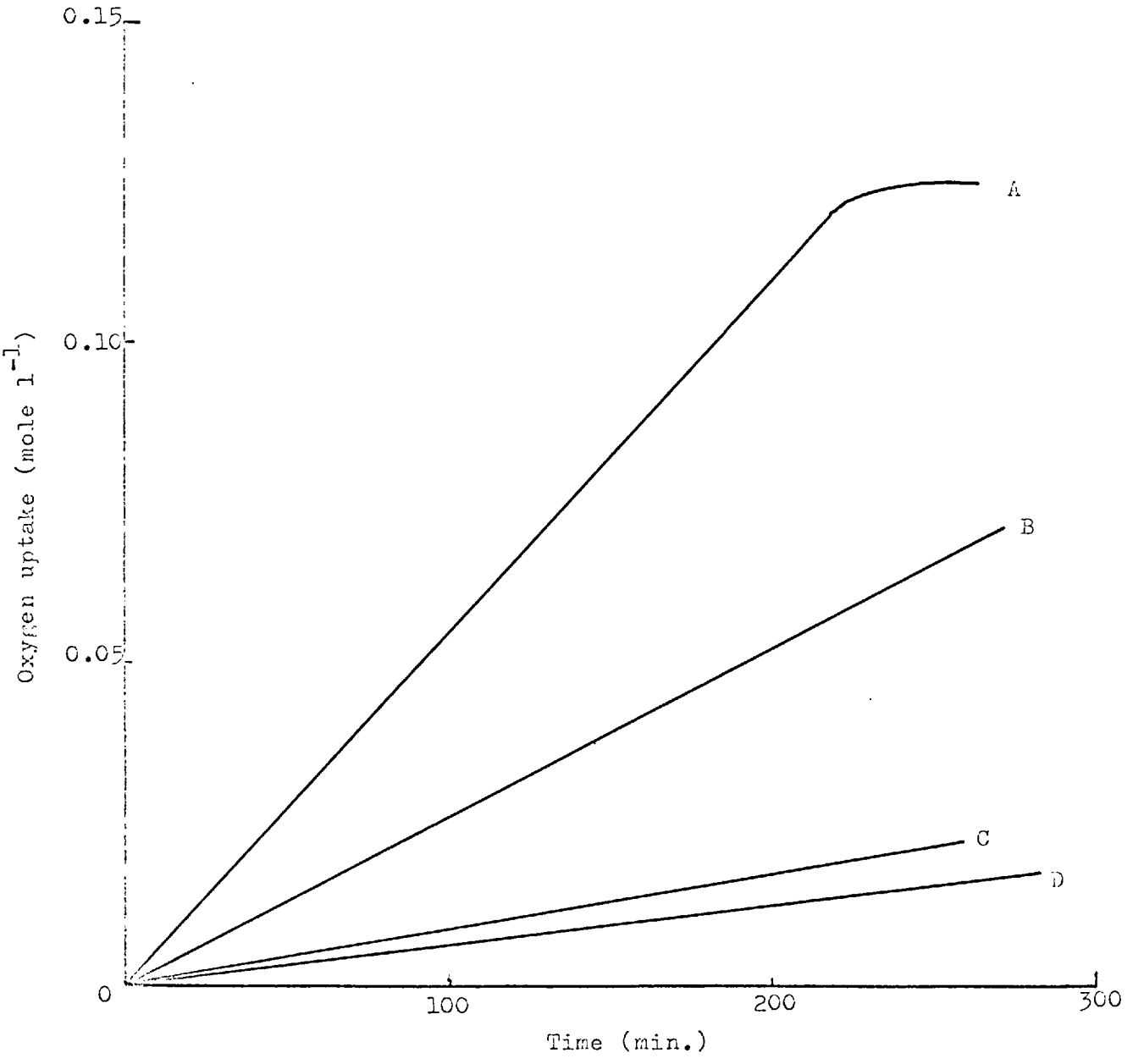


Fig.40 The oxidation of ethanethiol in the presence of chlorophyll.

Letters against curves refer to the following conditions.

A - 10^{-3} M chlorophyll, B - 10^{-3} M $MgSO_4.7H_2O$, C - Uncatalysed,

D - 10^{-3} M chlorophyll, 0.25 M KCN.

to the usual metal concentration of 10^{-3} M. The samples of phthalocyanines used in the following experiments were not sulphonated before use, with the exception of cobalt phthalocyanine, a small batch of which was sulphonated for comparison with the results of the other experiments. Since sulphonation results in the metal phthalocyanine disulphonate, which is appreciably soluble in the alkaline solutions, a higher rate of oxidation was expected for the sulphonated cobalt phthalocyanine. The results are given in Fig.41 and Table 30, which also includes results obtained with the corresponding simple metal salts. The metal-thiol complexes normally present in reactions catalysed by cobalt and iron were not evident in phthalocyanine-catalysed experiments, although the presence of such complexes would be very difficult to detect on account of the intense colours of the phthalocyanine solutions. The phthalocyanines are seen to act both as a catalyst (cobalt, iron) and as an inhibitor (copper, vanadium) in comparison to the corresponding simple metal salts.

i) Effect of pyrophosphates

Transition metal pyrophosphates have been reported to act as heterogeneous catalysts in the oxidation of thiols[105]. A series of experiments has been carried out on the oxidation of ethanethiol in the presence of four transition metal pyrophosphates. The results, which are given in Table 31 and Fig.42, show that in none of the cases was the pyrophosphate a better catalyst than the metal sulphate, when added to give the same concentration of metal. Cobalt pyrophosphate resulted in a higher rate of oxidation than the

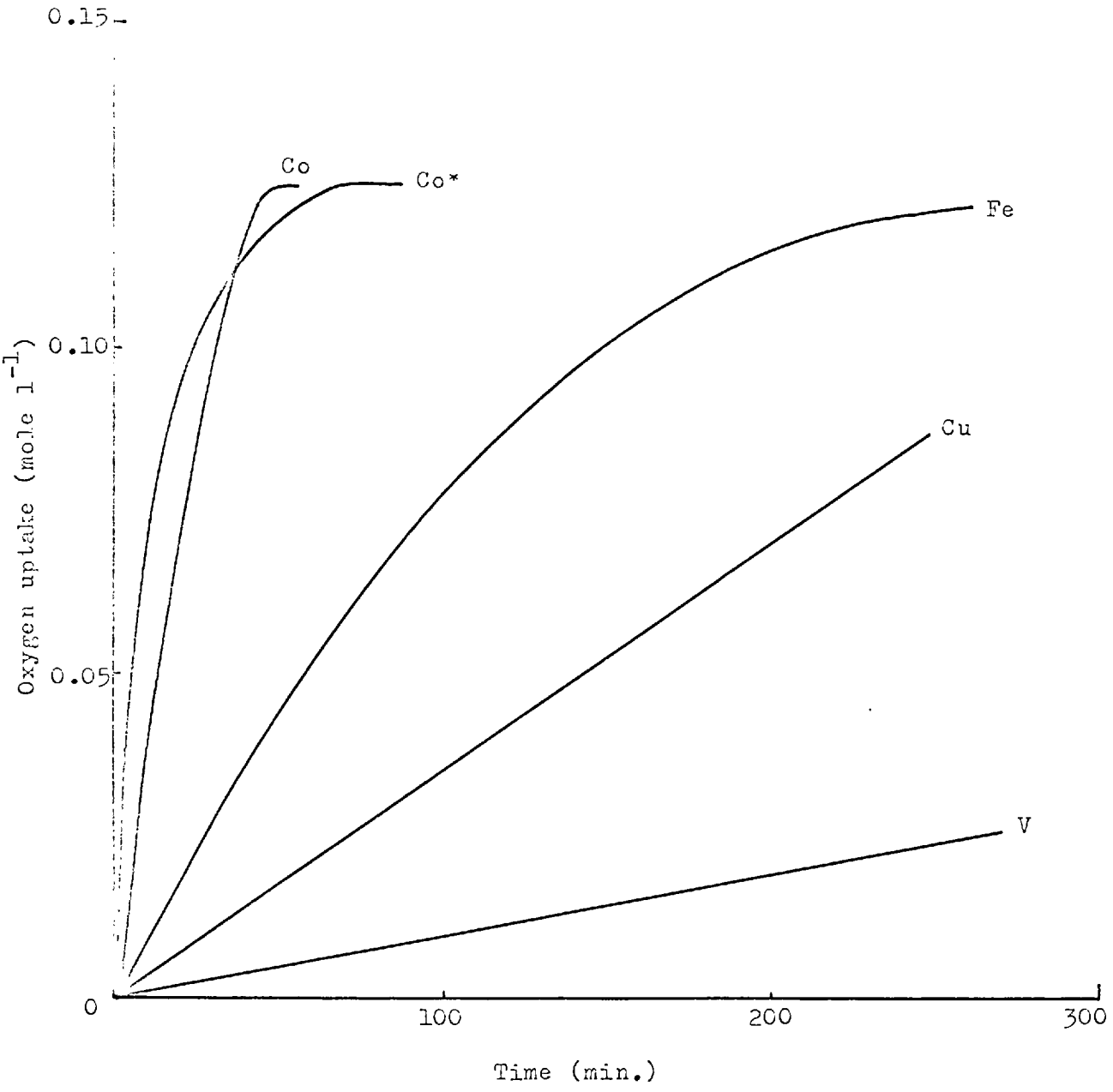


Fig.41 The oxidation of ethanethiol in the presence of transition metal phthalocyanines. Nature of metals is given against curves.

* Cobalt phthalocyanine disulphonate.

Table 30

The oxidation of ethanethiol, effect of transition metal phthalocyanines

Metal	Added as	Added conc^{n} M	Rate mole l^{-1} sec^{-1}
Co	$CoSO_4.7H_2O$	10^{-3}	12.34×10^{-6}
Co	Co phthalocyanine	3.5×10^{-3}	47.60×10^{-6}
Co	Co phthalocyanine disulphonate	3.5×10^{-3}	119.00×10^{-6}
Cu	$CuSO_4.5H_2O$	10^{-3}	26.75×10^{-6}
Cu	$CuSO_4.5H_2O$	10^{-5}	13.20×10^{-6}
Cu	Cu phthalocyanine	3.5×10^{-3}	5.36×10^{-6}
Fe	$FeSO_4.7H_2O$	10^{-3}	3.60×10^{-6}
Fe	Fe phthalocyanine	3.5×10^{-3}	14.70×10^{-6}
V	$VOSO_4$ + aq.	10^{-3}	2.60×10^{-6}
V	Vanadyl phthalocyanine	3.5×10^{-3}	1.70×10^{-6}

Table 31

The oxidation of ethanethiol, effect of transition metal pyrophosphates

Metal	Added as	Added concentration M	Rate mole l^{-1} sec^{-1}	% conversion in 1 hour
Fe	$FeSO_4.7H_2O$	10^{-3}	3.60×10^{-6}	10
Fe	$Fe_2P_2O_7$	10^{-3}	3.80×10^{-6}	10
Co	$CoSO_4.7H_2O$	10^{-3}	10.30×10^{-6}	32
Co	$Co_2P_2O_7$	10^{-3}	9.60×10^{-6}	26
		1.35×10^{-2}	19.64×10^{-6}	41
Co	$Co_3(PO_4)_2$	5.4×10^{-3}	15.20×10^{-6}	40
Cu	$CuSO_4.5H_2O$	10^{-3}	32.60×10^{-6}	100
Cu	$Cu_2P_2O_7$	10^{-3}	12.80×10^{-6}	36
		1.35×10^{-2}	24.16×10^{-6}	56
Ni	$NiSO_4$ + aq.	10^{-3}	15.10×10^{-6}	29
Ni	$Ni_2P_2O_7$	10^{-3}	8.62×10^{-6}	25
		1.35×10^{-2}	8.62×10^{-6}	25

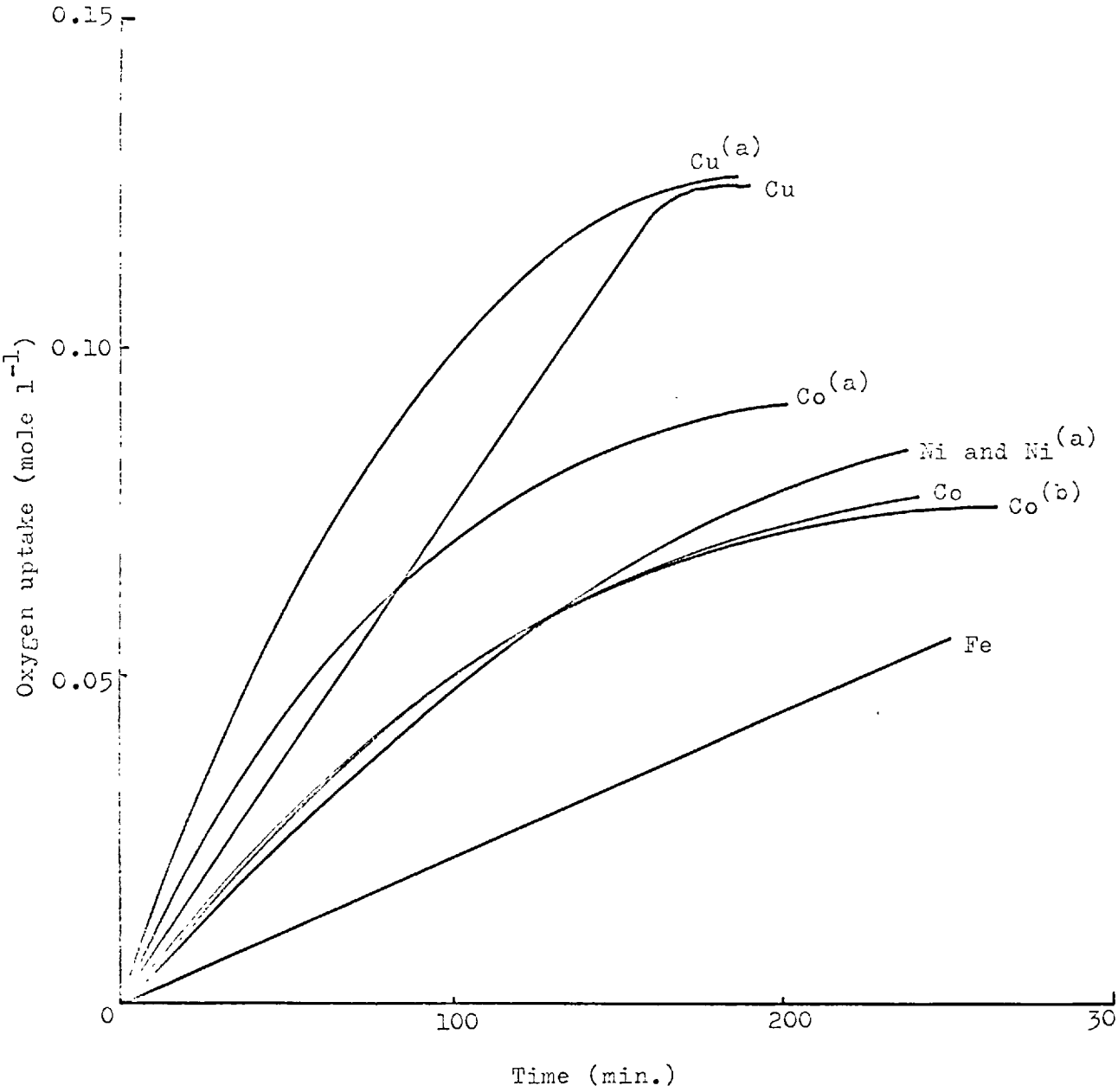


Fig.42 The oxidation of ethanethiol in the presence of transition metal pyrophosphates. Nature of metals is shown against curves.

(a) Metal concentration 1.35×10^{-2} M.

(b) Curve for 5.4×10^{-3} M cobalt phosphate.

sulphate when the concentration of pyrophosphate was increased to make the reactant solution 1.35×10^{-2} M with respect to cobalt.

In experiments with cobalt and nickel pyrophosphates, the normal coloured precipitates were present in the product mixture at the end of experiments, showing that the metal pyrophosphates apparently decompose as the oxidation proceeds. Further experiments showed that the catalytic activity of cobalt pyrophosphate was somewhat less than that of cobalt phosphate, the latter experiments also resulting in the production of the usual cobalt-thiol complex. Additional experiments with transition metal pyrophosphates are described in the following Section.

3(j) Effect of filtration of reactant solutions

In order to obtain evidence of the physical state of the active catalysts, experiments have been performed where the kinetics of oxidation under standard conditions in the presence of various metal salts were compared with the rates of reaction when solid residues have been filtered from solution.

Thus the rates of oxidation under standard conditions (case 1) were compared with the rates after filtration of the solutions before the addition of thiols, but after the addition of all other reagents (case 2), and with the rates of oxidation of solutions filtered immediately after the addition of all reagents (case 3). Whatman No.42 papers (pore size 1.1μ) were used throughout the experiments, and the results are given in Table 32.

i) Copper catalysed reactions

The effect of filtration on the rate of oxidation of

Table 32

The oxidation of ethanethiol, effect of filtration of reactant solutions, using Whatman No.42 papers (pore size 1.1 μ)

Metal	Added as	Added conc^{n} M	Rate mole l^{-1} sec^{-1}	Conditions*	Measured metal concentration in solution M	
Cu	$CuSO_4.5H_2O$	10^{-3}	32.63×10^{-6}	1	1.0×10^{-3}	(a)
Cu	$CuSO_4.5H_2O$	10^{-3}	27.04×10^{-6}	2	n.m.	(a)
Cu	$CuSO_4.5H_2O$	10^{-3}	24.42×10^{-6}	3	n.m.	(a)
Cu	$CuSO_4.5H_2O$	10^{-5}	13.22×10^{-6}	1	1.0×10^{-5}	(b)
Cu	$CuSO_4.5H_2O$	10^{-5}	13.22×10^{-6}	2	1.0×10^{-5}	(b)
Cu	$CuSO_4.5H_2O$	10^{-5}	13.22×10^{-6}	3	1.0×10^{-5}	(b)
Cu	$Cu_2P_2O_7$	1.35×10^{-2}	24.16×10^{-6}	1	n.m.	
Cu	$Cu_2P_2O_7$	1.35×10^{-2}	24.20×10^{-6}	3	n.m.	

(a) Rate of reaction diffusion controlled

(b) No solid material could be filtered from solutions

* Conditions are described in text

n.m. = not measured

Table 32 continued

Metal	Added as	Added conc^{n} M	Rate mole l^{-1} sec^{-1}	Conditions*	Measured metal concentration in solution M	
Cu	Cu phthalocyanine	3.5×10^{-3}	5.36×10^{-6}	1	n.m.	(c)
Cu	Cu phthalocyanine	3.5×10^{-3}	5.36×10^{-6}	2	n.m.	(c)
Co	$CoSO_4.7H_2O$	10^{-3}	10.30×10^{-6}	1	1.0×10^{-3}	
Co	$CoSO_4.7H_2O$	10^{-3}	7.62×10^{-6}	2	8.9×10^{-5}	
Co	$CoSO_4.7H_2O$	10^{-3}	9.91×10^{-6}	3	6.4×10^{-4}	
Co	$Co_2P_2O_7$	1.35×10^{-2}	19.65×10^{-6}	1	1.35×10^{-2}	(d)
Co	$Co_2P_2O_7$	1.35×10^{-2}	4.73×10^{-6}	2	8.50×10^{-5}	(d)
Co	$Co_2P_2O_7$	1.35×10^{-2}	18.07×10^{-6}	3	n.m.	(d)
Co	$Co_3(PO_4)_2$	5.40×10^{-3}	15.20×10^{-6}	1	5.40×10^{-3}	(d)
Co	$Co_3(PO_4)_2$	5.40×10^{-3}	15.84×10^{-6}	2	8.50×10^{-5}	(d)

(c) Catalyst appeared unchanged at the end of the reaction, no dissolution was evident.

(d) Red Co-thiol complex produced.

* Conditions are described in text.

n.m. = not measured.

Table 32 continued

Metal	Added as	Added conc^{n} M	Rate mole l^{-1} sec^{-1}	Conditions*	Measured metal concentration in solution M
Co	Vitamin B_{12}	10^{-3}	80.40×10^{-6}	1	1.0×10^{-3}
Co	Vitamin B_{12}	10^{-3}	80.40×10^{-6}	2	1.0×10^{-3}
Co	Co phthalocyanine	3.5×10^{-3}	47.60×10^{-6}	1	n.m.
Co	Co phthalocyanine	3.5×10^{-3}	47.60×10^{-6}	2	n.m.
Ni	$NiSO_4$ + aq.	10^{-3}	15.21×10^{-6}	1	1.0×10^{-3}
Ni	$NiSO_4$ + aq.	10^{-3}	3.42×10^{-6}	2	1.3×10^{-5}
Ni	$NiSO_4$ + aq.	10^{-3}	14.61×10^{-6}	3	5.3×10^{-4}
Ni	$Ni_2P_2O_7$	1.35×10^{-2}	8.62×10^{-6}	1	n.m. } (e)
Ni	$Ni_2P_2O_7$	1.35×10^{-2}	8.28×10^{-6}	3	n.m. } (e)

(e) Brown Ni-thiol complex produced.

* Conditions are described in text.

n.m. = not measured.

ethanethiol in the presence of 10^{-3} M copper sulphate was rather inconsistent, due to control of the rate by the rate of diffusion of oxygen into the alkaline solutions at this copper concentration. In the presence of 10^{-5} M copper sulphate, the rate was unaffected by filtration; no solid residues could be filtered from the solutions and the filtered solutions were shown on analysis to contain 1.0×10^{-5} M copper.

ii) Cobalt catalysed reactions

Filtration of solutions to which cobalt sulphate had been added showed that the active species was a soluble cobalt complex, since the rate in case 3 was approximately the same as that observed in case 1. The lower rate of oxidation in case 2 was consistent with the low cobalt concentration, as observed by analysis of the filtered solution.

iii) Nickel catalysed reactions

The effect of filtration on the rates in the presence of nickel sulphate was similar to that observed with cobalt sulphate. The rates in cases 1 and 3 were again very similar, and the rate in case 2 was considerably lower, which was consistent with the low nickel concentration observed by analysis of the filtered solution.

iv) Pyrophosphate catalysed reactions

Solutions containing pyrophosphates were filtered under the conditions of case 3, and for all three metals the rate was virtually unaffected by filtration. The results suggest that the active species in the case of cobalt and nickel is formed immediately upon the addition of thiol to the reactant solutions, since the red

and brown colourations were observed in the respective solutions.

v) Phthalocyanine catalysed reactions

Filtration of solutions containing phthalocyanines under the conditions of case 2 had no effect on the rate of reaction compared with the rate obtained in case 1. In experiments with copper phthalocyanine, no dissolution of the complex was evident in case 1, the phthalocyanine appearing unchanged at the end of the reaction.

4 The oxidation of other thiols in the presence of metallic catalysts

In addition to the work described in the previous Sections on the oxidation of ethanethiol, experiments have been carried out on the oxidation of certain other thiols in the presence of metal salt and metal complex catalysts.

4(a) Effect of nickel sulphate

The oxidation of a range of aliphatic and aromatic thiols in the presence of 10^{-3} M nickel sulphate is compared with the reaction with ethanethiol in Fig.43 and Table 33. Induction periods were not observed, and with the exception of thiophenol and tert-butanethiol, the rates of oxidation generally decreased as the reaction proceeded. The brown nickel-thiol complex associated with the nickel-catalysed oxidation of ethanethiol was not observed in experiments with thiophenol and tert-butanethiol. The rates of oxidation of the various thiols decreased in the order $Et > Hex^{n} > Bu^{i} > Bu^{n} > Bu^{s} > PhCH_2 > Ph > Bu^{t}$.

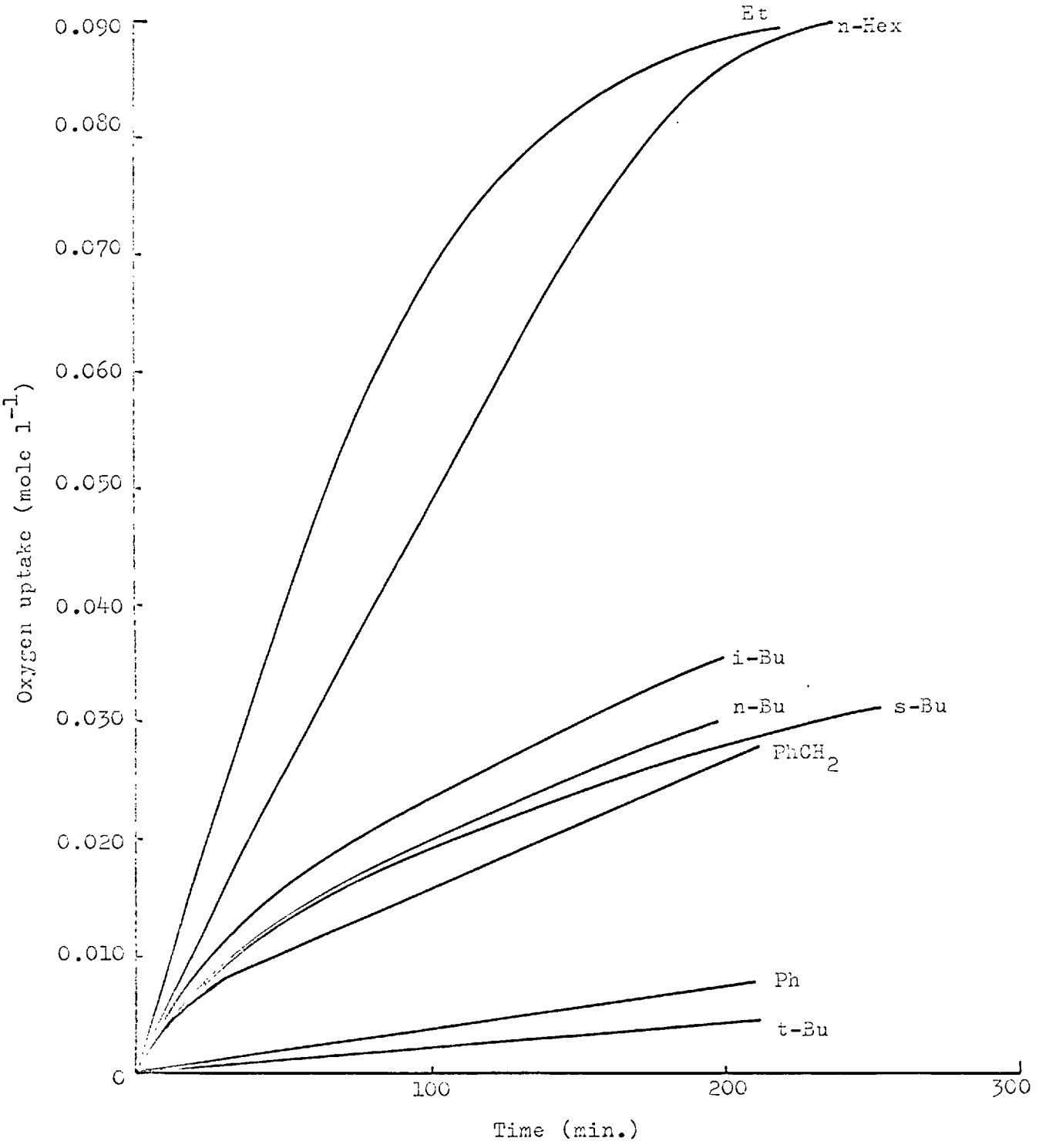


Fig.43 The oxidation of various thiols in the presence of 10^{-5} M nickel sulphate. Nature of thiols is shown against curves.

Table 33

The oxidation of various thiols in the presence of 10^{-3} M nickel sulphate

Thiol	Rate mole l^{-1} sec^{-1}	% conversion in 2 hours
EtSH	15.20×10^{-6}	64.0
Bu^nSH	7.00×10^{-6}	19.6
Bu^iSH	7.82×10^{-6}	23.2
Bu^sSH	5.82×10^{-6}	18.4
Bu^tSH	0.36×10^{-6}	2.4
Hex^nSH	10.70×10^{-6}	52.0
PhSH	0.59×10^{-6}	4.0
$PhCH_2SH$	5.44×10^{-6}	16.0

4(b) Effect of copper sulphate

The oxidation of iso- and sec-butanethiols was compared with the oxidation of n- and tert-butanethiols in the presence of 10^{-5} M copper sulphate. The results are given in Fig.44 and Table 34, which contain for comparison the rate for the oxidation of ethanethiol under similar conditions. No induction periods were observed, and with the exception of tert-butanethiol essentially quantitative oxidation of thiol to disulphide occurred within 3 hours.

4(c) Effect of cobalt sulphate

The effect of 10^{-3} M cobalt sulphate on the rate of oxidation of iso- and sec-butanethiols is shown in Fig.45 and Table 35.

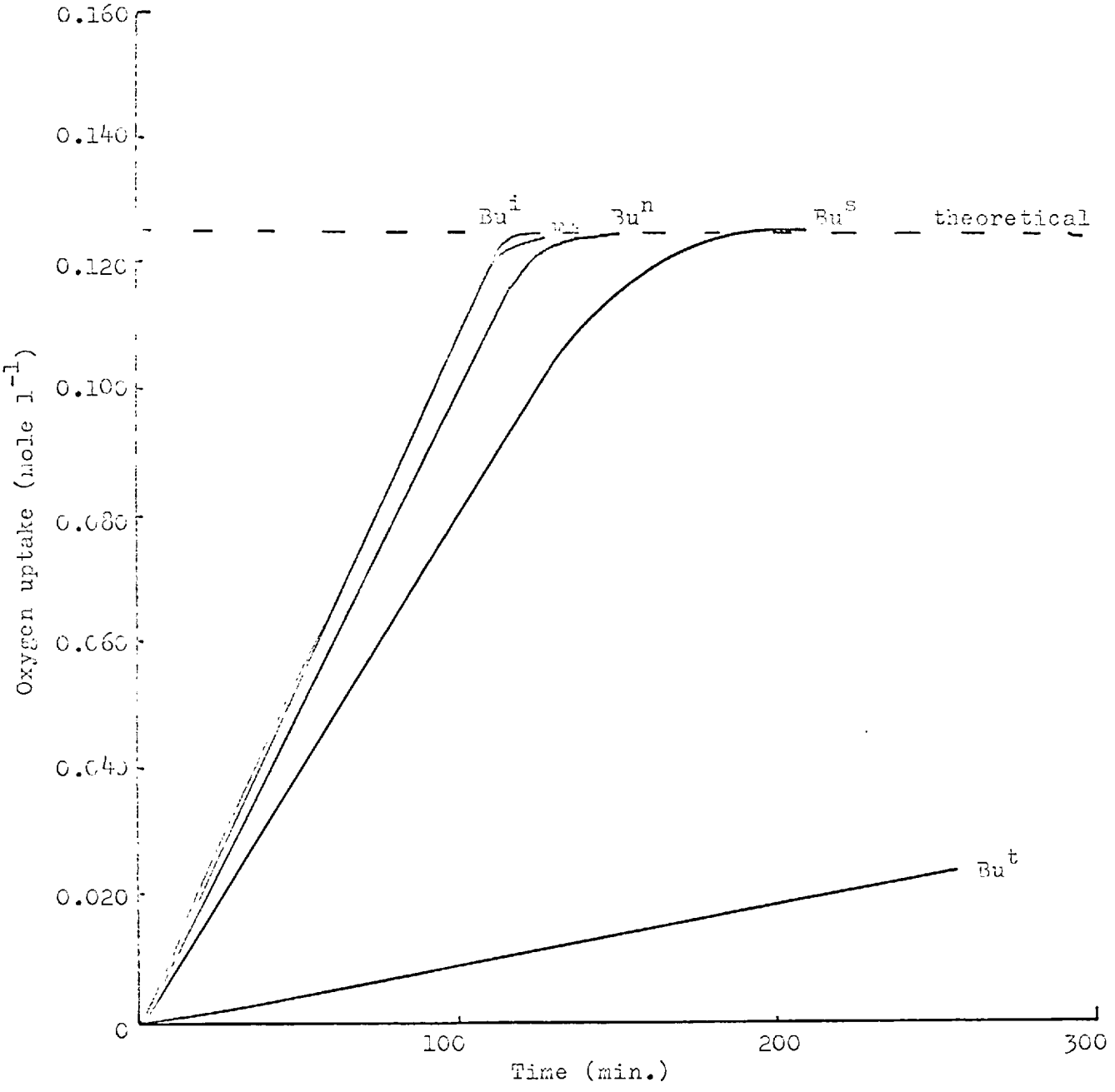


Fig.44 The oxidation of iso- and sec-butanethiols in the presence of 10^{-5} M copper sulphate; comparison with n- and tert-butanethiols, and ethanethiol.

Nature of thiols is shown against curves.

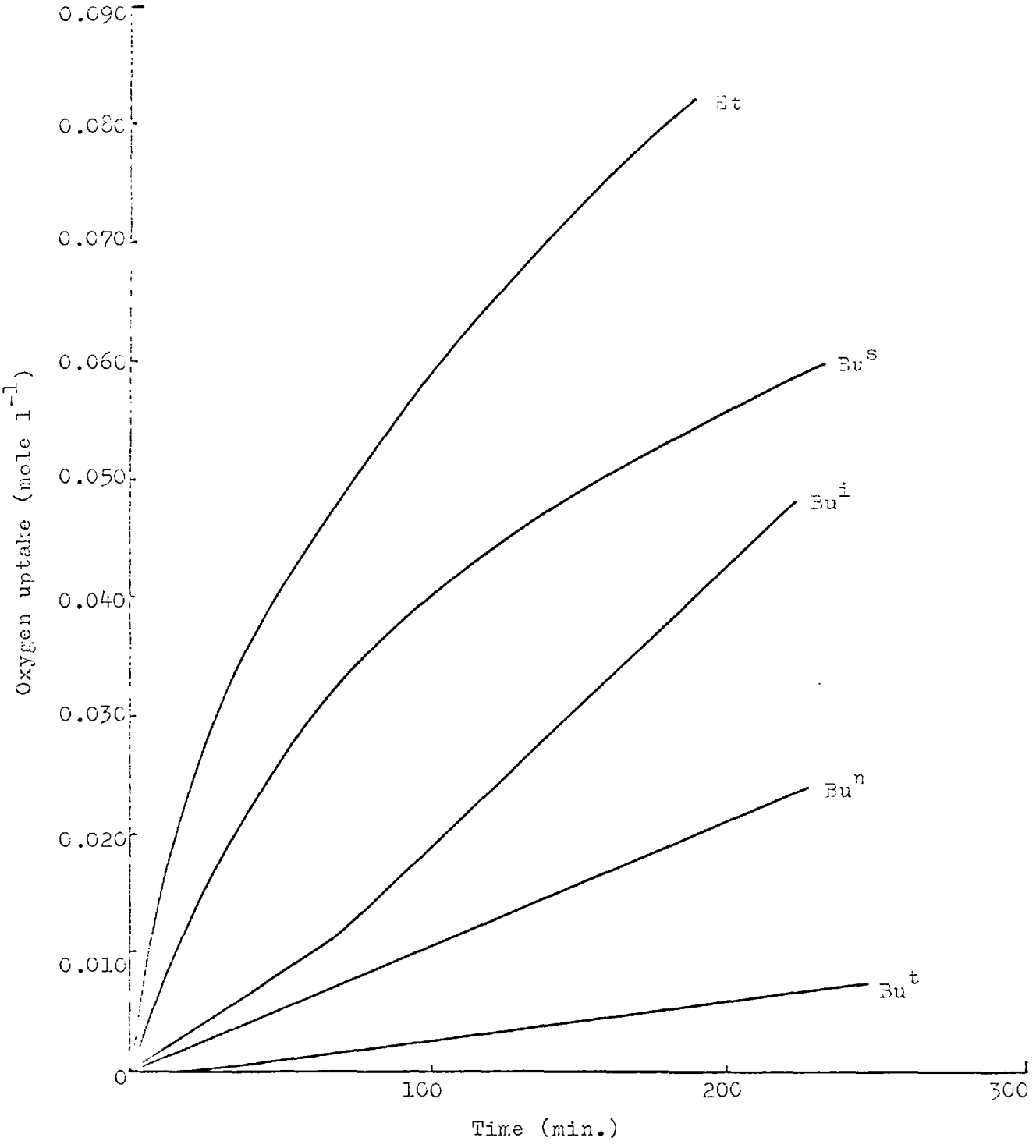


Fig.45 The oxidation of iso- and sec-butanethiols in the presence of 10^{-3} M cobalt sulphate, comparison with n- and tert-butanethiols and with ethanethiol.

Nature of thiols is shown against curves.

Table 34

The oxidation of iso- and sec-butanethiols in the presence of 10^{-5} M copper sulphate, comparison with n- and tert-butanethiols and with ethanethiol

Thiol	Rate mole l^{-1} sec^{-1}	% conversion in 2 hours
EtSH	17.30×10^{-6}	100
$Bu^{n}SH$	16.60×10^{-6}	96
$Bu^{i}SH$	17.90×10^{-6}	100
$Bu^{s}SH$	14.00×10^{-6}	76
$Bu^{t}SH$	1.50×10^{-6}	8

Table 35

The oxidation of iso- and sec-butanethiols in the presence of 10^{-3} M cobalt sulphate, comparison with n- and tert-butanethiols and with ethanethiol

Thiol	Rate mole l^{-1} sec^{-1}	% conversion in 2 hours
EtSH	12.80×10^{-6}	56
$Bu^{n}SH$	1.83×10^{-6}	12
$Bu^{i}SH$	3.00×10^{-6}	23
$Bu^{s}SH$	11.60×10^{-6}	38
$Bu^{t}SH$	0.42×10^{-6}	3

Results are compared with those obtained for the oxidation of n- and tert-butanethiol and ethanethiol. The red cobalt-thiol complex associated with experiments in the presence of ethanethiol was not observed in the oxidation of tert-butanethiol, and only small amounts were observed in the oxidation of sec-butanethiol. An induction period of approximately 25 min. was observed in reactions with tert-butanethiol.

4(d) Effect of vitamin B_{12}

The results of experiments on the oxidation of a range of thiols in the presence of 10^{-3} M vitamin B_{12} are given in Fig.46 and Table 36. The rates of oxidation of the various thiols are observed to decrease in ore order $Hex^n > Bu^n \approx Bu^i \approx Et \approx PhCH_2 > Bu^s > Ph \approx Bu^t$. The formation of cobalt-thiol complexes was not observed in reactions catalysed by vitamin B_{12}.

Table 36

The oxidation of various thiols in the presence of 10^{-3} M vitamin B_{12}

Thiol	Rate mole l^{-1} sec^{-1}	% conversion in 20 mins	Final % conversion
EtSH	93.80×10^{-6}	68.5	99
Bu^nSH	102.60×10^{-6}	65.5	100
Bu^iSH	94.00×10^{-6}	68.0	100
Bu^sSH	65.40×10^{-6}	58.5	102
Bu^tSH	16.32×10^{-6}	14.3	98
Hex^nSH	220.40×10^{-6}	96.5	99
PhSH	19.40×10^{-6}	18.0	100
$PhCH_2SH$	84.80×10^{-6}	71.5	101

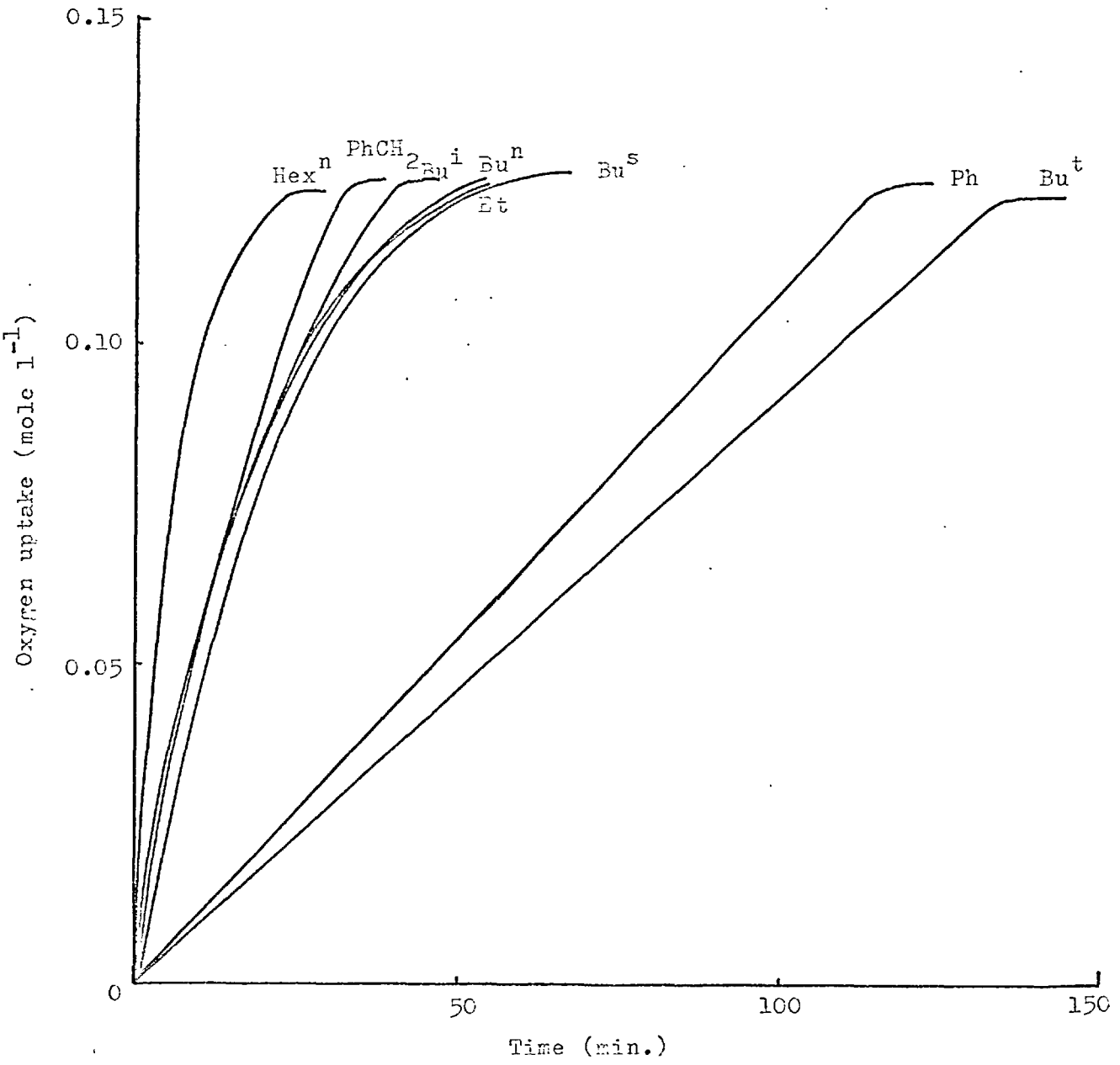


Fig.46 The oxidation of various thiols in the presence of 10^{-3} M vitamin B_{12}. Nature of thiols is shown against curves.

Essentially quantitative conversion of thiol to disulphide occurred in all cases. The effect of filtration of the solution from the vitamin B_{12} catalysed oxidation of ethanethiol is given in Table 32, from which the rate is observed to be unaffected by filtration before the addition of thiol.

I THE ISOLATION OF METAL-THIOL COMPLEXES

Experiments on the oxidation of ethanethiol in the presence of a number of metal ions were characterised by the formation of precipitates, some of which were brightly coloured (Table 11). In addition to the apparatus used in kinetic experiments, a reaction vessel was constructed specifically for the investigation of metal-thiol complexes under controlled conditions (Fig.5). Metal-thiol complexes have been prepared and investigated in a number of instances, and the results obtained are described in the following sections.

1 Nickel complexes

(a) Recognisable nickel complexes were obtained with a range of thiols (Table 37). Complexes were not obtained with the sterically hindered thiols, viz. Bu^tSH, PhSH and Ph_3CSH, and a complex with Bu^sSH was produced only slowly. All preparations were carried out under an atmosphere of de-oxygenated white spot nitrogen, using the following reagent concentrations: 50 ml solutions of aqueous sodium hydroxide (2.0 M) containing thiol (0.5 M) and metal salts at a concentration of 0.2 M. In experiments with triphenylmethanethiol, the thiol was added as a solution in a small amount of acetone, such that the final concentration was 0.1 M.

In all experiments samples were filtered from the solutions and were washed with distilled water and ethanol and dried, all in the complete absence of oxygen.

The dried precipitates were extracted with chloroform in a Soxhlet apparatus, and were found to consist of a soluble and an insoluble portion, of which the latter constituted 90-95% of the total. The soluble portion was examined spectrophotometrically, and the results obtained are given in Table 38. No difference could be detected between the spectra obtained for the soluble complex dissolved in carbon tetrachloride, cyclohexane or pyridine, and no clear distinction could be made between the spectra of various complexes.

Both the soluble and insoluble fractions were brown in colour, and both portions of the ethanethiol complex were diamagnetic. In some cases slight paramagnetism was observed in samples which had been stored for some time, and this was attributed to decomposition of the complexes (see below). Elemental analysis gave the following empirical formulae: insoluble fraction, $Ni(SEt)_2$, soluble fraction $Ni(SEt)_3(OH)$. The insoluble fraction apparently corresponds to the linear polymer proposed by Jensen[118]. The soluble fraction reacted readily with atmospheric oxygen, to give diethyl disulphide and a brownish black solid of empirical formula $Ni(OH)_2$ (possibly $NiO.H_2O$). After storage under nitrogen for a matter of weeks, the soluble portion in some cases was found to disproportionate to nickel sulphide. Definite melting points were not observed with either fraction; the insoluble fraction with all

thiols appeared to decompose at temperatures around 200 to 250° C, whilst the soluble fractions melted in the temperature range 80 to 120° C, most individual samples having melting ranges of up to 30° C.

1(b) Effect of ligands

The nature of the ligands present in the solutions had a profound effect on the ease of formation of nickel-thiol complexes. The presence of 0.25 M cyanide also completely inhibited the formation of complexes. At concentrations of 0.1 M, EDTA and en completely inhibited the formation of complexes, and o-phen and dipy had the effect of considerably reducing the amounts of complex formed. At concentrations of 10^{-2} M en and EDTA, reduced amounts of complexes were formed. During kinetic experiments in the presence of nickel pyrophosphate, nickel-thiol complexes were formed in amounts comparable to those obtained in the presence of nickel sulphate. Since the nickel-thiol complexes were formed in the presence of en and EDTA at concentrations of 10^{-3} M, the stability constant of the nickel-thiol complexes may be similar to those of the nickel complexes with en and EDTA (approximately 10^{18}) [151]. The nickel complexes could not be prepared from solutions which contained diethyl disulphide instead of ethanethiol.

2 Copper complexes

(a) Under the conditions used for the preparation of complexes, (0.2 M Cu), yellow precipitates were obtained with all of the thiols investigated (Table 37). These precipitates are well known to consist of cuprous mercaptides[127, 152]. Filtration of the ethanethiol complex in the complete absence of oxygen resulted in the

Table 37

The formation of complexes on addition of metal ions to alkaline solutions of thiols

Thiol	Metal and added concentration (M)					
	Co	Ni	Pd	Tl	Cu(a)	Cu(b)
	0.15	0.20	0.20	0.20	0.20	0.20
C_2H_5SH	f	f	f	f	f	f
n-C_4H_9SH	f	f	f	f	f	f
iso-C_4H_9SH	f	f	f	f	f	-
sec-C_4H_9SH	(f)	(f)	f	f	f	-
tert-C_4H_9SH	nf	nf	f	f	f	f
n-$C_6H_{13}SH$	f	f	f	f	f	f
n-$C_8H_{17}SH$	f	f	f	f	f	-
C_6H_5SH	nf	nf	f	f	f	-
$C_6H_5CH_2SH$	f	f	f	f	f	-
$(C_6H_5)_3CSH$	nf	nf	f	f	f	-

(a) formation of yellow precipitate

(b) formation of blue solution on filtration of yellow precipitate

f complex formed

(f) complex produced only slowly

nf complex not formed

isolation of a solution which was deep blue in colour. The solutions were also turbid (diethyl disulphide) and they were therefore extracted with chloroform, whereupon the blue complex went into the chloroform layer. The ultraviolet spectrum of this solution is given in Table 38. Concentration of the solution by evaporation resulted in a suspension of bluish-white particles in a small amount (<0.1 ml) of diethyl disulphide, but the amount of solid produced in this way was insufficient to allow analysis of a sample.

Similar blue solutions were observed on filtration of the mercaptides formed with n-butanethiol, tert-butanethiol and n-hexanethiol.

2(b) Effect of ligands

The effect of ligands on the formation of the yellow mercaptide with ethanethiol was investigated. In the presence of 0.1 M ethylenediamine, the complex formed readily, in contrast to the results obtained with nickel (see above). The complex was not formed, however, in the presence of potassium cyanide at concentrations of 0.25 M or 0.1 M. Complexes were not observed in solutions containing diethyl disulphide in the absence of ethanethiol.

3 Cobalt complexes

(a) The formation of cobalt complexes with various thiols is given in Table 37. In agreement with the results obtained with nickel, complexes were not formed with the sterically hindered thiols. The complexes were prepared under an atmosphere of oxygen in the presence of 0.15 M cobalt. The complexes were dark red in solution but dried samples were dark brown,

appearing green in reflected light. Spectral data for solutions of all complexes were similar one with another, and are reported in Table 38.

Elemental analysis of ethanethiol complexes gave the empirical formula $Co(SEt)_{3.1}$. Complexes prepared under carefully controlled conditions were found to be diamagnetic, although in some cases slight paramagnetism was observed, which was attributed to remaining traces of unreacted Co^{II}.

Under an atmosphere of carefully de-oxygenated nitrogen red complexes were not obtained if Co^{II} salts were used as starting materials. With all the thiols which formed red complexes normally, deep blue solutions were obtained, which were oxidised to the red complex by very small amounts of oxygen. As a result it proved impossible to isolate any of these blue complexes, and the spectral data given in Table 38 refer to the preparative solution. The absorption spectra of the blue solutions are not consistent with the presence of large amounts of cobalt hydroxides in solution, and it is possible that the blue coloration is due to the presence of Co^{II} mercaptides.

In the absence of oxygen red complexes were formed from Co^{III} salts at concentrations of 0.15 M, but at cobalt concentrations of 10^{-2} to 10^{-3} M, blue solutions were produced. In the presence of oxygen and metal ions, ethanethiol anions are oxidised to diethyl disulphide and Co^{II} should be oxidised to Co^{III}. The addition of diethyl disulphide to the blue solutions produced in the absence of oxygen did not result in the formation of red complexes.

Table 38

Spectral data of solutions of complexes in carbon tetrachloride and cyclohexane

Complex	λ max (mμ), and relative peak height ratios
Red $Co(SR)_3$ complexes	265 (8.8), (275) (5.3), (285) (3.8) (330) (1.0), 418 (1.2), 508 (3.4)
Blue Co^{II} complexes*	(475) (1.0), (505) (1.2), (625) (2.6), 680 (2.8), (722) (2.5), (755) (1.8)
Soluble $Ni(SR)_3OH$ complexes	265 (8.5), 340 (6.6), 438 (4.2), (520) (2.0), (550) (1.5), (600) (1.0)
$Pd(SR)_2$	(350) (1.1), (400) (1.0)
Blue Cu complex+	(600) (1.0), 665 (3.3), (800) (1.0)

* spectra of preparative solution, not of complex dissolved in carbon tetrachloride.

+ spectra of chloroform solution.

Parentheses around λmax values indicate shoulders.

In view of the fact that the red precipitates are produced from Co^{III} salts in the absence of oxygen, a series of experiments were carried out to investigate the effect of oxidising agents on the formation of the red complexes from Co^{II} salts in the absence of oxygen. In these experiments the cobalt was added as a solution of cobalt^{II} sulphate, such that the reactant solution was 5×10^{-3} M in cobalt. Oxidising agents were added as de-oxygenated solutions such that their concentrations in the reactant solutions were 2×10^{-2} M. In experiments with hydrogen peroxide, ceric ammonium sulphate, potassium dichromate, and potassium permanganate, the red complexes were produced in all cases, and since aqueous solutions of the latter three oxidising solutions are not known to oxidise thiol anions directly, the red complexes were evidently formed between thiol anions and Co^{III}.

3(b) Effect of ligands

Table 39 shows the effect of ligands on the formation of the red cobalt-ethanethiol complex. Thus the formation of complexes did not occur when the cobalt was present as cobalt phthalocyanine, vitamin B_{12} or as $K_3Co(CN)_6$, and reduced amounts of complex were formed from $Coen_3Cl_3$, suggesting that the en could not be displaced completely from co-ordination with cobalt. Thus it would appear that the stability constant of the red cobalt thiol complex lies somewhere between that of $[Coen_3]^{3+}$ (10^{49}) and that of $[Co(CN)_6]^{3-}$ (10^{64}) [151]. Neither the red nor the blue complex was observed in experiments where the ethanethiol had been replaced by diethyl disulphide.

Table 39

The effect of the ligand environment on the formation of cobalt-ethanethiol complexes

Initial complex (10^{-3} M Co, unless otherwise stated)	Formation of Co-thiol complex
$CoSO_4.7H_2O$	f
cis-$[Co(NH_3)_4(H_2O)Cl]Cl_2$	f
$[Co(NH_3)_5CO_3]NO_3$	f
cis-$[Coen_2Cl_2]Cl$	f
trans-$[Coen_2Cl_2]Cl$	f
$Coen_3Cl_3.3H_2O$	(f)
$K_3Co(CN)_6$	nf
$Na_2Co(EDTA)$	f
$Co_2P_2O_7$	f
$Co_3(PO_4)_2$	f
Co phthalocyanine (3.5×10^{-3} M)	nf
Vitamin B_{12}	nf
$Copy_2Cl_2$	f

f complex formed

nf complex not formed

(f) complex formed only in small amounts

4 Palladium complex

Palladium formed complexes with all of the thiols investigated (Table 37). The colours of the complexes produced varied with the nature of the thiol, being brick red with thiophenol, brown with triphenyl methanethiol and orange with all other thiols. All complexes were soluble in carbon tetrachloride and cyclohexane, and moderately soluble in most other common solvents. Spectral data are given in Table 38. Elemental analysis of the ethanethiol complex gave the empirical formula $Pd(SEt)_2$. In contrast to the complexes with other metals, palladium complexes were formed when diethyl disulphide was substituted for ethanethiol, as expected from the work of Akerfeld[153]. The amount formed was, however, small; spectral data of a carbon tetrachloride extract of the preparative solution were in agreement with results obtained for the ethanethiol complex.

5 Thallium complex

All of the thiols investigated formed complexes with thallium salts, (Table 37). The complexes were yellow, and were insoluble in all common solvents. Elemental analysis of the ethanethiol and n-butanethiol complexes gave the empirical formulae Tl(SEt) and $Tl(Bu^n)$ respectively. On heating, the n-butanethiol complex turned red at 70-75° C, melted between 75 and 100° C, and decomposed above 100° C.

J STOPPED-FLOW EXPERIMENTS

1 The reaction of thiols with potassium ferricyanide

During experiments on the effect of cyanide on the oxidation of thiols, the reaction of ethanethiol with potassium ferricyanide was investigated. Whilst the yellow colour of the ferricyanide, present at a concentration of 10^{-3} M, disappeared very rapidly on injection of the thiol into the reactant solution, the actual rate of oxidation of the thiol proceeded at a very low rate (2.22×10^{-6} mole l^{-1} sec^{-1}).

Using the stopped-flow apparatus described in Section E.3 the kinetics of the reaction of potassium ferricyanide with a variety of thiols were investigated. The two syringes respectively contained the ferricyanide ($1\text{-}3 \times 10^{-3}$ M) and the thiol (10^{-3} - 2.5×10^{-2} M), both being in 50% v/v aqueous alcoholic solutions which were 0.02 M with respect to sodium hydroxide. The use of alcoholic solutions was found to be necessary to minimise turbidity produced during the reaction. Both solutions were carefully de-oxygenated before use. By arrangement of the mixing chamber close to the spectrophotometric cell, it was possible to study the rate of disappearance of ferricyanide within $\leq$0.1 sec of the solutions being mixed. A time scan of 6 min. was found to be suitable for following the reactions.

1(a) Ethanethiol

Whereas the initial rate of oxidation of ethanethiol was 2.22×10^{-6} mole l^{-1} sec^{-1}, the initial rate of disappearance of ferricyanide, at an initial ferricyanide concentration of 3×10^{-3} M,

and an initial thiol concentration of 5×10^{-3} M, was 8.92×10^{-4} mole l^{-1} sec^{-1}, i.e. approximately 400 times greater than the rate of oxidation of the thiol. The reaction was found to have first-order dependence on the ferricyanide concentration, and a zero-order dependence on the thiol concentration, (Table 40).

I(b) Other thiols

The results of experiments with a variety of thiols other than ethanethiol are given in Table 40 together with the results obtained for ethanethiol. In all cases, the rates of reaction had a first-order dependence on the ferricyanide concentration, and with the exception of thiophenol had a zero-order dependence on the thiol concentration. The reaction of thiophenol was found to have a first-order dependence on the thiol concentration. Initial rates of reaction of the thiols with ferricyanide are given in Table 40 for comparison. These values were obtained for the reaction at an initial thiol concentration of 5×10^{-3} M, and an initial ferricyanide concentration of 3×10^{-3} M. From these rates the order of thiol reactivity with potassium ferricyanide is $Et > PhCH_2 > Bu^i > Ph > Bu^n > Bu^s > Hex^n > Bu^t$. This order is interesting in that the rate of reaction of thiophenol is relatively high, and that of n-hexanethiol is relatively low compared to the rates of the overall oxidation of these thiols in the presence of metal ions (Section H.3).

Table 40

The reaction of thiols with potassium ferricyanide

Thiol	Order w.r.t thiol	Order w.r.t. ferricyanide	Rate constant	Initial Rate* mole l^{-1} sec^{-1}
EtSH	0	1	2.96×10^{-1} sec^{-1}	8.92×10^{-4}
Bu^nSH	0	1	6.67×10^{-2} sec^{-1}	2.09×10^{-4}
Bu^iSH	0	1	1.22×10^{-1} sec^{-1}	3.50×10^{-4}
Bu^sSH	0	1	2.01×10^{-2} sec^{-1}	6.75×10^{-5}
Bu^tSH	0	1	5.80×10^{-3} sec^{-1}	1.97×10^{-5}
Hex^nSH	0	1	1.18×10^{-2} sec^{-1}	4.02×10^{-5}
PhSH	1	1	16.8 l $mole^{-1}$ sec^{-1}	2.40×10^{-4}
$PhCH_2SH$	0	1	1.32×10^{-1} sec^{-1}	4.07×10^{-4}

* values obtained for the following initial concentrations:

$[\text{Ferricyanide}] = 3 \times 10^{-3}$ M

$[\text{Thiol}] = 5 \times 10^{-3}$ M

DISCUSSION

DISCUSSION

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DISCUSSION

K. KINETIC OXYGEN-UPTAKE EXPERIMENTS

Prior to the investigation of the oxidation of thiols in the presence of metal-containing catalysts, a number of experiments were carried out in the absence of such additives. A knowledge of the uncatalysed oxidation of thiols provides a necessary background to the subsequent investigation in the presence of metallic compounds. Furthermore, since an increasing volume of data on the uncatalysed reaction is now available[66], this reaction may be used as a convenient indication of the impurities present in any particular series of oxidation experiments.

1. The oxidation of thiols in the absence of added metal-ion catalysts

The two initial series of experiments on the uncatalysed oxidation of ethanethiol, described in Section H.2(a), show that progressive refinements in the experimental procedure (Section G.1) resulted in the respective mean initial rates of the series being reduced from 1.72×10^{-6} mole l^{-1} sec^{-1} (standard deviation 19%) to 1.50×10^{-6} mole l^{-1} sec^{-1} (standard deviation 9%). This reduction in rate is ascribed to the partial elimination of the influence of impurities such as metal ions.

The stoichiometry of the oxidation of ethanethiol was found to conform with equation (78) at all stages of the reaction, and this result is in agreement with that found by Hopton[66] and by Wallace, et al.[44, 56]. Oxygen uptake values and thiol analyses were consistent with the stoichiometry of equation (78), but low results were obtained for the disulphide analyses, particularly in the

presence of more concentrated alkaline solutions. These low results were accompanied by slight decreases in the alkali concentration, and may indicate the presence of small amounts of acids in the products. The apparent correlation between the decrease in alkali strength and the disulphide deficiency was not good, probably as a result of the rather poor reproducibility of the disulphide determination. The results are not in agreement with those of Xan, et al.[49], who observed oxygen uptakes of up to 50% more than the predicted value, but it must be remembered that these workers used ratios of thiol to alkali considerably smaller than those employed in the present work. Under these conditions, hydrolysis of disulphides may well become important, and result in substantially increased oxygen uptakes. Yields of sulphinic and sulphonic acids have been shown to increase with the basicity of the solution and with the temperature[61]. Since saturated disulphides are generally inert to oxidation[25, 26, 27], the formation of higher oxidation products probably results from the hydrolysis of the disulphide, (equation (33), Section C.2(b)), the sulphenic acid thus produced being further oxidised to sulphinic and sulphonic acids. Hydrolysis of the disulphide may be expected to become more important as the size of the alkyl group is increased, and in agreement with this, oxygen-uptake values in the oxidation of n-hexanethiol have been found to be higher than those predicted on the basis of equation (78)[66].

The oxidation of ethanethiol was found to be first order with respect to oxygen but the order with respect to thiol varied with the experimental conditions. The graph of rate of oxidation versus

oxygen pressure (Fig.11), did not pass through the origin, a small intercept (ca.1.5 cm.) being observed on the oxygen pressure axis. This intercept is attributed to the vapour pressure of the reagents. In a number of experiments in the absence of additives, the shape of the kinetic curves changed slightly after ca.10-20% of the reaction had occurred. In the initial period the rate of oxidation appeared to be first order with respect to thiol, changing to zero order after ca.20% of reaction. This change in order was not expected on the basis of the behaviour of a first order plot at high conversions. The rate was zero order both with respect to initial EtSH and to EtSH present at the time of rate measurement. On the basis of first order kinetics, the rate plot would not become pseudo zero order until much higher conversions. Two rate constants, k_1 and k_2, can thus be assigned to the oxidation of ethanethiol, these being the respective rate constants before and after the change in shape of the kinetic curves. The rate equation therefore becomes:

$$\frac{-d[EtSH]}{dt} = \frac{-4d[O_2]}{dt} = k_1[O_2][EtSH]$$

for the first part of the oxidation, and

$$\frac{-d[EtSH]}{dt} = \frac{-4d[O_2]}{dt} = k_2[O_2]$$

for the remainder. Taking the value of 0.0114 for the Bunsen absorption coefficient for oxygen in 2M aqueous NaOH at 30° C (Appendix 3), the values of k_1 and k_2 can be shown to be 4.86×10^{-2} mole l^{-1} sec^{-1} and 2.01×10^{-2} sec^{-1} respectively.

In agreement with the results of Hopton[66] the oxidation

of ethanethiol had a positive dependence on the alkali concentration; this is unlikely to have been due to increasing ionisation of the thiol, which would have been 99% ionised in the weakest alkali used (1.0 M). The effect may have been due to catalytic impurities introduced with the thiol or alkali.

The observed kinetics can be explained in terms of the mechanism proposed by Wallace and Schriesheim[51]:

$$RSH + B^- \rightleftharpoons RS^- + BH \qquad (20)$$

$$RS^- + O_2 \longrightarrow RS^{\cdot} + O_2^- \qquad (21)$$

$$RS^- + O_2^- \longrightarrow RS^{\cdot} + O_2^{2-} \qquad (22)$$

$$2RS^{\cdot} \longrightarrow RSSR \qquad (23)$$

$$O_2^{2-} + H_2O \longrightarrow 2OH^- + \tfrac{1}{2}O_2 \qquad (24)$$

where reaction (21) is rate-determining, and B represents a suitable base which may be the solvent. Theobserved order of unity with respect to both thiol and oxygen for the initial reaction is consistent with the above reaction scheme. The relationship between the rate of reaction and the concentration of hydroxide is a complicating factor, but this may be accounted for in terms of the fast equilibrium (20) and of the increasing effect of the hydrolysis of disulphide with high concentrations of hydroxide ion. Thus, although it has been suggested that only disulphides containing aryl, carbonyl, or α-unsaturated groups are susceptible to hydrolysis by nucleophilic reagents such as the hydroxide ion, only a very small degree of hydrolysis may have a comparatively large effect on the low rates of the uncatalysed reaction.

The catalytic effect of disulphides, and in particular

dithioglycolic acid, is now fairly well established[99], their influence being ascribed to a cyclic process involving sulphenic and persulphenic acids[60]. Since sulphenic acids are produced by the hydrolysis of disulphides[72], the autocatalytic effect of disulphide should increase with the alkali concentration. However, sulphenic and sulphinic acids normally disproportionate according to the scheme[154]:

$$2RSOH \longrightarrow RSH + RSO_2H \quad (79)$$

$$2RSO_2H \longrightarrow RSOH + RSO_3H \quad (80)$$

$$RSH + RSOH \longrightarrow RSSR + H_2O \quad (81)$$

$$RSO_2H + RSOH \longrightarrow RSO_2SR + H_2O \quad (82)$$

These reactions would lead to the formation of higher molecular weight oxidation products, such as sulphonic acids but thesewere not formed in any considerable quantity during the present work.

With the exception of experiments involving cyanide, the results of uncatalysed experiments are rather irreproducible, and it seems likely that metal ions are being introduced with the reagents. As a result, attempts were made to deactivate any metal ions by the production of metal complexes thought to be inert, such as cyanide, ethylenediamine and EDTA derivatives. The presence of cyanide ions in the reactant solutions has a profound effect both on the oxygen uptake and on the production of disulphide. Because of these large changes it is premature to assume that the reactions in the presence and absence of CN^- are similar, particularly since analytical methods for the estimation of sulphinic and sulphonic acids do not operate satisfactorily in the presence of cyanide. The addition of

potassium cyanide to alkaline solutions of disulphide which could result in decomposition in the manner proposed by Schoeberl[73] (equation (83)), had no noticeable effect.

$$RSSR + CN^- \longrightarrow RSCN + RS^- \qquad (83)$$

Any thiocyanate which could be produced by this reaction has been shown to be inert to oxidation, but to be hydrolysed to disulphide in 2 M NaOH.

Further evidence for the effect of impurities on the rates of oxidation of the nominally uncatalysed system is obtained by consideration of the oxidation of ethanethiol in the presence of nitrogen-containing ligands. Additives such as pyridine, dipy and o-phen readily form complexes with any metal ions in the system. In the presence of these ligands, the rate of oxidation was in general found to increase, (Table 8) and in particular large increases were observed with certain batches of dipy. Metal complexes involving these ligands would be expected to be relatively inert[151], and it seems likely that instead of removing catalytic metal ions from the reaction, these additives are in fact responsible for the introduction of traces of metal ions. This is supported by the fact that, according to the analysis given on the maker's label, a 0.1 M solution of pyridine could contain up to 5×10^{-7} M copper. The catalytic role of copper in this concentration range has amply been demonstrated[66].

Apparent impurity effects were also observed in experiments using different alkaline solutions. Thus in two experiments carried out in 1.0 M caesium hydroxide, rates differing

by a factor of 1.9 were observed. In view of this difference it is perhaps unrewarding to discuss the rates of oxidation for the reaction in solutions of the four alkali metal hydroxides reported in Section H.2(a). However, in the presence of 0.25 M potassium cyanide, the results show a definite trend, the rates being lowest for lithium hydroxide and highest for caesium hydroxide. Although these rates appear to bear some relationship to the first ionisation potential of the alkali metals, a more important factor is perhaps the solubility of oxygen in the alkaline solutions. Bunsen coefficients do not appear to have been reported for the solubility of oxygen in solutions of lithium hydroxide and caesium hydroxide, but the "salting out" effect of an ion in solution on the solubility of gases in that solution generally increases with decreasing ionic size[155]. Thus the rate of oxidation would be expected to be lowest for lithium hydroxide and highest for caesium hydroxide.

For ethanethiol, it is unlikely that physicochemical factors such as diffusion of oxygen into the liquid phase, or partitioning of thiol between the aqueous phase and the disulphide affect the course of the reaction. Direct examination of diffusion-controlled reactions has shown that this effect is irrelevant in the uncatalysed system. It may be suggested that the change in the rate of oxygen uptake which was observed in some experiments is related to the partition of thiol in the system, since the high initial rate disappeared when disulphide was added to the reactant solutions. It seems unlikely, however, that thiol anions would dissolve to a significant extent in a solvent such as disulphide.

The detailed comparison of the kinetics of the oxidation of various thiols, may be unrewarding since the systems are complicated by individual values of physicochemical factors such as the degree of ionisation of the thiol, and partition coefficients of thiols between the alkaline solution and the disulphide layer. It is possible, however, to explain the relative order of rates of oxidation in terms of electron-donating tendencies and steric effects associated with individual thiols. In a series of n-alkanethiols, $CH_3(CH_2)_nSH$, the electron-directing influence of the methyl group would be expected to decrease as n increases. Similarly, for the butanethiols, electron-donation to the sulphur atom, and hence the rate of oxidation, would be expected to increase in the order $Bu^n < Bu^i < Bu^s < Bu^t$. On the other hand, steric hindrance would be expected to increase in the order $Bu^n \approx Bu^i < Bu^s < Bu^t$, and the rate of oxidation would be expected to decrease in this order. The importance of the latter effect is confirmed by the experimentally observed order of ease of oxidation, namely $Bu^i \geqslant Bu^n > Bu^s \gg Bu^t$. Further confirmation is obtained from the fact that the rate of oxidation of phenylmethanethiol is greater than that of the sterically hindered thiophenol (see Section H.3). It is clear, however, that the results for the oxidation of n-butanethiol are anomalous with respect to those for ethanethiol, and are consistent with an impurity in the n-butanethiol system.

The importance of impurities is further emphasised by consideration of the rates of oxidation obtained with n-octanethiol (Table 10). Thus, although it is possible to explain the rapid

oxidation of n-octanethiol in terms of autocatalysis by the compounds formed as products of disulphide hydrolysis, a tentative explanation of the observed order of reactivity in terms of metal-ion catalysis appears preferable. Certain metal-thiol complexes are known to be volatile[119], the volatility increasing with the size of the alkyl group. Purification of thiol samples by double distillation would therefore be expected to become less efficient with increasing molecular weight of the thiol.

Although there is little doubt that electron transfer reactions (e.g. equations (21) and (22)) are involved in the overall reaction, the suggestion that quantitative yields of disulphide arise from the dimerisation of thiyl radicals is inconsistent with the observed behaviour of other free radicals[156]. In agreement with published work[66], peroxidic substances have been shown to play no part in the reaction, and free radical inhibitors did not result in a decrease in the rate of oxidation. On the basis of the uncatalysed results, however, it is difficult to suggest alternative and plausible reaction mechanisms except in so far as metal catalysis may be affecting the nature and kinetics of reaction. Clarification of the role of such impurities was obtained from studies of the reaction in the presence of added metal ions.

2. The oxidation of thiols in the presence of metal-containing catalysts

The oxidation of ethanethiol has been studied in the presence of a wide variety of transition metals, added as simple salts. More detailed investigations of the oxidation of ethanethiol and certain other thiols have been carried out in the presence of

copper, cobalt and nickel catalysts, since these metals were found to exert the most powerful catalytic action when added to the solutions as simple salts.

2(a) Comparison of different metals

Since an electron transfer from thiol anions has been shown to be an important reaction, it might be expected that some correlation would be observed between the catalytic activities of metal ions and their redox potentials, the metals acting as electron acceptors. No such correlation was in fact observed presumably since reactions were carried out in 2 M alkaline solutions, in which the metals would be present mainly as hydroxides or hydrated oxides, which are known to be largely insoluble.

If the catalytic activity of any one metal ion is dependent upon the degree of dissolution of the metal in the solutions, and on the ease with which an electron is transferred from the thiol anion to the metal, then some metals may be poor catalysts in alkaline solution either because the hydroxides are insoluble or because the co-ordination atmosphere of the hydroxyl groups does not easily allow the passage of an electron. Alternatively, metals may be poor catalysts because of the difficulty of replacement of hydroxyl groups by ligands such as thiol or disulphide. If such complexes are formed, then the possibility of increased solubility, or increased facility of electron transfer, may result in enhanced catalytic properties. It would thus seem feasible to correlate catalytic activity with the nature and solubility of metal complexes in solution. In general, the predicted relationship holds although

obvious discrepancies do appear. Thus in the presence of a tin salt, which is soluble in alkaline solutions, the observed rate of oxidation was low (Table 11), being only marginally higher than the uncatalysed rate. Similarly, low rates were observed in the presence of palladium and thallium, both of which form complexes with the thiol. However, the three most efficient catalysts, copper, cobalt and nickel, all formed complexes with the thiol which were partially soluble in alkaline solution. Further evidence for the suggested correlation is discussed below.

2(b) The isolation of metal-thiol complexes

The formation of metal-thiol complexes was observed with a number of metals (Section H.3(a), but only in relatively few cases was the formation of such complexes associated with efficient catalysis of the oxidation of thiols. Thus, experiments in the presence of a palladium salt were characterised by low rates and by the formation of bright orange precipitates. These precipitates were formed with all of the thiols investigated, and the colours varied with the nature of the thiol, being orange with aliphatic thiols and brick red with thiophenol. Elemental analysis of the ethanethiol complex suggested that this was a palladous mercaptide. Since these mercaptides were formed with all the thiols investigated, including sterically hindered thiols such as tert-butanethiol and thiophenol, the structure of the mercaptides is evidently such that their formation is not impaired by the presence of bulky groups attached to the sulphur atom. The ready solubility of these complexes in organic solvents suggests that they are not co-ordination polymers

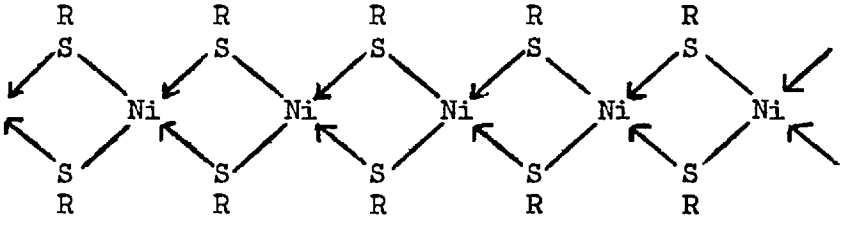
as was once suggested[119]. It is interesting that a complex with a similar ultraviolet spectrum to the Pd-EtSH complex was formed from diethyl disulphide and palladous chloride. Such behaviour was not observed with the other metals investigated.

Thallium complexes were also obtained with all of the thiols investigated, and elemental analysis showed these to be thallous mercaptides. Complexes were not formed from the dialkyl disulphide (cf. palladium). In view of the insolubility of these compounds in all common solvents, they are most probably co-ordination polymers.

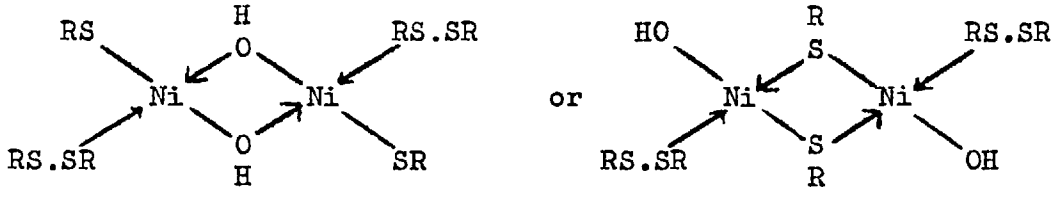
Kinetic experiments in the presence of copper sulphate were not accompanied by the formation of highly coloured precipitates, but in experiments designed specifically for the preparation of complexes, yellow precipitates of empirical formula CuSR were obtained with all the thiols investigated. Unfortunately the deep blue complex observed in solution following filtration of the yellow cuprous mercaptides was not positively identified, but it is possible that this may be a dissolved copper^{II}-thiol complex. Since the cuprous ethyl mercaptide was formed in solutions containing 0.1 M en, but was not formed in the presence of cyanide, the stability constant of this complex presumably lies between that of $Cuen_3^{2+}$ (10^{21}) and $Cu(CN)_4^{3-}$ (10^{28}). The mercaptides are possibly co-ordination polymers.

Nickel complexes were not obtained with the sterically hindered thiols, in contrast to the complexes of palladium, thallium and copper. Furthermore, Soxhlet extraction with chloroform

yielded both a soluble and an insoluble portion, of which the latter accounted for 90-95% of the total. Both complexes were diamagnetic, indicating that they have a square planar structure[150]. The ultra-violet spectra of the soluble complex dissolved in carbon tetrachloride was identical with that obtained in pyridine solution, suggesting that the pyridine was not becoming co-ordinated to give an octahedral complex. The insoluble residue from the Soxhlet extraction was of high melting point with an empirical formula $Ni(SEt)_2$ for the ethanethiol complex; it is possible that these insoluble fractions are linear co-ordination polymers of the type suggested by Jensen[118]:-



The soluble complex possessed a lower melting point, and it seems unlikely that this complex is polymeric in view of the empirical formula, $Ni(SR)_3(OH)$, two possible structures may be proposed:



The effect of ligands on the formation of nickel-thiol complexes has been discussed (Section K.2(c)), and it seems likely that the stability constants of these complexes are of the order 10^{18}.

In agreement with the observed behaviour of nickel-thiol complexes, cobalt-thiol complexes were not formed with the

sterically hindered thiols. The empirical formula of the red ethanethiol complex $Co(SEt)_{3.1}$ is in agreement with the published analysis of the n-hexanethiol complex[120], and it is possible that the red cobalt-thiol complexes are polymeric, as suggested for the n-hexanethiol complex. Under an atmosphere of carefully deoxygenated nitrogen no red complexes were observed when cobaltous salts were used as starting materials. In these experiments deep blue solutions were formed, which were oxidised to the red complexes by traces of oxygen. It seems possible that these blue complexes are Co^{II} mercaptides, and in the presence of oxygen, a balance exists between the equations:

$$Co^{III} + xRS^- \longrightarrow Co^{II}(SR)_x \text{ (blue complex)} \quad (84)$$

$$Co^{II}(SR)_x + O_2 \longrightarrow Co^{III}(SR)_x + O_2^- \text{ (red complex)} \quad (85)$$

Thus in a system where either $[Co]$ is low, or where $[RS^-] \gg [O_2]$, formation of the blue complex will be favoured. In agreement with this, blue solutions were produced in the absence of oxygen from Co^{III} salts at concentrations of 10^{-2} to 10^{-3} M, whereas at cobalt concentrations of 0.15 M, red complexes were produced. It has also been shown to be unnecessary for oxygen to be present to ensure the formation of the red complexes, provided that oxidising agents are present to convert Co^{II} to Co^{III}. Solid samples of the blue complexes could not be isolated owing to the extreme ease with which they were oxidised to the red complexes.

2(c) The effect of nickel sulphate

The rate of oxidation of ethanethiol in the presence of nickel sulphate was observed to increase with temperature, and an

activation energy of 8.0 kcal mole^{-1} was recorded. This is generally similar to values obtained for redox reactions involving metal ions, but it is not possible at present to derive mechanistic details from such data[157]. The rate of oxidation of ethanethiol was found to increase linearly with the oxygen pressure, but extrapolation of the graph to zero rate gave an intercept of slightly less than 5 cm on the oxygen pressure axis. The positive intercepts obtained on the plots of rate versus oxygen pressure show marked similarities with one another and with calculated partial pressures of the components of the system, the existence of these intercepts being attributed to this cause. At concentrations of ethanethiol greater than 0.5 M the rate of reaction was found to be independent of the thiol concentration, and to depend on the rate of diffusion of oxygen into the system. Under these conditions, the rate of oxidation was dependent on the rate at which the reaction vessel was shaken. Diffusion was not rate-controlling however, in experiments where the nickel concentration varied from 10^{-7} M to 10^{-3} M at a constant ethanethiol concentration of 0.5 M or less. At these concentrations of ethanethiol the rate of reaction was first order with respect to thiol. The rate of oxidation apparently increased with decreasing alkali concentration, but this increase disappeared on correction by the Bunsen coefficients, for the solubility of oxygen in the alkaline solutions.

The rate of reaction was very dependent on the nature of the metal complex in solution. Both EDTA and en decreased the amount of the brown nickel-thiol complexes formed, and at ligand

concentrations of 10^{-1} M, brown complexes were not produced in either case. The addition of this concentration of EDTA or en also markedly decreased the overall rate of oxidation, possibly as a result of a reduction in the amount of brown nickel-thiol complexes in solution. Since the competition between EDTA, en, and thiol anions for nickel ions markedly favours the formation of EDTA or en complexes, even when [EDTA] and [en] are considerably less than the thiol concentration, it is likely that the stability constants of the nickel-thiol complexes are of the same order as those of the nickel-EDTA complex (10^{18}) and the nickel-en complex (10^{18}) [151]. The addition of diethyl disulphide to nickel-catalysed oxidations had virtually no effect on the rate of oxidation (Table 13).

The presence of 0.25 M potassium cyanide in the reacting solutions resulted in a large reduction in the rate of oxidation and in the complete inhibition of the formation of nickel-thiol complexes. Cyanide is known to form stable complexes with nickel, the stability constant of $Ni(CN)_4^{2-}$ being 10^{22}, and that of $Ni(CN)_6^{4-}$ being 10^{26} [151]; it is therefore evident that the cyanide is competing more favourably than thiyl entities for the nickel co-ordination sites. The reaction in the presence of cyanide evidently follows a different mechanism from the other nickel-catalysed reactions, as no disulphide was detectable in the reaction products (see above).

Experiments in the presence of pyridine, dipy and o-phen have also shown that the stability of the metal-ligand complexes in solution has a profound effect on the subsequent rate of oxidation of the thiol. The addition of pyridine would be expected to have

little influence on the nature of complexes in solution and on the catalytic activity of the nickel, (stability constants of nickel-pyridine complexes $<10^{9}$; stability constant of $Ni(OH)_2$ $\approx 10^{11}$). On the other hand dipy and o-phen, whose respective stability constants for the complexes $Ni(L)_3^{2+}$ are 10^{21} and 10^{26}, would be expected to have a considerable influence on the formation of metal-thiol complexes and hence on the rate of oxidation of the thiol. These predictions have been confirmed by the experimental results, (Table 15).

The observed order of reactivity of a variety of thiols in the presence of nickel sulphate, viz. $Et > Hex^{n} > Bu^{i} > Bu^{n} > Bu^{s} > PhCH_2 > Ph > Bu^{t}$ is in reasonable agreement with that expected on the basis of electron-directing properties and steric effects (see above). The order of reactivity of thiols is approximately the same as for the uncatalysed system, although rates of oxidation of individual thiols are higher. In the thiophenol and tert-butanethiol systems, the formation of brown nickel-thiol complexes was not observed. Furthermore the rates of oxidation of these two thiols did not decrease as the reaction proceeded, in contrast to the other thiols under investigation. The oxidation of these two thiols was found to be independent of the thiol concentration in the system.

2(d) <u>The effect of copper sulphate</u>

Copper was found to be the most efficient of a range of metal-ion catalysts for the oxidation of thiols, and at copper contrations equal to 10^{-3} M in the presence of ethanethiol the rate of oxidation was controlled by the rate of diffusion of oxygen into

the system. Copper catalysed reactions were in general carried out at a concentration of 10^{-5} M Cu. Copper-thiol complexes, some of which were cuprous mercaptides (Section I) were produced, but were not normally as conspicuous as those of nickel and cobalt. Kinetically the copper-catalysed oxidation of ethanethiol was first order with respect to oxygen and zero order with respect to thiol. In agreement with the results obtained in the presence of nickel sulphate, the graph of rate versus oxygen pressure did not pass through the origin, an intercept of 6 cm.Hg being obtained on the oxygen pressure axis. Apparent autocatalysis was observed in a number of experiments, as the rate of oxygen uptake increased as the reaction proceeded. If autocatalysis resulted from disulphide hydrolysis (equations (33), (79) to (82)), the overall oxygen uptake would be expected to be higher than that theoretically required for conversion of thiol to disulphide. This was not observed in the present system.

An increase in the alkali strength appeared to result in a decrease in the rate of oxidation, but the rates became almost identical on correction for the solubility of oxygen in the alkaline solutions (Appendix A.3). The reaction rate increased with temperature, and for solutions of ethanethiol containing 10^{-5} M copper the measured activation energy was 3.3 kcal $mole^{-1}$.

The presence of en, EDTA or cyanide has been shown to inhibit oxidation in the presence of copper sulphate[66], and it is likely that these ligands are competing for the co-ordination sites of the metal, as has been proposed for nickel catalysis. The

addition of pyridine, dipy or o-phen had virtually no effect on the rate of oxidation, and this may be explained in terms of the stability constants of these ligands with copper[151]. Thus in the presence of cyanide, complete inhibition of oxidation occurred, and in the presence of en and EDTA, partial inhibition was observed. The respective stability constants are: $Cu(CN)_4^{3-}$, 10^{28}; $Cuen_3^{2+}$, 10^{21}; $Cu\ EDTA^{2-}$, 10^{19}. Using similar concentrations of pyridine, dipy and o-phen (Table 19), no serious inhibition occurred in the presence of pyridine, and the rate was only slightly reduced in the presence of dipy and o-phen. In this case the respective stability constants are $Cupy_6^{2+}$, 10^{10}; $Cu(dipy)_3^{2+}$, 10^{18} and $Cu(o\text{-}phen)_3^{2+}$, 10^{17}. If the active species is a copper thiol complex, the stability constant would thus be expected to be around 10^{20}, in which case little effect would be expected from ligands such as pyridine, whereas cyanide might be expected to displace thiol completely from the metal co-ordination atmosphere.

The rates of oxidation of the four butanethiols in the presence of copper sulphate were in the same order as those observed in the presence of nickel sulphate, viz. $Bu^i > Bu^n > Bu^s \gg Bu^t$. In contrast to the nickel-catalysed system, there was evidence for the formation of a copper complex with tert-butanethiol (see Section I.2). The curves of oxygen uptake versus time were all approximately linear, suggesting that the kinetics of the oxidation are independent of thiol concentration.

2(e) <u>The effect of cobalt sulphate</u>

The results of experiments in the presence of cobalt

sulphate are generally comparable with those obtained with nickel sulphate and copper sulphate. Thus the rate has a first order dependence on oxygen pressure, and a plot of rate versus oxygen pressure resulted in an intercept being obtained on the oxygen pressure axis. Differences were apparent in the effect of thiol concentration on the rate of oxidation. At low thiol concentrations, a marked decrease in the rate of oxidation was observed after approximately 30% conversion of thiol to disulphide. On the basis of these "initial high" rates of oxidation, there appeared to be a zero order dependence on thiol, but this dependence became first order with respect to thiol if values of the final "steady" rate were used. This will be discussed further in terms of the mechanisms proposed for cobalt catalysis (see below). This change in order could not be explained in terms of the expected behaviour of a first order rate curve at high concentrations.

Further similarities with systems catalysed by nickel and copper were observed in the dependence on temperature of the rate of oxidation of ethanethiol in the presence of cobalt sulphate. The measured activation energy over the range 20-40° C was found to be 7.5 kcal $mole^{-1}$. The presence of EDTA, en and cyanide has been reported to cause a decrease in both the rate of oxidation, and the amount of characteristic red complex formed during the oxidation[66]. In agreement with the results obtained for nickel and copper catalysis, both dipy and o-phen caused the rate to decrease, although the amounts of red cobalt thiol complex appeared to be virtually unaltered. The order of reactivity of the four butanethiols in the presence of

cobalt sulphate differed from that observed in the presence of nickel sulphate or copper sulphate in that the rate of oxidation of sec-butanethiol was considerably higher than that of n-butanethiol or of iso-butanethiol. The characteristic cobalt-thiol complex was produced only slowly, although it is possible that a sufficient quantity to produce noticeable catalysis was formed soon after the reagents had been mixed. The rate of oxidation of sec-butanethiol did, however, decrease fairly rapidly with time, and after ca.40% of the reaction had taken place the rate was lower than that for iso-butanethiol or n-butanethiol. No cobalt-thiol complex was formed with tert-butanethiol in agreement with the results obtained in the presence of nickel sulphate. The rate of oxidation of tert-butanethiol was also very low, being only $\sim$3% of the initial rate of oxidation of ethanethiol.

2(f) The effect of filtration of reaction solutions containing simple metal salts

If heterogeneous catalysis is involved in the oxidation of thiols in the presence of simple metal salts, efficient filtration of reactant solutions should result in a decrease in the rate of oxidation of the thiol. The results obtained in Section H.3(j) have shown that solid material does not take part in the reaction. Thus rates observed in unfiltered solutions (case 1) are almost identical to those obtained with solutions which had been filtered after addition of the thiol (case 3), where the amounts of metal in solution are determined by the solubility of metal thiol complexes formed in solution. Analyses of the cobalt- and nickel-containing solutions

after filtration (case 3) have shown the amounts of metal present to be 6.4×10^{-4} M and 5.3×10^{-4} M respectively, the metal concentration originally added being 10^{-3} M.

On the other hand the rate of reaction in case 2 (solution filtered before addition of thiol is determined by the solubility of the metal hydroxide or hydrated oxide, and in general the solubilities of such compounds are low[151]. In experiments with cobalt sulphate and with nickel sulphate, these rates were found to be considerably lower than those obtained in cases 1 and 3 as were the amounts of the two metals analysed in the filtered solutions (8.9×10^{-5} M and 1.3×10^{-5} M respectively). It is apparent from this work that the amount of metal in solution markedly affects the efficiency of catalysis. Many of the metals which were ineffective as catalysts (Section H.3(a)) may well be inefficient either because they form only relatively insoluble hydroxides or hydrated oxides or because, although they form metal-thiol complexes, these complexes are insoluble in alkaline solution.

2(g) Proposed mechanisms

In the light of the results discussed above, the general reaction scheme for the metal catalysed oxidation of thiols (equations (55) to (58)) does not adequately account for all experimental results. This scheme can therefore be replaced by two inter-related mechanisms which account more fully for the observed results.

There is no doubt that any mechanism suggested must explain the observed electron directing and steric effects of thiols,

and a mechanism can be proposed on the basis of the co-ordination chemistry of metal ions. For the sake of clarity, let us consider first the reaction in the presence of cyanide in which the ligand is tightly bound to the metal ion. In these circumstances no replacement reactions are likely to occur and electron transfer probably involves an"outer-sphere"reaction[158].

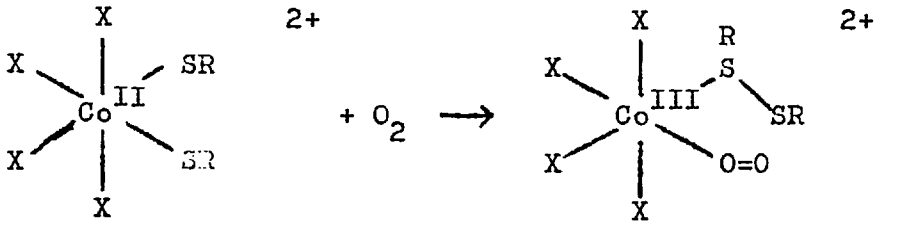
$$\begin{array}{lll} RS^- + M^{n+}(X)_6 + O_2 \longrightarrow & RS^-.....M^{n+}(X)_6.....O_2 & \\ & \downarrow & \\ & RS^{\bullet}.....M^{(n-1)+}(X)_6.....O_2 & (86) \\ & \downarrow & \\ RS^{\bullet} + M^{n}(X)_6 + O_2^- \longleftarrow & RS^{\bullet}.....M^{n+}(X)_6.....O_2^- & \end{array}$$

Any disulphide formed in such a reaction must be produced by radical dimerisation provided that no substitution of thiol occurs into the metal co-ordination atmosphere. Results obtained in the presence of CN^- point to the conclusion that no substitution of thiol takes place and that radical dimerisation, even if it occurs, is unimportant compared with other reactions of thiyl radicals. In these circumstances, it is no longer possible to entertain a reaction mechanism in which quantitative yields of disulphide are produced as a supposed result of radical dimerisation (reaction (58)).

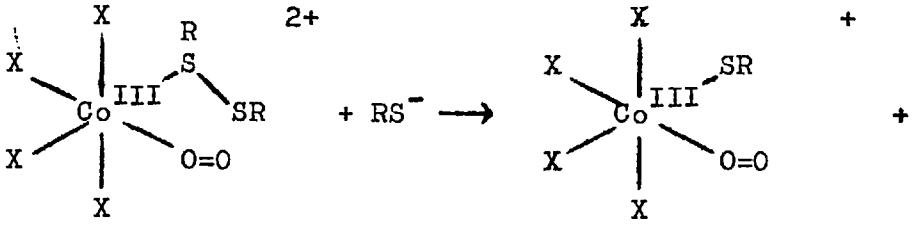
A number of other possible mechanisms based on a "ligand transfer" type of reaction[159] can be suggested:

$$M^{n+}(X_5Y) + R^- \longrightarrow M^{(n-1)+}(X_5R) + Y \qquad (87)$$

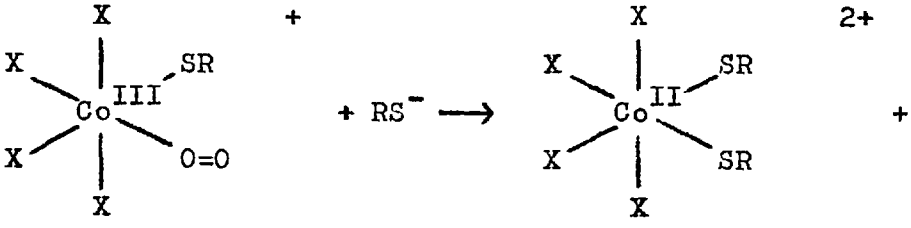
Thus in the case of cobalt catalysis the following reaction sequence may be advanced:



(88)



(89)



(90)

$$2O_2^{2-} + 2H_2O \longrightarrow 4OH^- + O_2 \qquad (91)$$

Such a reaction scheme satisfies all of the observed facts, provided that as the kinetic results indicate, reaction (88) is assumed to be rate-determining. The four co-ordination positions $(X)_4$ play no part in the reaction, but would be expected to have a small but definite influence on the rate of reaction[158]. In the initial stages of the oxidation, X will presumably be a hydroxy or thiyl ligand, but as the reaction proceeds (or in the presence of a complexing agent) there will be competition by the disulphide (or the complexing agent) for such sites. The rate of oxidation would be expected to alter as the disulphide competes more successfully for these sites, or to alter in the presence of a complexing agent. This

effect may be clearly seen in practice by examination of the change in rate of oxidation from the initial "high" rate to the final "steady" rate. However, at high concentrations of complexing agents, the co-ordination positions would not be available to thiyl ligands and the reaction would proceed by an "outer sphere" mechanism.

In the case of catalysis by copper, a similar mechanism can be proposed which embraces possible changes in the number of co-ordination sites available. Since the most favoured co-ordination numbers of Cu^{I} are 4(tetrahedral) and 2(linear) and those of Cu^{II} are 4(square or tetrahedral) and 6(tetragonally distorted octahedral), the following mechanism may be suggested:

$$Cu^{I}\left[(\overset{*}{S}R)_2\right]^- + O_2 \longrightarrow Cu^{II}\left[(\overset{*}{S}R)_2(\overset{*}{O}_2)\right]^- \quad (92)$$

$$Cu^{II}\left[(\overset{*}{S}R)_2(\overset{*}{O}_2)\right]^- + 2RS^- \longrightarrow Cu^{I}\left[(\overset{*}{S}R)_2(R\overset{**}{S}\overset{**}{S}R)\right]^- + O_2^{2-} \quad (93)$$

$$Cu^{I}\left[(\overset{*}{S}R)_2(R\overset{**}{S}\overset{**}{S}R)\right]^- \longrightarrow Cu^{I}\left[(\overset{*}{S}R)_2\right]^- + RSSR \quad (94)$$

$$2O_2^{2-} + 2H_2O \longrightarrow 4OH^- + O_2 \quad (95)$$

In this scheme, in which atoms co-ordinated to the metal atom are marked with an asterisk, the addition of oxygen (equation (92)) must be assumed to be rate-determining. This reaction is stabilized by the "inner-sphere"[158] transfer of an electron from the copper atom to oxygen. Peroxide is then displaced by thiol anions, and the resulting complex returns to the original two co-ordinate complex by the elimination of disulphide.

The reaction mechanisms suggested for copper and cobalt catalysis (see above) appear unrealistic in the case of nickel

catalysis, since any mechanism involving Ni^{III} or Ni^{I} seems unlikely[150]. The nickel catalysed oxidation is first order with respect to oxygen and thiol, and it could be suggested that thiolic and oxygen entities are held adjacent to one another by incorporation into the co-ordination atmosphere of Ni^{II} ions, which can exist with co-ordination numbers of both 4 and 6. In these circumstances, nickel ions of other valencies may exist in solution as short-lived intermediates, allowing catalysis to occur by means of a rapid electron-transfer reaction. Some support for this view is obtained from the work of Coucouvanis and Fackler[160], who showed that complexes formed by the oxidation of $nickel^{II}$ dithiobenzoate and $nickel^{II}$ N-phenyldithiocarbamate do not contain $nickel^{IV}$, but are ligand-oxidised $nickel^{II}$ species.

In the reactions discussed above, the geometric structure and electron-directing properties of the thiol anion affect the overall catalytic activity of the complex, although the rate of oxidation is zero order in thiol for cobalt and copper catalysis and for nickel catalysis at low thiol concentrations. π-bonding of the thiol anions may be consistent with this behaviour[157]. The first order kinetics with respect to thiol in nickel catalysed reactions may be due to difficulty of substitution of thiol anions into the nickel co-ordination atmosphere.

2(h) <u>The effect of cobalt complexes</u>

Whilst the rate of an outer-sphere reaction involving metal ions is relatively insensitive to changes in the ligands attached to the metal ion[161], the ligands $(X)_4$ co-ordinated to the

metal atom in reactions (88) to (90) have a small but definite influence on the rate of reaction[158]. Thus in a series of experiments in the presence of various cobalt complexes, the rate of oxidation of ethanethiol was found to vary with the nature of the complex. In addition the amount of red cobalt-thiol complex produced in individual cases varied both with the ligands present in the system, and in some cases with the concentration of such ligand-forming additives. Only in the case of $K_3Co(CN)_6$ was the red complex not produced, and the rate of oxidation in the presence of this complex was extremely low. Complexes containing only monodentate ligands such as NH_3, py or H_2O resulted in rates of oxidation very similar to that observed in the presence of cobalt sulphate. Bidentate ligands, (e.g. en) however, decreased the rate of oxidation and the amounts of red cobalt-thiol complex produced.

Since reactions (88) to (90) envisage catalysis via a complex which contains disulphide in two co-ordination positions of the octahedral Co^{III} co-ordination shell, any ligand which can prevent the formation of this cobalt-disulphide complex should have a profound effect on the rate of oxidation of the thiol. Unfortunately the only simple ligand which could completely displace disulphides or thiols was cyanide, in the presence of which the reaction evidently proceeds via an outer-sphere mechanism. Again, dimerisation of thiols should be hindered if the thiyl entities are not adjacent to each other. However, attempts to discover an alkali-stable cobalt^{III} complex in which only the trans- co-ordination positions are available to substitution by thiols or disulphides were

unfortunately unsuccessful. Thus in the presence of alkali, complexes such as trans- $[Coen_2Cl_2]Cl$ rapidly form the cis-hydroxy complex[157], where disulphide can either replace the hydroxy groups, or the en. That this latter substitution can occur, is evident from the results obtained with $Coen_3Cl_3$, where all the cobalt co-ordination positions are occupied by three molecules of en. This complex was found to catalyse the oxidation of ethanethiol, and although the rate of oxidation was little more than half that observed in the presence of the red catalytic complex from cobalt sulphate, a certain amount of red cobalt-thiol complex was present in the reaction products. Evidently the reaction proceeds mainly by an outer-sphere mechanism with some little substitution occurring to give a "ligand-transfer" reaction as a minor mechanistic route.

(i) The effect of metal-thiol complexes

The reaction schemes proposed for the metal-catalysed oxidation of thiols involve metal-thiol complexes as intermediates. Experiments have been completed in which it is shown, for the cobalt- and nickel-catalysed systems, that the nature and concentration of the dissolved complex markedly affects the rate of reaction.

In experiments with ethanethiol in the presence of cobalt-thiol complexes, the rate of oxidation of the thiol was found to be identical when the metal was added in various forms. Thus, in the first case, the cobalt-thiol complex was produced in the reaction solution, cobalt sulphate being added to the solution initially so that the cobalt concentration was 10^{-3} M. Secondly the oxidation was carried out in the presence of the red cobalt-

ethanethiol complex, which had been separately prepared, and which was added to the solution to give a cobalt concentration of 10^{-3} M. The third case involved a sample of the red cobalt-ethanethiol complex which had been collected from a previous reaction in the presence of cobalt sulphate. In this case the cobalt concentration in the solution would be $\leqslant 10^{-3}$ M, depending on the extent to which the cobalt-thiol complex was originally produced from the cobalt sulphate, and upon the amount that could be filtered from the original solution. The fourth and fifth cases were similar to the second and third respectively except that the complexes added were red cobalt-n-hexanethiol complexes, prepared under conditions similar to those used in cases 2 and 3.

By consideration of the results in Section H.3(f), it is evident that the overall pattern of oxidation was similar in all cases, although slight differences in initial rates were observed. It is thus apparent that the cobalt-thiol complexes produced in the third and fifth cases were formed in almost quantitative yields from cobalt sulphate and the respective thiol, since the oxidation of thiols in the presence of cobalt salts has been shown to be dependent on the amount of cobalt present in the system[66].

Confirmation of the above results was obtained from a similar series of experiments in the presence of nickel complexes where it was possible to isolate soluble and insoluble products. Thus the oxidation of ethanethiol in the presence of nickel sulphate was compared with experiments in which the nickel was added respectively as the soluble brown complex with ethanethiol, the

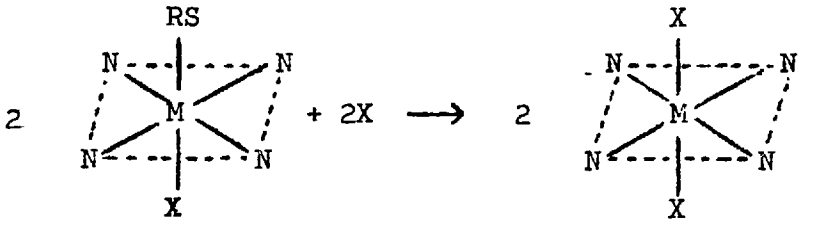
insoluble complex with ethanethiol, and the mixed complex removed from the reaction products of a reaction in the presence of nickel sulphate. In all cases the rates of oxidation were very similar, again suggesting that the mixed complex added in the final case was produced in quantitative yield from nickel sulphate in the reaction in which it was prepared, and that the soluble complex could be produced from the insoluble complex and vice versa.

Slight differences were observed in the kinetic curves for the oxidation of ethanethiol in the presence of metal-thiol complexes, the curves of oxygen uptake versus time tending to be almost linear in some cases. In particular the initial "high" rate observed in the presence of cobalt sulphate was not evident in the presence of cobalt-thiol complexes. Since the final "steady" rates have been suggested to be due to increased participation of metal-disulphide complexes in the reaction mechanism, the elimination of the initial "high" rate in the presence of added complexes would be expected, since in these cases the catalyst is possibly being added to the solutions as a metal-disulphide complex.

2(j) The effect of macrocyclic tetrapyrrolic complexes

In contrast to the majority of experiments described in the previous sections, the use of macrocyclic tetrapyrrolic complexes permits the addition of metal atoms to reactant solutions in a form which is both stable and is soluble in alkali. The structures of the three complexes (haemin, vitamin B_{12} and chlorophyll) used in the present investigation are given in Appendix A.4. In the majority of cases considered in the previous sections, the metal complex

originally added to the reactant solution is substituted by thiyl entities, and metal-thiol complexes are produced. If the complex cannot be substituted, then the rate of reaction will depend on the ease with which an electron can be transferred across the co-ordination system to the metal ion. Alternatively if disubstitution or monosubstitution occurs in the two co-ordination positions not occupied by the porphyrin ring, then the production of disulphide must involve two metal centres:



(96)

Although haemin, chlorophyll and vitamin B_{12} do not form coloured metal-thiol complexes, the conjugated double bonds in the porphyrin ring provide a means for the facile transfer of an electron to the central metal atom. Furthermore these complexes are soluble in alkaline solution, a factor which would be expected to enhance the homogeneous catalytic activity of the metal. This was found to be the case and indeed in certain cases the rates of reaction were greater than the rate of diffusion of oxygen into the solution (cf reaction in the presence of 10^{-3} M copper sulphate, Section H.3(c)). This increase above the value dictated by diffusion control is probably due to oxygen uptake by metal complexes at the liquid-gas interface, such complexes acting as oxygen "carriers"[162,163,164].

The rate of oxidation of ethanethiol in the presence

of haemin was found to increase with increasing haemin concentration and to have a first order dependence on oxygen pressure. Extrapolation of a plot of initial rate versus oxygen pressure gave an intercept of 5.7 cm.Hg, which is comparable to the values obtained in the previous Sections. The rate of oxidation was found to have a first order dependence on thiol concentration for $[EtSH] \leq 0.5$ M, a zero order dependence being observed at higher thiol concentrations. These results, which are similar to those obtained with nickel sulphate (Section H.3(b)), suggest that at the higher thiol concentrations the rate of oxidation is diffusion-controlled.

In contrast to the results observed in all other systems, the addition of cyanide increased the rate of oxidation of ethanethiol in the presence of haemin, and almost quantitative yields of disulphide were produced. A possible explanation of this behaviour is that the dicyano ferroporphyrin complex produced under these conditions can easily be oxidised and reduced[164] and thus the resulting outer-sphere electron transfer from the thiol anion to the metal would be rapid.

No evidence was obtained for the formation of red cobalt-thiol complexes during the oxidation of ethanethiol in the presence of vitamin B_{12} and the rate of oxidation of ethanethiol was approximately seven times greater than that found in the presence of cobalt sulphate (Table 29). In the presence of cyanide the rate dropped to almost the same value as that obtained with cobalt sulphate in the presence of cyanide and no disulphide was detected

amongst the reaction products. This similarity suggests that the complex produced in this case is not easily oxidised and reduced, and the subsequent outer-sphere reaction is slow. In the absence of cyanide the order of ease of oxidation of various thiols in the presence of vitamin B_{12} is in general agreement with that predicted on the basis of electron directing properties and steric effects (Table 36). In all cases essentially quantitative yields of disulphide were produced.

The rate of oxidation of ethanethiol in the presence of chlorophyll was considerably lower than the rates obtained with haemin and vitamin B_{12}. It is difficult to envisage the magnesium atom being able to accept an electron from a thiol anion, and the apparent catalytic activity of chlorophyll may well be due to the fact that commercial samples of chlorophyll are frequently stabilized with copper compounds[165]. In the presence of cyanide, the rate of oxidation decreased considerably, and no disulphide could be detected amongst the reaction products.

2(k) The effect of phthalocyanines

In view of the general similarity of the phthalocyanine structure to that of the porphyrin-type complexes discussed above, transition metal phthalocyanines may be expected to catalyse the oxidation of thiols, and indeed, commercial petroleum-sweetening processes involving phthalocyanines have been patented[21]. In the present investigation metal phthalocyanines are seen to act both as a catalyst (cobalt, iron) and an inhibitor (copper, vanadium) by comparison with the respective simple metal salts (Table 30).

The phthalocyanine structure should allow the easy passage of an electron between thiol anions and the metal in all cases, and the inhibition of reaction in the presence of copper phthalocyanine is apparently due to the fact that this complex, as prepared, was relatively insoluble in the alkaline solutions. This argument is strengthened by the fact that sulphonation of cobalt phthalocyanine to give the alkali-soluble phthalocyanine disulphonate, resulted in a noticeable increase in the initial rate of oxidation. Whilst low solubility may also be a factor in the case of vanadyl phthalocyanine, it is possible that the vanadyl sulphate, used for comparison, was impure compared with vanadyl phthalocyanine. (Vanadyl sulphate was available only as the "Fine Chemical" grade material, whereas the starting material for the preparation of vanadyl phthalocyanine was "AnalaR" grade ammonium metavanadate). Reactions in the presence of metal phthalocyanines will be discussed further in Section K.2(m).

2(l) The effect of pyrophosphates

The oxidation of thiols on the presence of transition metal pyrophosphates has been reported to involve a heterogeneous mechanism[105], the reaction occurring at the solid pyrophosphate-liquid interface. In the present investigation the pyrophosphates of iron copper, cobalt and nickel, prepared from solutions of the metal sulphates and sodium pyrophosphate, were added to reactant solutions to provide a metal concentration of 10^{-3} M, and the rates of oxidation of the thiol were compared with those obtained in the presence of the corresponding simple metal salts. In all experiments the rates of oxidation for any given metal were found to be

comparable. Furthermore, in the case of cobalt and nickel pyrophosphates, the usual coloured metal-thiol complexes were present at the end of the reactions, and there was no trace of the original solid pyrophosphate in the reaction vessel. These observations support the suggestion that in the present system, the mode of action of metal ions in the catalysis of the oxidation of thiols is via a metal-thiol complex, which is formed in the reaction whenever strong competition does not exist for metal co-ordination sites. Pyrophosphate ligands do not compete for co-ordination sites, as is seen by the fact that the stability constants of the four pyrophosphates are all low[151].

Wallace, et al.[105] have also suggested that pyrophosphates are active catalysts because of a six membered ring structure which favours transference of an electron. In the present system cobalt phosphate, which does not possess a ring structure is as active a catalyst as the pyrophosphate, which supports the contention that both these types of complex break down to give metal-thiol complexes. The results of further experiments in the presence of transition metal pyrophosphates will be discussed in the following Section.

2(m) The effect of filtration of reaction solutions containing metal complexes

Filtration of transition metal pyrophosphate solutions confirms that solids do not play any part in the catalysis in this system. The pyrophosphates of nickel, cobalt and copper were each found to give rise to identical rates of oxidation of ethanethiol in cases 1 and 3 (see Section K.2(f)). Since the characteristic red

and brown metal-thiol complexes have been observed in solutions containing respectively cobalt and nickel pyrophosphates, and the rates of reaction are similar to those obtained when the metals are added as simple salts, it is evident that metal-thiol complexes are the catalytically active species. In agreement with this, the rate of oxidation in the presence of cobalt pyrophosphate was considerably lower in case 2, and the amount of cobalt present in the filtered solution was also found to be low.

The rate of oxidation in the presence of both cobalt and copper phthalocyanine was found to be identical in cases 1 and 2. This supports the view that the catalytic activity of phthalocyanines is determined solely by the solubility of the complex in question. The characteristic metal-thiol complexes were not observed in experiments involving phthalocyanines, and it appears reasonable to suggest that with these complexes the catalysis take place either via a fast outer-sphere mechanism or via a two centre inner-sphere mechanism similar to that proposed for porphyrins. The rates observed in the presence of vitamin B_{12} were identical in cases 1 and 2, which would be expected since the complex was observed to be completely soluble and to be stable in the alkaline solutions.

L STOPPED-FLOW EXPERIMENTS

In the outer-sphere reactions discussed above, it has been suggested that the rate of electron transfer controls the overall rate of thiol oxidation. By use of the stopped-flow technique, it was found possible to measure the rate of electron transfer from thiol anions to ferricyanide.

Although the overall rate of oxidation of thiols in the presence of cyanides was low, reactions involving potassium ferricyanide were somewhat unusual. Thus, the yellow colour of the complex was observed to vanish with great rapidity on addition of thiols to the reaction mixture. The rate of disappearance of ferricyanide, measured from the light absorption at 420 mμ, was found to be first order with respect to the initial ferricyanide concentration, and zero order with respect to initial thiol concentration for all thiols except thiophenol, where a first order dependence was observed. The nature of the thiol was found to affect the rate of reaction, the rate decreasing in the order $Et > PhCH_2 > Bu^i > Ph > Bu^n > Bu^s > Hex^n > Bu^t$. No metal-thiol complexes could be detected among the products of reaction.

It is difficult to understand exactly what processes are being studied. It is unlikely that the disappearance of the yellow colour of the ferricyanide is due to substitution of one CN^- group[166]. Furthermore, cyanides are known to be stable, and are normally involved in outer-sphere, non-substituted reactions. It seems most likely that the disappearance of the yellow colour results from the reduction of ferricyanide to ferrocyanide, which produces thiyl radicals. The rate of disappearance of the yellow colour is thus the rate of electron transfer between thiol anions and the ferricyanide. Application of the electron transfer rate constant for ethanethiol (2.96×10^{-1} sec^{-1}) to the conditions employed for measurement of the rate of overall oxidation of the thiol (10^{-3} M metal cyanide) gives a value of 2.96×10^{-4} mole l^{-1} sec^{-1} for the rate of electron transfer,

compared with a value of 2.22×10^{-6} mole l^{-1} sec^{-1} for the rate of oxidation of the thiol. Clearly electron transfer cannot be the rate-determining step in the oxidation of ethanethiol by ferricyanide. It therefore appears that the rate-determining step is the rate of reoxidation of the reduced ferricyanide. The nature of the thiol should not affect the rate of reaction, and the variation in rate of reaction observed with different thiols is difficult to understand in terms of an outer-sphere electron transfer mechanism unless such transfer involves the close approach of the thiol anion to the metal atom by means of some favoured position. The anomalous behaviour observed with thiophenol may be due to some extent to the low pK_a value of this thiol (6.5 at 25° C)[167].

M CONCLUSIONS

The autoxidation of alkane and arane thiols to the corresponding disulphides or higher oxidation products is a reaction of considerable academic and commercial interest. In the present investigation, attention has been focussed on reactions which terminate with the production of disulphides. In aqueous solution, the oxidation of a number of alkane and arane thiols has been found to lead to yields of up to 100% of the corresponding disulphides. The reaction occurs comparatively slowly in the nominal absence of catalysts, but may be accelerated considerably by the addition of certain metal ions. Of the numerous additives investigated, copper, cobalt and nickel ions have been found to be the most effective catalysts. Metals were also added to the reaction mixtures in the form of salts and complexes, but in most cases the actual catalytic

species appears to involve metal-thiol complexes.

The catalytic activity of additives has been found to be affected by the solubility of the particular complex and to vary according to the nature of the ligand attached to the metal ion. The kinetics of the reaction have been studied in the absence and in the presence of various additives, and reaction mechanisms have been suggested. The nature and role of metal additives has been discussed in the light of these mechanisms. Contrary to previous reports, in the present system the catalyst has always been found to act homogeneously.

The most important reaction mechanism involves the transfer of an electron from a co-ordinated thiol anion to the metal complex, which is then reoxidised by molecular oxygen. At the same time, thiolic ligands dimerise and disulphide is eliminated. In certain circumstances, a second reaction resulting in the formation of thiyl free radicals becomes important, and only small amounts of disulphide are produced. Distinction is drawn between different co-ordination atmospheres of a given metal ion which favour one or other of these reaction paths. As a result of these discussions, the solubility, stability, and facility of electron transfer are shown to be important in determining the mode of action of metal-containing homogeneous catalysts. The rates of reaction obtained in the presence of a series of complexes of one metal, and the rates of oxidation of various thiols in the presence of various metals, are in agreement with predictions made on the basis of these mechanisms.

APPENDICES

APPENDICES

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APPENDICES

A.1 Boyle's law correction for gas burette readings

Corrections were applied to the gas burette readings for variations in the water bath temperature and in the operating pressure. Corrections were calculated from the following Boyle's law treatment. If the effect of reagent vapour pressures is ignored, the observed and corrected gas burette readings are related by the equation:

$$\frac{P_{sw}(V_2-r_2)}{RT_{sw}} + \frac{P_{sw}V_1}{RT_o} = \frac{P_w(V_2-r_1)}{RT_w} + \frac{P_wV_1}{RT_o} \qquad (1)$$

where P_{sw} and T_{sw} are the standard pressure and water bath temperature

P_w and T_w are the observed pressure and water bath temperature

T_o is the oil-bath temperature

V_1 is the volume of gas in the reaction vessel (at T_o)

V_2 is the volume of the working line at T_w, with the burette at the zero mark, and excluding the volume T_o

r_1 and r_2 are the observed and corrected gas burette readings respectively.

Equation (1) may be rearranged to give:

$$r_2 = r_1 + \frac{P_{sw}(T_w-T_{sw}) - T_{sw}(P_w-P_{sw})}{T_wP_{sw}}(V_2-r_1) + \frac{V_1T_{sw}}{T_oP_{sw}}(P_{sw}-P_w) \qquad (2)$$

The apparatus was calibrated, and the volumes were found to be $V_1 = 89$ cm^3 (with 50.0 cm^3 of reagent solution in the reaction vessel), $V_2 = 602$ cm^3. Taking T_o as 303° K, equation (2) becomes:

$$r_2 = r_1 + \frac{P_{sw}(T_w - T_{sw}) - T_{sw}(P_{sw} - P_w)}{T_{sw}P_{sw}} (602 - r_1) + 0.2937 \frac{T_{sw}}{P_{sw}} (P_{sw} - P_w) \quad (3)$$

The value $T_{sw}P_{sw}$ in this equation is an approximation to the true value, T_wP_{sw}. Values of P_{sw} and T_{sw} may be chosen to minimise the corrections needed in each experiment.

A.2 Operation of manostat sensing cell

The manostat sensing cell is shown schematically in Fig.47. The fall SA in the electrolyte level in the reference limb (Δh_2) and the corresponding rise SB in the limb attached to the working line (Δh_1) are caused by a pressure decrease from P_1 to $P_1 - \Delta P_1$ in the working line, the corresponding decrease in the reference limb being from P_2 to $P_2 - \Delta P_2$. Thus for the gas enclosed in the reference limb:

$$P_2V_2 = (P_2 - \Delta P_2)(V_2 + \pi r_2^2 \Delta h_2) \quad (4)$$

For equilibrium at level A:

$$P_2 - \Delta P_2 = P_2 - \Delta P_1 + dg(\Delta h_2 + \Delta h_1) \quad (5)$$

where d represents the density of the fluid in the cell.

Now, since the volume of the cell is constant,

$$\pi r_2^2 \Delta h_2 = \pi r_1^2 \Delta h_1, \text{ or } \Delta h_1 = \Delta h_2 \frac{r_2^2}{r_1^2} \quad (6)$$

Thus from equations (5) and (6):

$$\Delta P_2 = \Delta P_1 - dg \Delta h_2 \left[1 + \frac{r_2^2}{r_1^2} \right] \quad (7)$$

and from equations (4) and (7), the sensitivity of the cell is expressed by:

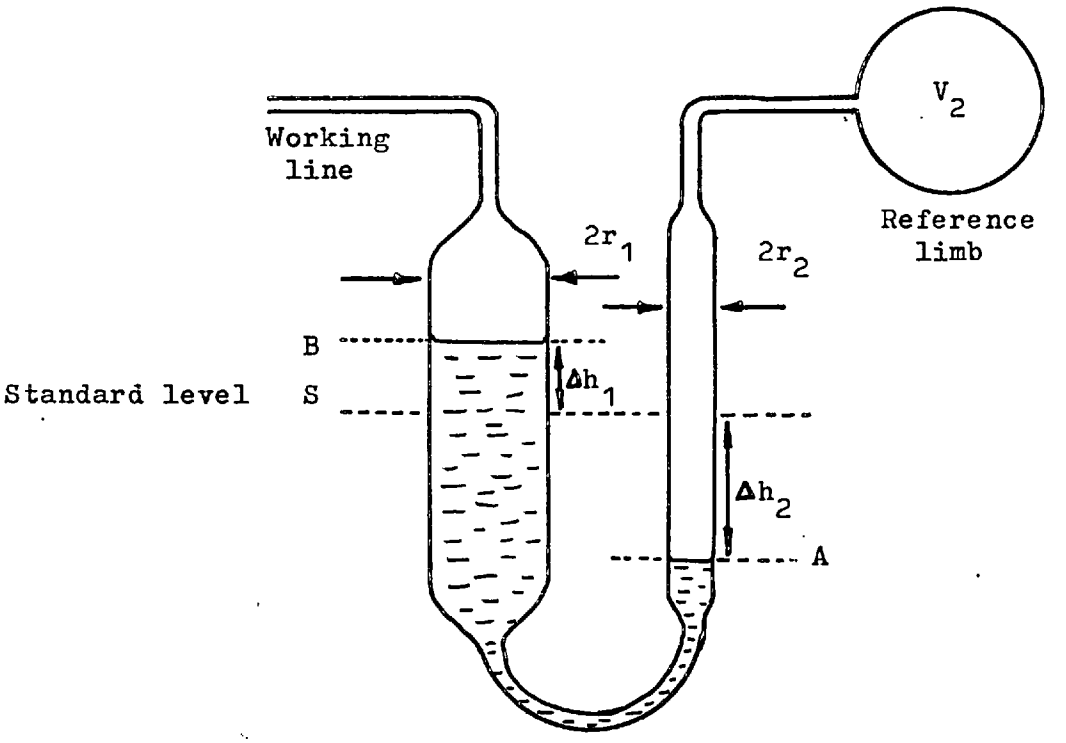


Fig. 47. Manostat sensing cell (schematic) showing dimensions

$$\frac{\Delta h_2}{\Delta P_1} = \frac{V_2}{P_2 \pi r_2^2 - V_2 dg(1+r_2^2/r_1^2)}$$

Thus for high sensitivity, the volume of reference limb, V_2, should be large, and the tube diameter r_2, should be small.

A.3 Solubility of oxygen in aqueous alkali

Values are available of the solubility of oxygen in aqueous solutions of sodium and potassium hydroxides[168]. The Bunsen absorption coefficient, α, is defined as the volume of oxygen, corrected to 0° C, dissolved in unit volume of solution. For use in the present work, data were interpolated and extrapolated using the equations[159]:

$$\ln \alpha = \frac{-\Delta H}{RT} + \text{constant}$$

at constant alkali concentration, c, and

$$\ln \alpha = kc + \text{constant}$$

at constant temperature, T, where k is a constant.

The data thus obtained are given in Table 41.

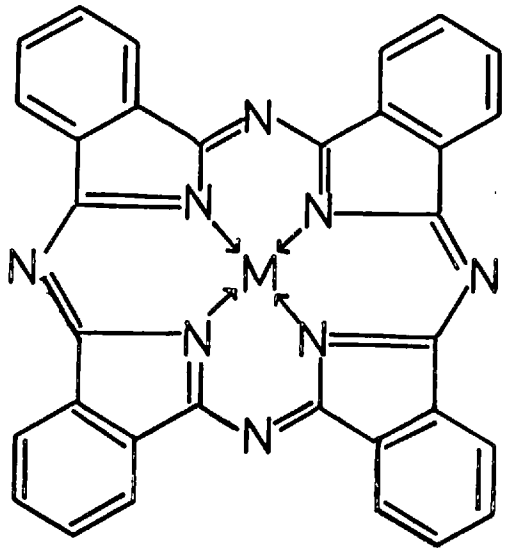
Table 41

Bunsen absorption coefficients for the solubility of oxygen in aqueous alkaline solutions

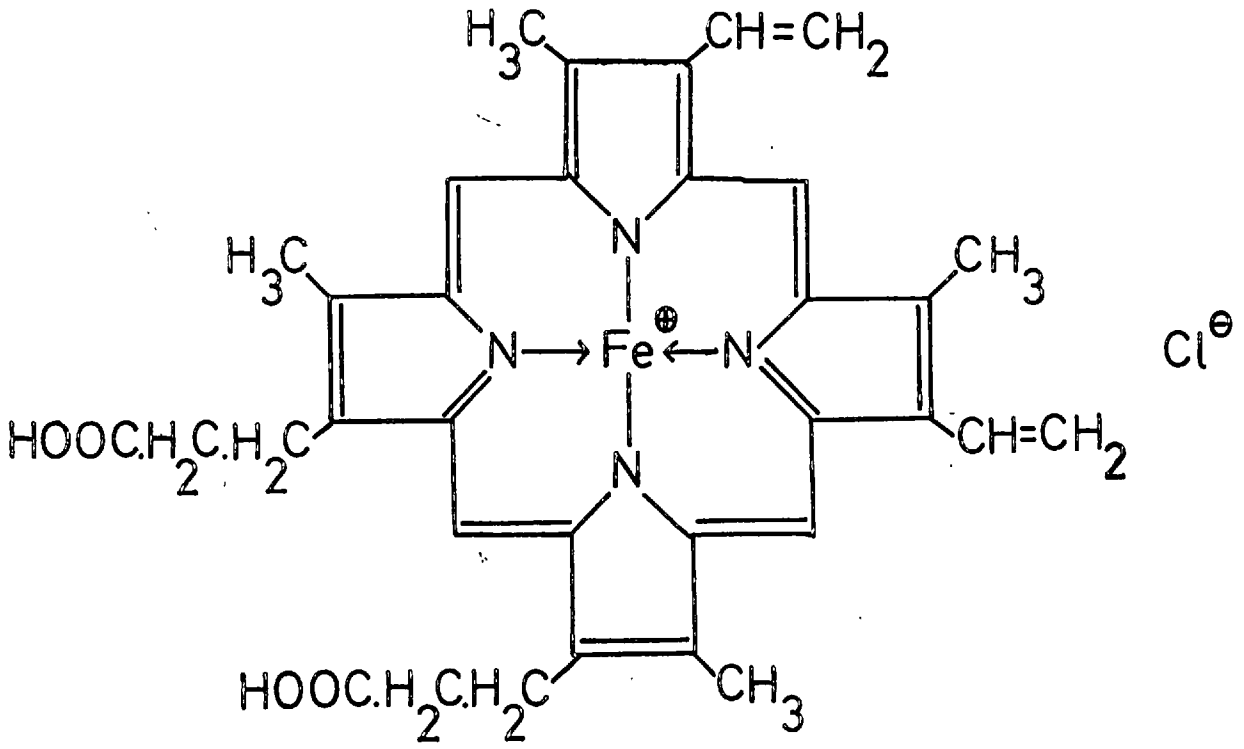
Solution	Bunsen coefficient, α		
	15° C	25° C	30° C
0.5 M NaOH	0.02730	0.02290	0.02070
1.0 M NaOH	0.02190	0.01868	0.01707
2.0 M NaOH	0.01440	0.01220	0.01110
3.0 M NaOH	-	-	0.00480
0.5 M KOH	0.02758	0.02308	0.02083
1.0 M KOH	0.02218	0.01886	0.01720

A.4 The structures of some additives

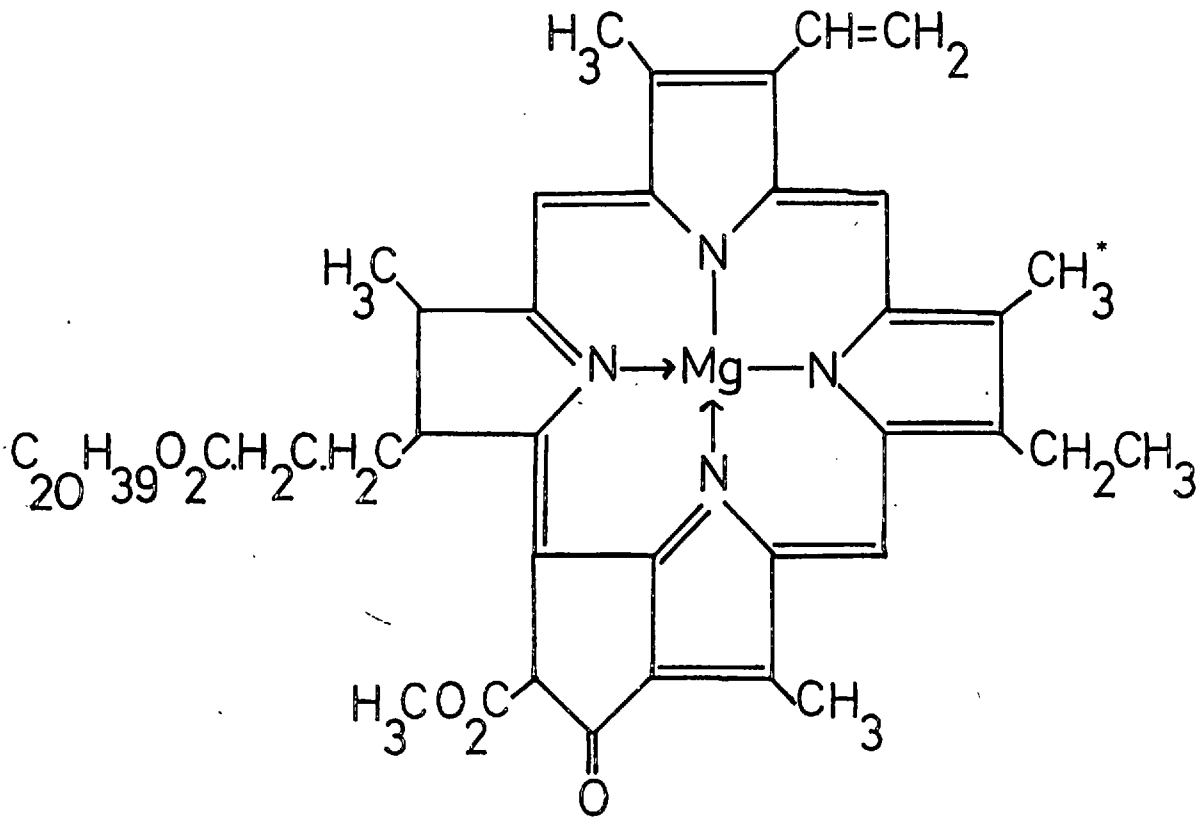
(a) The structure of a metal phthalocyanine



(b) The structure of haemin

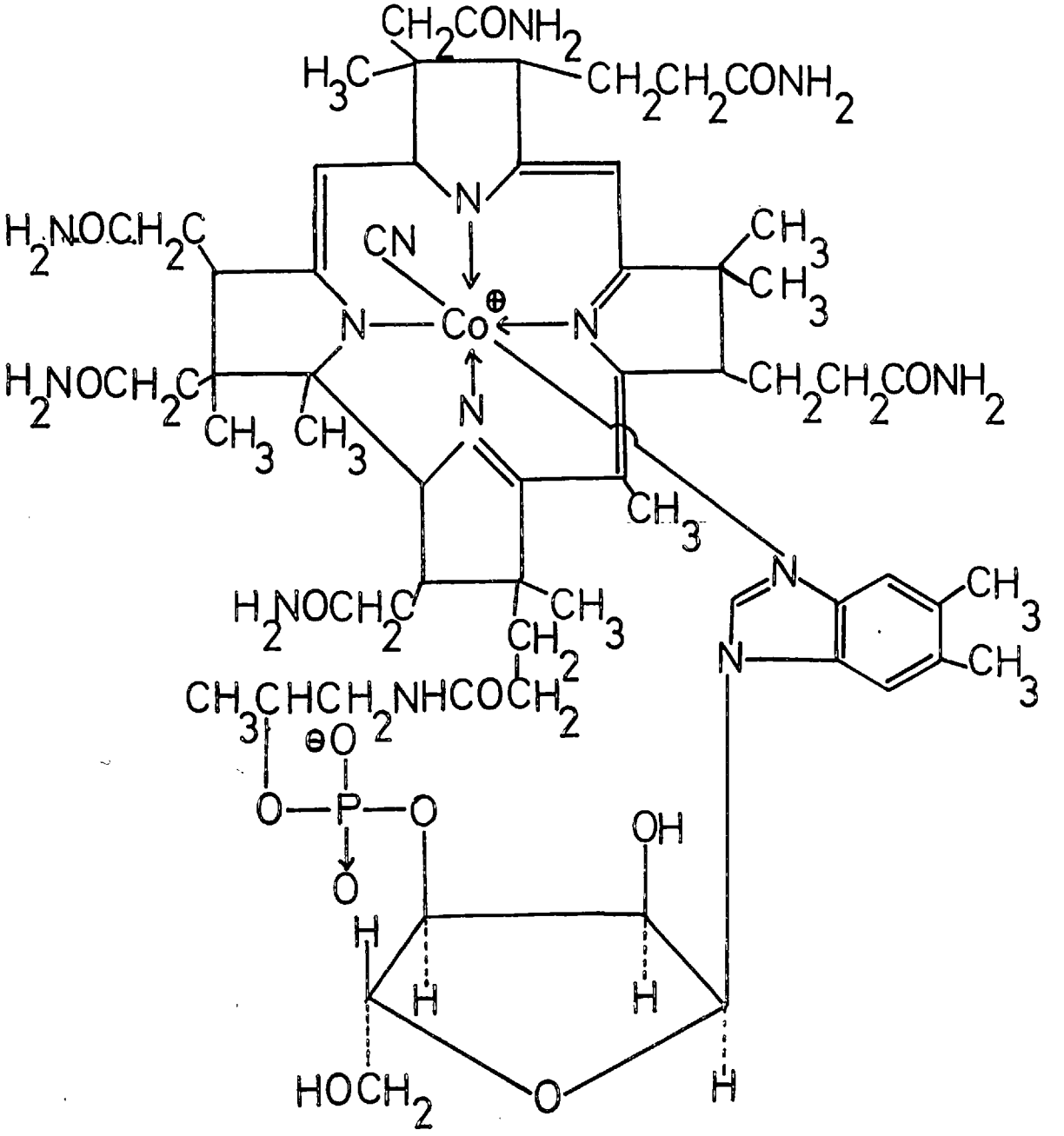


(c) The structure of chlorophyll (a)



In chlorophyll (b) the methyl group marked with an asterisk is replaced by a formyl group.

(d) The structure of vitamin B_{12}



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