'THERMOCHEMISTRY OF

ALCOHOLS AND KETONES'

A thesis submitted by

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In part fulfilment of the requirements
for admittance to the Degree of
Doctor of Philosophy
in the
University of London

Royal College of Science,
South Kensington,
London, S.W.7.

March, 1963.

Contents

	Page No.
Introduction	1
Part A	
I. Equilibration reactions	
Materials and Purifications	16
Spectrophotometric determination of the amount of fluorenone in benzene solution	21
Method of equilibration	22
Polarography	29
II. Heats of hydrogenation	
Direct gas-phase hydrogenation	37
Direct liquid-phase hydrogenation	41
Liquid-phase hydrogenations by Skinner	43
Liquid-phase hydrogenation reactions by Turner	49
Hydrogenation reactions in solution by Jackman	53
Part B	
I. Experimental	
(1) Materials; preparation and purification	60
(2) Oxygen	70
(3) Carbon dioxide analysis	70
(4) Examination of completeness of combustion	72
(5) Correction for the amount of nitric acid formed	73

Page No.

(6) Calorimetry 75

(7) Determination of the corrected temperature rise 80

(8) Determination of the energy equivalent with benzoic acid 83

(9) Experimental Proceedure 86

(10) Units and auxiliary quantities 93

(11) Results 95

II. Discussion

(1) The heats of combustion of some alcohols and carbonyl compounds 120

(2) Substituent effects in reaction energies 125

(3) The heats of hydrogenation of six carbonyl compounds 133

(4) Conclusions 144

References 146

Abstract

The heats of combustion of nine carbonyl compounds and carbinols have been determined at 25° in an isothermal static bomb calorimeter. The heats of hydrogenation of the carbonyl compounds were calculated as the difference between the heats of formation in the gas state at 25° of the carbinols and the corresponding carbonyl compounds. The results obtained gave support to those accurately determined either by catalytic hydrogenation in the vapour phase, or by hydrogenation in solution using metal hydrides as a source of hydrogen.

Bond energy terms and the deviation from additivity of the heats of combustion of alcohols and carbonyl compounds agreed with the literature values. Substituent effects in heats of hydrogenation were discussed in some detail. No quantitative analysis of our results can be given at present. Concerning the relative importance of the various effects, it is thought that the influences of the intramolecular kinetic energy make a considerable contribution to the overall substituent effects observed.

Adkins' equilibration method was shown to be unsound. The effect of varying the catalyst concentration on the carbonyl carbinol equilibrium constants was investigated in more detail.

An account was given of the thermochemically studied reduction reactions and an agreement was shown in many cases between the results obtained and those from combustion calorimetry.

Acknowledgements

The author is deeply indebted to Professor L.M. Jackman for his constant guidance and encouragement.

The author is greatly indebted to Professor D.H.R. Barton for admittance and to Professor G. Wilkinson for his help and interest in building up the calorimeter.

After Professor L.M. Jackman's transfer to Australia, Dr. D.W. Turner continued the supervision of this work. The author is deeply indebted to him for much helpful discussion and criticism during the preparation of this thesis.

The author would like to express his appreciation to Dr. E.S. Waight and to Dr. J.M. Lawlor.

The author thanks Mr. R.H. Young, Mr. F.W.L. Croker, Mr. J.C. Watson and the staff of the College Workshop.

The author would like to express his gratitude to the Government of the United Arab Republic for financial support.

Finally the author wishes to thank his parents who have made his University education possible, his wife and Mrs. C.H. Hammerton of Putney, London.

March, 1963. Mahmoud N.E.D.H. Moussa.

INTRODUCTION

Thermo chemical data has been used in the development of the concepts of inductive, mesomeric and steric factors affecting the reactivities of organic molecules.

Pauling[1] made an electronegativity scale for atoms, based on bond energies, by adopting the principle of additivity. These electronegativities contribute to the inductive effect of an atom or a group of atoms in a molecule.

The heats of formation of compounds, in which resonance operates, include energy terms due to this effect. The additivity principle established by L. Pauling and J. Sherman[2] ought not to hold true for these compounds and therefore their heats of formation should be greater than the sum of the heats of formation of the separate bonds. They found that a large number of compounds disobeyed the additivity principle, and mesomerism or resonance in them corresponds to an increase in molecular stability. The difference between the heats of formation of the substances represented as 'resonance hybrids' of classical structures and those predicted from bond energies are called resonance energies.

The most outstanding contribution to the calorimetry of organic reactions has been concerned with heats of hydrogenation. The classic researches of Kistiakowsky and his co-workers[3] in this field played an important part in the

development of theories of mesomeric and steric effects in organic chemistry. More recently this work has been extended by Turner[4] and by Skinner[5].

H.C. Brown and his co-workers[6] made extensive studies of steric effects using the thermal equilibrium method. Brown obtained the dissociation constants of addition compounds, such as trialkylborons, with amines.

$$R_3N : BR_3^1 \rightleftharpoons R_3N + BR_3^1$$

On these dissociation constants many conclusions were based.

Kinetic reactivity evidence made the largest contribution to the development of the electronic theory of organic chemistry. The ionization of carboxylic acids has been more extensively studied than has any other type of organic chemical equilibrium. Inductive effects of groups can be illustrated by comparing dissociation constants of acids or pk values.

Hammett[7] derived polar substituent constants, σ constants, representing the electron attracting ability of the substituents being considered in terms of dissociation constants of carboxylic acids. Hammett selected the ionisation of p- and m- substituted benzoic acid in water at 25° as the standard reaction series. The Hammett equation may be written:

$$\log (K/K_o) = \rho\sigma$$

where K is the equilibrium constant for a substituted benzoic acid and K_o is that of benzoic acid. If rate constants are

being considered the term on the left is log (k/k_o). The constant ρ is a measure of the sensitivity of a given reaction series to ring substituents. It is fixed at unity for the standard reaction series. Hammett, then examined the data for reactions of other p- and m- substituted phenyl derivatives (e.g. the rates of hydrolysis of the esters of p- and m- substituted benzoic acids) and found that the equation $\log (k/k_o) = \rho\sigma$ was applicable. It was also found that p- and m- substituted derivatives obeyed the relationship:- $\log (K/K_o) = \rho\Sigma\sigma$, demonstrating that the inductive effects were additive.

An estimate of inductive effects is also obtained by comparing the rates of acid and base catalyzed hydrolyses of substituted esters. Taft's[8] inductive substituent effect, σ^*, is defined as

$$\sigma^* = \frac{1}{2.48}\left[(\log K/K_o)\, B - \log (K/K_o)A\right]$$

K refers to the rate constant of the hydrolysis of the ester of a substituted acid, $R.CO_2H$, and K_o to that of the standard of comparison, (K_o, R= $-CH_3$). The factor $\frac{1}{2.48}$ represents an attempt to put the σ^* values on the same scale as Hammett's values. Taft was able to extend the application of Hammett's theory to a wide range of reactions using the equation:-

$$\log (K/K_o) = \rho^* \sigma^* \qquad (1)$$

where the constant ρ^* is a measure of the susceptibility of

a given reaction series to inductive effects. Taft's treatment, unlike Hammett's, employs additive substituent effects (σ^* values) applicable to both aliphatic and aromatic molecules whether the substituent is capable of resonance interaction with the functional group or not.

Discussion of resonance effects may be based upon the influence of substituents on acidities, as with inductive effects because of the large quantity of available data. In Taft's treatment, if within a reaction series a compound is not correlated by the equation, the deviation is ascribed to other substituent effects and is taken as a measure of them. The type of effect is indicated by the nature of the reaction, the substituents and their deviations. This use of equation (1) is regarded as its most valuable one for it permits the quantitative evaluation of steric and resonance effects. The reality of a mesomeric effect of alkyl groups arising from hyperconjugation in the ground state of the molecule was proved by J.W. Baker and Hemming[9] in their study of the cyanohydrin equilibria.

$$p\text{-}R.C_6H_4.\ cH{:}o + HCN \underset{k2}{\overset{k1}{\rightleftharpoons}} p\text{-}R.C_6H_4\ .\ cH(oH).CN$$

$(K = k2/_{k1})$.

The hyperconjugation effect decreases in the order $Me \rangle Et \rangle Pr^i \rangle Bu^t$. De La Mare and his co-workers[10] studies the exchange reaction of Br^- for the bromine atom in alkyl bromides. The rate was

followed by using radioactive bromide ion in solution and measuring the speed in which radioactivity was incorporated into the organic bromide. A quantitative treatment of steric effects was based on this reaction.

$$*Br^- + RBr \xrightarrow{\text{acetone}} *Br - R + Br^- \quad \text{rate} = k_2 (*Br^-)(RBr).$$

The quantitative treatment of the inductive, mesomeric and steric effects and the relation between structure and reactivity is based mostly on kinetic reactivity evidence. This evidence however is difficult to interpret as such a quantitative interpretation requires a knowledge of the transition state. Therefore, it is desirable to obtain estimates of these effects on ground state energies.

Heats of reaction and free-energies of reaction may frequently be referred to the gas state where the chemical properties of the substance are those of the individual molecules (ignoring departures from the ideal gas state). From the point of view of obtaining parameters to compare with those derived mathematically from first principle, heatssof reaction would appear to be more valuable than free-energies of reaction and certainly more valuable than free-energies of activation. Heats of reaction and free energies of reaction have the disadvantage that they are not nearly as sensitive to structural effects as rate constants (free

energies of activation). However, this drawback may be outweighed by the sensitivity of rate constants to reaction conditions and the inability to refer liquid-phase transition states to the gas phase. Heats of reaction have the disadvantage that more effort is required to measure them than either free-energies of reaction or free-energies of activation.

One attempt to obtain heats of reaction data is that of Lawlor[11] which gave results which were immediately intelligible in terms of simple theories. Lawlor determined the heats of hydrogenation of some aldehydes and ketones at 25°. The method involves the measurement of the heats of reaction of liquid carbonyl compounds and the corresponding alcohols with lithium aluminium hydride. Subtraction of the heats of reaction of the alcohols from those of the corresponding carbonyl compounds gave the hydrogenation heats in the liquid state. Lawlor determined also the heats of vaporisation at 25° in order to refer the heats of hydrogenation of the aliphatic compounds to the gas state. Lawlor's results are represented in the following table:-

The heats of hydrogenation of ten carbonyl compounds.

Compound	ΔH (K cal.mole^{-1})
acetone	-13.2 ± .2 gas state, 25°C.
Butan-2-one	-13.7 ± .2 " " "

Compound	ΔH (K cal.mole^{-1})			
3-methyl-butan-2-one	-14.0 ± .3	gas	state,	25°C.
3:3-Dimethyl-butan-2-one	-15.4 ± .2	"	"	"
Pentan-2-one	-13.1 ± .2	"	"	"
2-Methyl-pentan-2-one	-13.8 ± .2	"	"	"
2:2-Dimethyl-pentan-2-one	-15.3 ± .3	"	"	"
Trimethylacetaldehyde	-16.7 ± .2	"	"	"
Benzophenone	-14.6 ± .2	solid	"	"
p-Chlorobenzaldehyde	-18.3 ± .2	"	"	"

Some well defined trends can be readily seen in a plot of the heats of hydrogenation against the corresponding carbon-atom contents of the molecules examined. The methyl ketones fall into a group with an almost linear increase (within the experimental error) in the heats of hydrogenation. Similarly, the ethyl ketones show a near linear increase but the increase is more rapid than in the methyl ketone series. The heats of hydrogenation of the ethyl ketones are considerably less exothermic than those of the methyl ketones. The heats of hydrogenation of the ketones increase as the electronegativities of the substituents decrease. The number of α-hydrogen atoms per molecule decreases as the heats of hydrogenation increase.

It was concluded that the influences of intramolecular kinetic energy make a considerable contribution to the

overall substituent effects observed. If no kinetic effects occur in the energies of hydrogenation, Taft's equation would give the same correlation for the heats of reaction and the free energies of reaction. The parameters employed in applying Taft's equation were obtained from Adkins[12] results. It was found that there was not the slightest agreement between Lawlor's measurements and Taft's correlation of Adkins' results.

Because of the importance of these findings it was highly desirable to measure these quantities by an entirely independent technique.

Adkins and his associates have determined a large number of carbonyl-carbinol equilibrium constants in dilute toluene solution at 333° K. Their results yielded the free energies of hydrogenation of a number of ketones in which we are interested. We first made some equilibration experiments in dilute benzene solution at 333°K the results of which showed that Adkins' method was basically unsound. It can be said that carbinols present exchanged with the t-butoxy--groups of the catalyst and set up equilibria between the catalyst and alcohols present.

Our independent way of tackling this problem is the determination of the heats of combustion of the ketones and the corresponding carbinols. From these the heats of

hydrogenation of the ketones can be calculated. The heats of vaporisation necessary to refer the results to the gas state are those determined by Lawlor. The details of the experimental technique are described in part B together with a discussion of the results obtained. The results of the combustion method reveal certain well-defined trends in support of those obtained by Lawlor. In part A a review of heats of hydrogenation is made as well as a discussion of Adkins' work and our extension.

PART A

I. EQUILIBRATION REACTIONS

The carbonyl-carbinol equilibrium reactions studied by Adkins[13] and his associates are formulated as follows:-

$$R_2CO + R_2^1CHOH \longleftrightarrow R_2CHOH + R_2^1CO$$

assuming the alcohols to be at least in part present as their alkoxides and the ketones form addition products in the presence of aluminium t-butoxide used as a catalyst.

A polarographic[13(a)] method of analysis was developed to determine the ratio or amounts of ketones with an error of less than 2%. However, the determination of the concentrations of acetone, acetylacetone and presumably other saturated aliphatic ketones by this method, cannot be carried out in the presence of ammonium chloride and tetramethyl ammonium hydroxide used as electrolytes.

The equilibration procedure consisted of weighing into a test tube with a constricted neck equimolecular amounts (.01 mole) of a ketone and an alcohol. Fifteen c.c. of toluene containing 2.5 g. aluminium t-butoxide (.01 mole) was added and the tube sealed off and suspended in a thermostat at 100° for 20 to 620 hours. The procedure was modified so that equilibrium would be reached in a shorter time. The reaction mixtures were made up containing both ketones and

both alcohols under comparison the concentration in one set of reaction mixtures being somewhat to the right and somewhat to the left of the roughly known value. The average of the two values from both directions was taken as the true concentration of the ketones at equilibrium.

Adkins found that in equilibrating most ketones against benzophenone a period of 3 to 4 days at 100° was required while with fluorenone a few hours at 60° was sufficient. The equilibrations were then made in .05M solutions rather than 1M solutions. It was considered that condensation reactions of the Aldol or Tischenko type, which the carbonyl compounds are capable of undergoing, are improbable at the lower concentration of reactants and temperatures used. Also the more rapid the oxidation by the reference compound the less chance there is for a significant amount of a side reaction.

Adkins claimes that, with one exception, the equilibrium was approached from both sides so that there was experimental evidence that the equilibria were true and did not come to a constant value due to exhaustion of the condensing agent. However, with a few exceptions the reaction mixtures were made up so that the sum of the moles of a ketone and its alcohol was equal to the sum of the moles of the second ketone and its alcohol.

The reaction of benzophenone, diphenyl carbinol, fluorenol and fluorenone was studied in order to find if the values of K (the equilibrium constant) for different proportion of reactants were really constant. This is summarized in table 1[13(d)].

TABLE 1

Moles x 10^3 in 11 ml. toluene at beginning of reaction.

A	B	C	D	E	Hr. at 60°	Ratio C/A	K	%C[a]
.43	.43	.57	.57	.7	25	1.66	2.77	62.4
.43	.43	.57	.57	4.2	25	1.57	2.46	61.1
1.50	1.00	00	00	.7	113	.90	2.23	59.9
2.00	1.00	00	00	1.4	20	.67	2.69	62.2
1.00	1.00	00	00	.7	21	1.65	2.72	62.3
1.00	1.00	00	00	3.5	88	1.45	2.10	59.3

a) calculated from the various values of K for the amount of fluorenone that would be present at equilibrium if fluorenone and diphenyl carbinol (or fluorenol and benzophenone) were originally present in equimolecular amounts. A, B, C, D and E refer to benzophenone, fluorenol, fluorenone, diphenyl carbinol and aluminium t-butoxide respectively.

It was assumed that the ratio of two ketones at equilibrium with their alcohols at 60, 80 and 100° would be the same as at 25° and that the heats of reaction appeared to be small. In case of benzaldehyde and fluorenone the concentration of the reactants were determined experimentally at both 25° and 60°. The oxidation potentials calculated from the two sets of data were .197 and .200 volts respectively.

It must be remembered that Adkins actually measured the free energies of reduction of carbonyl compounds i.e. ΔG and not ΔH their heats of reduction. In order to obtain the latter quantities the equilibrium constant should be determined over a range of temperatures and then the following relation applied by plotting ΔG against T.

$$-RT \ \text{Ln}\ K = \Delta G = \Delta H - T\Delta S$$

The interception of the straight line drawn with the Y axis (representing ΔG values) gives ΔH and its slope gives ΔS. Reference to the gaseous state is possible since a number of latent heats of vaporization has already been determined by Lawlor. Only heats of dilution will be required and these may be determined calorimetrically. In this way the heats of reduction of a number of carbonyl compounds are obtained and can be compared with those determined directly by Lawlor to see if there is any agreement between the results of the two methods. The equilibrium concentrations of the systems acetone against fluorenone and ethyl methyl ketone against

fluorenone were measured over a range of temperatures and the results obtained are represented in tables 2 and 3. It is obvious from these results that the concentration of fluorenone per cent. at equilibrium (from which the equilibrium constant is calculated) does not vary regularly with temperature and is nearly constant.

However, it is suspected that there are consecutive alkoxide equilibria of the type

$$(RO)_3Al + R'OH \rightleftharpoons (RO)_2R'OAl + ROH$$

$$(RO)_2R'OAl + R'OH \rightleftharpoons RO(R'O)_2Al + ROH$$

not mentioned by Adkins and that the catalyst plays an important role in determining the equilibrium concentrations in the carbonyl carbinol equilibria. The effect of using different proportions of reactants including the catalyst and of varying the temperature on the equilibrium constant is not clear from Adkins experiments (table 1) on the reaction of benzophenone against fluorenone. The effect of changing the catalyst concentration alone or the temperature alone was not studied in detail. However, it was shown that the equilibrium constant did change although if the equilibrium constant is translated into per cent. of fluorenone at equilibrium in a reaction mixture originally containing equimolecular amounts of fluorenone and diphenyl carbinol the actual variation is seen to be small. Taking this in consideration

experiments were carried out on the equilibration reactions of acetone against fluorenone and pinacolone against fluorenone using different catalyst concentrations and the catalyst concentration used in Adkins work (.07 M). These are summarized in tables 4 and 5. It is evident from the results obtained that the equilibrium concentrations do change with changes in catalyst concentration (fig. 2). The terms arising from alkoxide equilibria can be eliminated by performing a large number of experiments at different catalyst concentrations and extrapolation to zero catalyst concentration. For this reason Lawlor's results are strongly supported and moreover they agree well with those obtained by us from heats of combustion.

The analytical method used to determine the amount of fluorenone, against which the other saturated aliphatic ketones are equilibrated, is a spectrophotometric one. Fluorenone absorbs in the visible region and the absorption being a maximum at $\lambda = 380$ millimicrons.

A polarographic method was tried to determine the amounts of both ketones in a reaction mixture at equilibrium. Tetrapropyl ammonium iodide was used as a base electrolyte in 75% dioxan. The proceedure of analysis as well as a discussion of the results obtained will be given in detail.

EXPERIMENTAL

MATERIALS AND PURIFICATIONS.

A Pye 'Argon Chromatograph' was used. The ionisation detector fitted was extremely sensitive so that very small samples could be analysed. A polyethylene glycol 400/celite packed column was used throughout. Ether, because of its volatility, produced a peak in the same region as those caused by air and water. In order to be confident that no ether was present in the liquid materials large distillation foreruns were rejected.

Aluminium t-butoxide. - Thin aluminium foil sheet (15 g.) was polished with emery paper, washed with ether and rubbed with cotton-wool. It was cut into small pieces and left under vacuum for one hour in a 1-litre round-bottomed flask. t-Butyl alcohol (150 g.), distilled from calcium oxide, was added together with a few milligrams of mercuric chloride to facilitate the start of the reaction. The flask was attached to a reflux condenser, protected from moisture, by a calcium chloride drying tube. After a few hours heating on a steam bath the contents of the flask turned dark and dry benzene (60 ml.) was added to keep the aluminate in solution. The reaction mixture was left on the steam bath overnight and during that period most of the aluminium dissolved. Dry benzene (500 ml.) was added, then the solution was centrifuged.

The completely clear solution was separated and concentrated under vacuum with shaking. The last traces of alcohol were removed by evacuation on a steam bath. The white crystalline powder was put in a dark bottle and kept in a desiccator. Yield 80 g. (59%).

Fluorenone. - Fluorenone (B.D.H.) was recrystallised from benzene to constant m.p. (85 - 6°). In order to remove occluded solvent the purified solid was vacuum-sublimed.

Fluorenol. - Fluorenone (10 g. m.p. 85-6°) in ether (50 ml.) was added dropwise, with stirring, to lithium aluminium hydride (2 g.) suspended in ether (150 ml.). The reaction mixture, which became red in colour, was stirred overnight. The hydrides were decomposed by the dropwise addition of water (the red coloration was rapidly discharged) and the precipitate which formed was dissolved with diluted sulphuric acid. The ether solution was separated, washed first with aqueous sodium bicarbonate, then with water, and dried over magnesium sulphate. The magnesium sulphate was filtered off and the ether evaporated at the pump. The residue was recrystallised to constant melting point (155-6°) from benzene and finally sublimed to remove solvent. Yield 7 g. (70%).

Acetone. - Acetone (Analar). No impurities were found by gas-liquid chromatography.

Iso-propanol. - Iso-propanol (Hopkins and Williams) was distilled, then refluxed with potassium borohydride for twenty-four hours to remove any oxidation products present. The alcohol was then fractionated through a two-foot Stedman column. Nearly all the iso-propanol distilled at 82°, nevertheless large head and tail fractions were rejected. The product gave only one peak on the gas-liquid chromatograph.

Butan-2-one. - Butan-2-one (Hopkins and Williams) was fractionally distilled through an 8" column of Fenske helices and the material obtained, b.p. 80°, was shown to contain no impurities by gas-liquid chromatography.

Butan-2-ol. - Butan-2-ol (Hopkins and Williams) was purified in the same way as iso-propanol. The product, b.p. 99.5° contained no impurities as shown by gas-liquid chromatography.

Pinacolone. - Pinacolone (L. Light's) was found impure and the impurities were not removed by repeated fractional distillation. The ketone was prepared as follows:

Pinacol hydrate. - (Vogel, p.347). Magnesium turnings (100 g.) and anhydrous benzene (1 L.) were placed in a 5 L. flask fitted with a condenser. A solution of mercuric chloride (100 g.) in dry A.R. acetone (dried over calcium chloride and distilled) (600 ml.) was added at a rate sufficient to cause vigorous refluxing. After the addition, and while the mixture still refluxed, dry acetone (250 ml.) in dry benzene was introduced. When the reaction slowed down the flask was heated on a steam-bath for two hours. The mass of magnesium pinacolate which was formed was broken up and the mixture refluxed for a further three hours to complete the reaction of the magnesium. Water (250 ml.) was introduced and the mixture heated for an hour, with occasional shaking, to hydrolyse the pinacolate. The reaction product was cooled to 50° and filtered at the pump. The residue was refluxed for thirty minutes with benzene (750 ml.) to extract the remaining pinacol. The main pinacol solution, together with the filtered extract, was distilled to one-half of the original bulk in order to remove acetone. Ether (400 ml.) was added and the mixture cooled to 0° with stirring. After an hour of stirring at 0° the pinacol hydrate, which had crystallised out, was filtered off at the pump. The mother liquor was treated with water (200 ml.) and left overnight at 2°. In this way a further quantity of pinacol

hydrate, nearly equal in bulk to the first crop, was obtained. The combined crops were washed with a little benzene and allowed to dry in air. Yield 440 g. (90% based on the magnesium). The hydrate was recrystallised (charcoal) from an equal volume of boiling water.

Pinacolone. - The recrystallised pinacol hydrate was refluxed with diluted sulphuric acid. (Water, 1 l./sulphuric acid 250 ml.) for two hours. The liquid product, which separated out in the flask, was distilled out in steam until the organic layer in the flask disappeared and there was as much water as ketone in the receiver. The aqueous layer of the steam distillate was saturated with potassium carbonate and the aqueous and organic phases shaken to remove acid sprayed over during the distillation. The ketone was separated from the aqueous layer which was then extracted with ether (100 ml.). The combined ketone and ether extract were given a preliminary drying with potassium carbonate and were left over anhydrous magnesium sulphate overnight. The dry ether solution was fractionally distilled through an 8'' column of Fenske helices. The ketone, (115 g.) b,p. 105 - 5,5° was found to be pure by gas-liquid chromatography.

Pinacolyl alcohol. - (40 g.) pure pinacolone dissolved in sodium dried ether (100 ml.) was added slowly, with stirring, to lithium aluminium hydride (6 g.) in dry ether (200 ml.). When the addition has been completed the mixture was refluxed for half an hour. The hydrides were decomposed by the dropwise addition, with stirring, of water. The inorganic precipitate was dissolved by the addition of diluted sulphuric acid. The ether solution of alcohol was separated and the aqueous layer extracted with ether (3 x 50 ml.). Concentrated aqueous potassium carbonate was used to remove acid from the combined ether solutions which, after a preliminary drying with potassium carbonate, were dried over anhydrous magnesium sulphate. The alcohol was isolated by fractional distillation through an 8" column of Fenske helices. The material obtained, b.p. 120°, contained no impurities as shown by gas-liquid chromatography. Yield 29 g. (75%).

Spectrophotometric determination of the amount of fluorenene in benzene solution. - Standard solutions of fluorenone in dry benzene, covering the range of concentration used in the equilibration experiments, were prepared. 1 ml. of each solution was quantitatively diluted to 10 ml. with dry benzene. The extinction co-efficient (E) was measured, in 1 cm. cell, on the Spectracord at λ=380 millimicrons using the tungsten lamp.

By applying the relation, $E = \varepsilon c l$ and plotting E against C, the concentration in gram mole/litre, a straight line was obtained. The standard deviations of the points not lying on the line is within $\pm$ 1% as shown in fig. 1.

C	Calc. E. from line	Deviation in E.	Deviation %.
.0010	.327	- .017	5.3
.0015	.465	- .015	3.2
.0020	.600	0.0	0.0
.0025	.737	+ .002	.34
.0030	.872	+ .007	.86
.0035	1.007	+ .012	1.2
.0040	1.142	+ .037	3.3
.0045	1.280	0.0	0.0
.0050	1.410	- .010	.71

Method of equilibration:

Equilibration reactions were made in .05 M solution as were those of Adkins. Also in order to minimise the time of reaction and the extent of side reactions, mixtures were made up which contained equimolecular amounts of two ketones and their corresponding carbinols in concentrations somewhat to the right or the left of the equilibrium value reported by Adkins.

Acetone VS Fluorenone. - Dry benzene solution (25 ml.) was prepared which is .05 M in total ketones and .07 M in catalyst concentration. In one representative reaction mixture there were -

.875 millimole of fluorenone i.e. 70% of the total ketones

.875 millimole of iso-propanol i.e. 70% of the total alcohols

.375 millimole of fluorenol i.e. 30% of the total alcohols

.375 millimole of acetone i.e. 30% of the total ketones,

and finally,

1.75 millimole of catalyst i.e. catalyst concentration is .07 gram mole/litre.

Immediately after adding the catalyst to the ketones and their corresponding carbinols in solution and mixing, (2 ml.) aliquots were removed and introduced into previously constricted glass tubes. The tubes were kept in a freezing mixture and after all had been sealed off, they were placed in a thermostat at a certain temperature for about twenty-four hours. At specified times these tubes were cooled, opened and (1-ml.) of their contents quantitatively diluted to (10-ml.) with dry benzene. The (E) of the solution was measured until a constant value and the corresponding concentration of fluorenone at equilibrium per cent. of the total amount of ketones present is computed from the calibration curve set before (fig. 1). The average of the value from one direction with that from the other was taken as the true concentration at

equilibrium. From the value of the concentration of fluorenone at equilibrium the equilibrium constant of the reaction can be calculated.

TABLE 2

Moles x 10^3 in 25 ml. benzene at beginning of reaction.

A	B	C	D	E	Temp.	Fluorenone % at equilibrium	Mean
.375	.375	.875	.875	1.75	60°	66.5	65
.875	.375	.375	.375	1.75	60°	63.5	
.375	.375	.875	.875	1.75	55°	66	66
.500	.500	.750	.750	1.75	55°	66	
.375	.375	.875	.875	1.75	50°	68.5	68.5
.500	.500	.750	.750	1.75	50°	68.5	
.375	.375	.875	.875	1.75	45°	67	66
.500	.500	.750	.750	1.75	45°	65	
.500	.500	.750	.750	1.75	40°	67.5	68.45
.250	.250	1.000	1.000	1.75	40°	69.4	

A, B, C, D and E refer to acetone, fluorenol, fluorenone, iso-propanol and aluminium t-butoxide respectively.

TABLE 3

Moles x 10^3 in 25 ml. benzene at beginning of reaction.

A	B	C	D	E	Temp.	Fluorenone % at equilibrium	Mean
.500	.500	.750	.750	1.75	60°	59	59.25
.625	.625	.625	.625	1.75	60°	59.5	
.375	.375	.875	.875	1.75	55°	59	59.0
.625	.625	.625	.625	1.75	55°	59	
.375	.375	.875	.875	1.75	50°	58.5	58.5
.625	.625	.625	.625	1.75	50°	58.5	
.562	.562	.688	.688	1.75	45°	56	56.75
.437	.437	.813	.813	1.75	45°	57.5	
.437	.437	.813	.813	1.75	43°	58.5	58.5
.562	.562	.688	.688	1.75	43°	58.5	
.562	.562	.688	.688	1.75	40°	56.8	56.84
.437	.437	.813	.813	1.75	40°	56.8	

A, B, C, D and E refer to Butan-2-one, fluorenol, fluorenone, butan-2-ol and aluminium t-butoxide respectively.

TABLE 4

Moles x 10^3 in 25 ml. benzene at beginning of reaction.

A	B	C	D	E	Temp.	Fluorenone % at equilibrium	Mean
.375	.375	.875	.875	1.75	60°	66.5	65.0
.875	.875	.375	.375	1.75	60°	63.5	
.375	.375	.875	.875	.875	60°	67.5	66.375
.625	.625	.625	.625	.875	60°	65.2	
.375	.375	.875	.875	2.500	60°	67	65.5
.500	.500	.750	.750	2.500	60°	64	
.375	.375	.875	.875	5.000	60°	64.9	62.95
.500	.500	.750	.750	5.000	60°	60.9	
.375	.375	.875	.875	.250	60°	72.5	67
.500	.500	.750	.750	.250	60°	61.5	

A, B, C, D and E refer to acetone, fluorenol, fluorenone, iso-propanol and aluminium to-butoxide respectively.

TABLE 5

Moles x 10^3 in 25 ml. benzene at beginning of reaction.

A	B	C	D	E	Temp.	Fluorenone % at equilibrium	Mean
.500	.500	.750	.750	1.25	60°	57.5	56.25
.625	.625	.625	.625	1.25	60°	55.0	
.500	.500	.750	.750	1.25	60°	57.0	56.52
.625	.625	.625	.625	1.25	60°	56.0	
.500	.500	.750	.750	2.50	60°	55.0	54.75
.625	.625	.625	.625	2.50	60°	54.5	
.500	.500	.750	.750	2.50	60°	56.5	54.75
.625	.625	.625	.625	2.50	60°	54.0	
.500	.500	.750	.750	2.50	60°	56.5	54.75
.625	.625	.625	.625	2.50	60°	54.0	
.500	.500	.750	.750	5.00	60°	56.1	54.3
.625	.625	.625	.625	5.00	60°	52.5	
.500	.500	.750	.750	5.00	60°	56.1	54.3
.625	.625	.625	.625	5.00	60°	52.5	

A, B, C, D and E refer to pinacolone, fluorenol, fluorenone, pinacolyl alcohol and aluminium t-butoxide respectively.

Polarography.

An account of the polarographic method tried to determine the concentrations of both ketones, the saturated aliphatic ketone and fluorenone against which it is equilibrated, will be given here. Adkins found that the cations of the electrolytes used in his study (ammonium chloride and tetra-methyl ammonium hydroxide) begin to be reduced at about 1.8 and 2.1 volts respectively and for this reason acetone and other saturated aliphatic ketones did not show a reduction potential since it is higher than 2.1. However, the potential range of the dropping-mercury electrode may be extended to -2.6V[14,15] or -2.8V[16] by using tetra-alkyl ammonium salts. Neiman and Markina[17] determined acetone and ethyl methyl ketone in tetramethyl ammonium iodide solution. Acetone was reduced at -2.20V and ethyl methyl ketone at -2.25V at the dropping mercury cathode.

Procedure for analysis.

A Tinsley recording polarograph was used. The cell was kept at room temperature and polarograms were made on solutions of acetone and fluorenone of nearly the same concentrations as those used in the equilibration experiments. Oxygen free nitrogen was allowed to bubble through the solution for five minutes. Carefully purified mercury from a reservoir whose upper level was about 40 cm. above the tip

of the capillary, was then allowed to drop through the solution. The gas flow was stopped and the polarograph set to OV and started. After one polarogram was made the instrument was reset and the process repeated.

Electrolyte.

Tetra-n-propyl ammonium iodide (Eastman Kodak) was used as base electrolyte in 75% dioxan. It was recrystallised from 95% dioxan.

Dioxan.

(Vogel, p.175). Dioxan was purified by refluxing over sodium and fractional distillation through an 8" column of Fenske helices.

Result:

The polarograms obtained are shown graphically. Before going into the details of a quantitative method, the ketones (acetone and fluorenone) were determined qualitatively and separately. However, the determination of both ketones together does not seem easy because fluorenone (reduced at -.6V) shows another two waves, also shown by reduction of fluorenol, the second of which will be confused with the wave of acetone. This is obvious from the polarogram of acetone and fluorenone together.

FIG. 1.

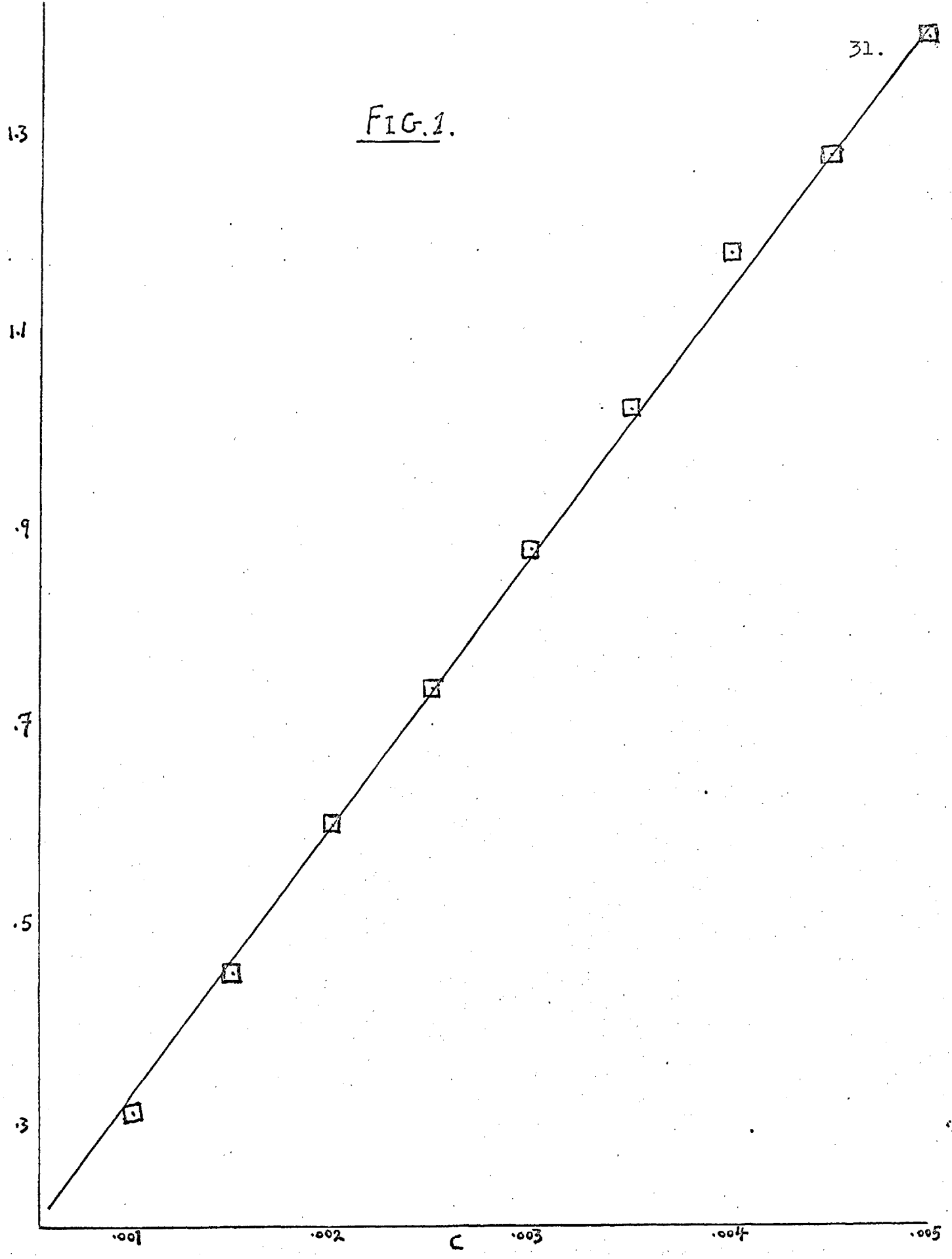
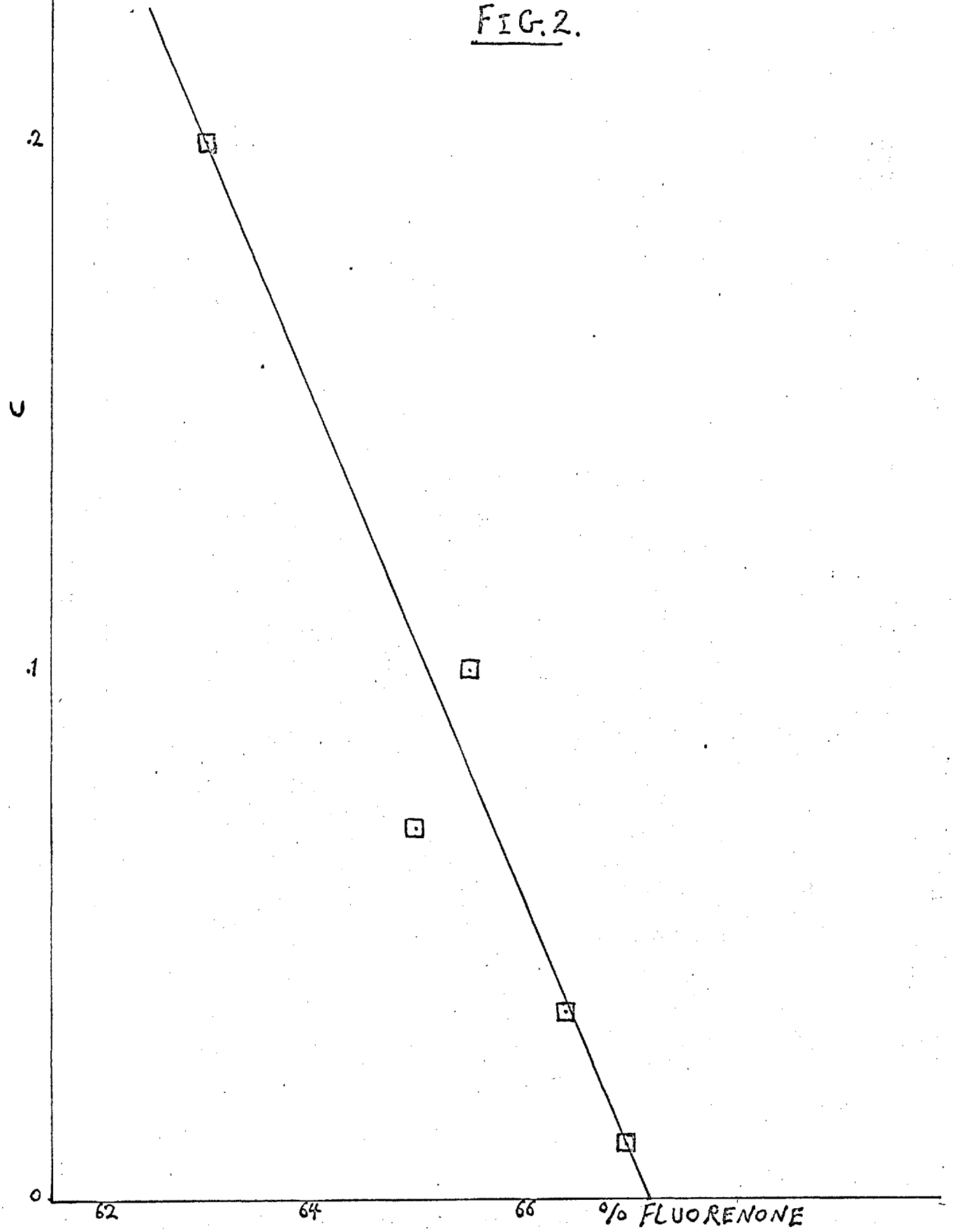
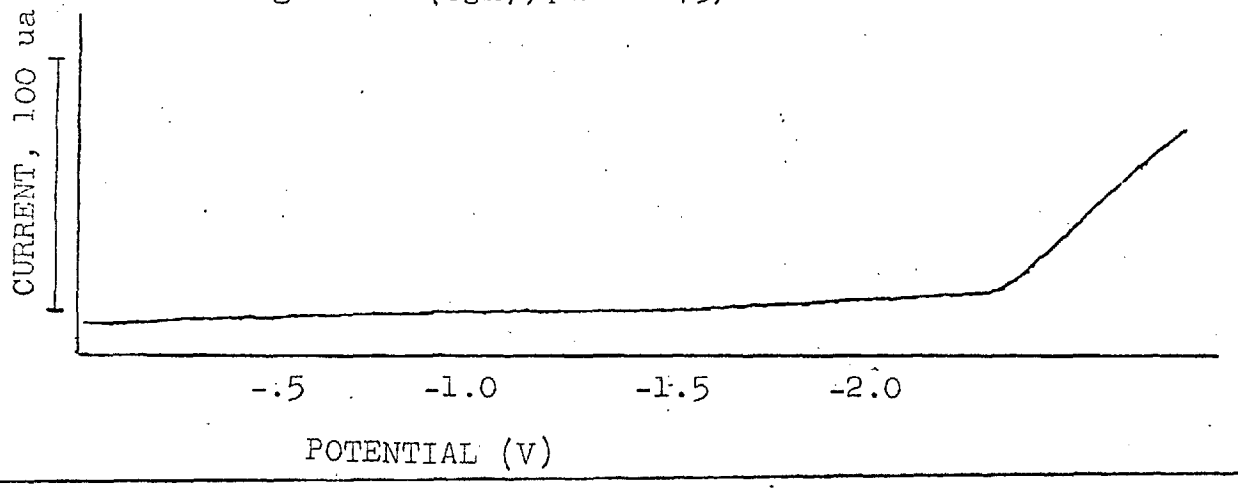


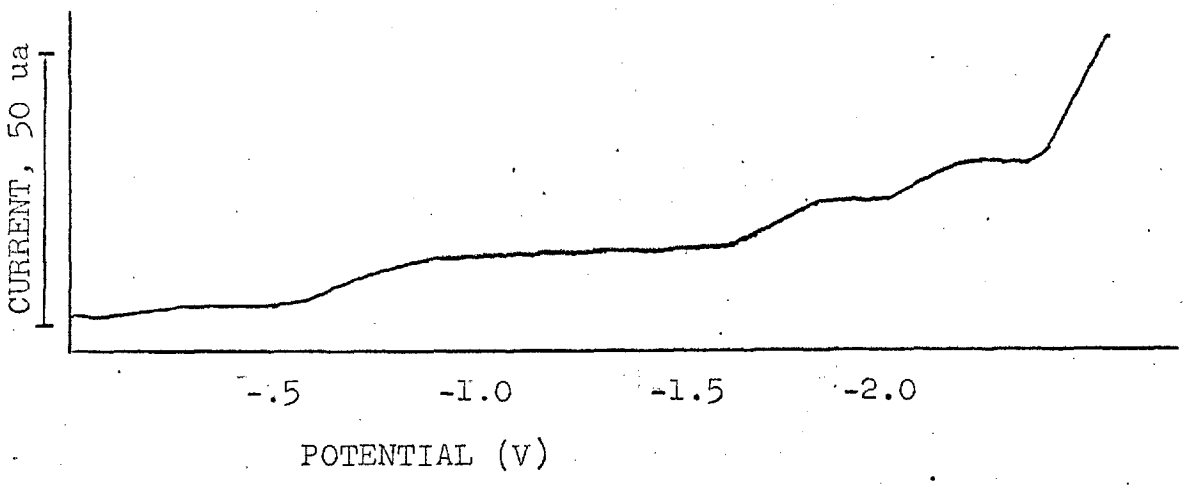
FIG. 2.



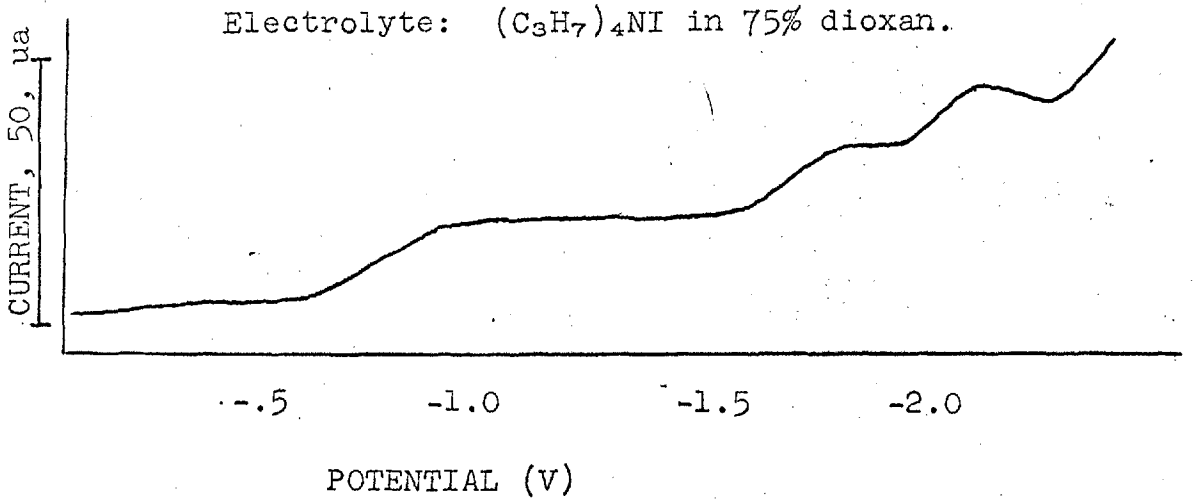
Polarogram of $(C_3H_7)_4NI$ in 75% dioxan



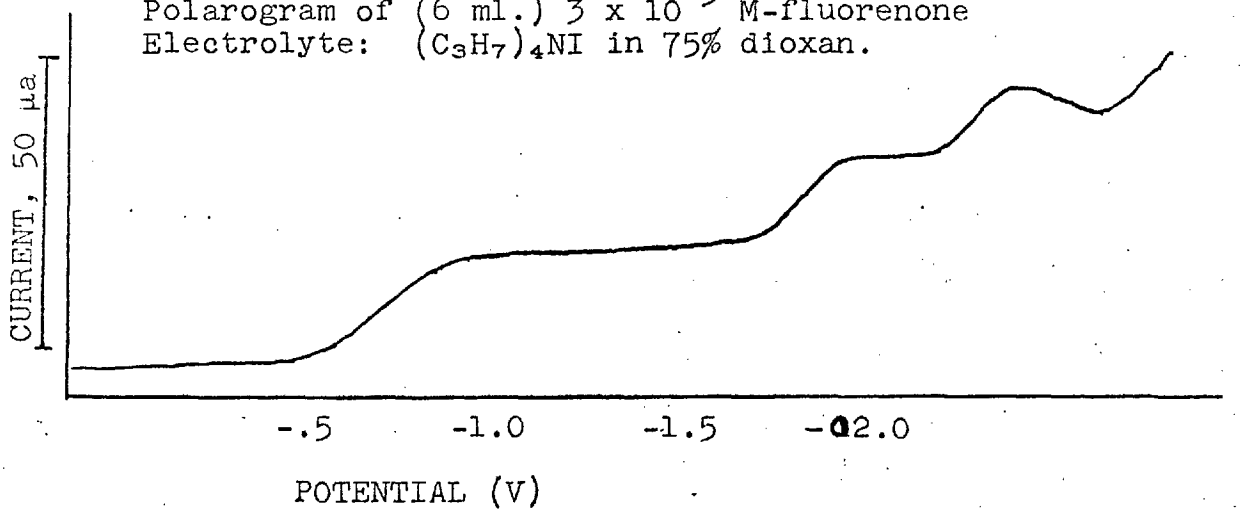
Polarogram of (2 ml.) 3 x 10^{-3} M-fluorenone
Electrolyte: $(C_3H_7)_4NI$ in 75% dioxan.



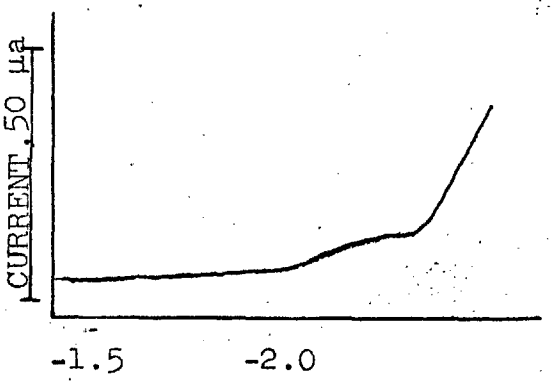
Polarogram of (4 ml.) 3 x 10^{-3} M-fluorenone
Electrolyte: $(C_3H_7)_4NI$ in 75% dioxan.



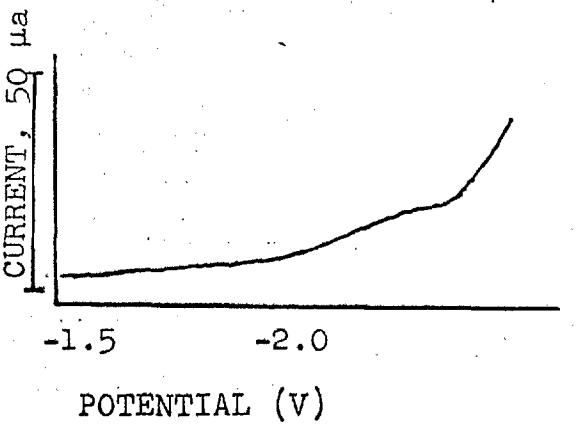
Polarogram of (6 ml.) 3 x 10^{-3} M-fluorenone
Electrolyte: $(C_3H_7)_4NI$ in 75% dioxan.



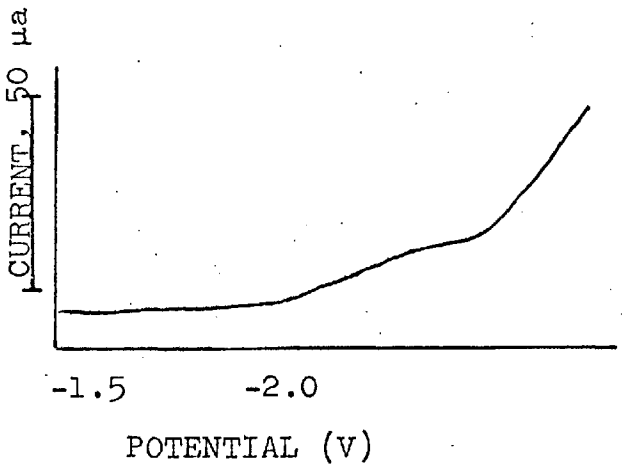
Polarogram of (2 ml.) 3 x 10^{-3} M-acetone
Electrolyte: $(C_3H_7)_4NI$ in 75% dioxan.



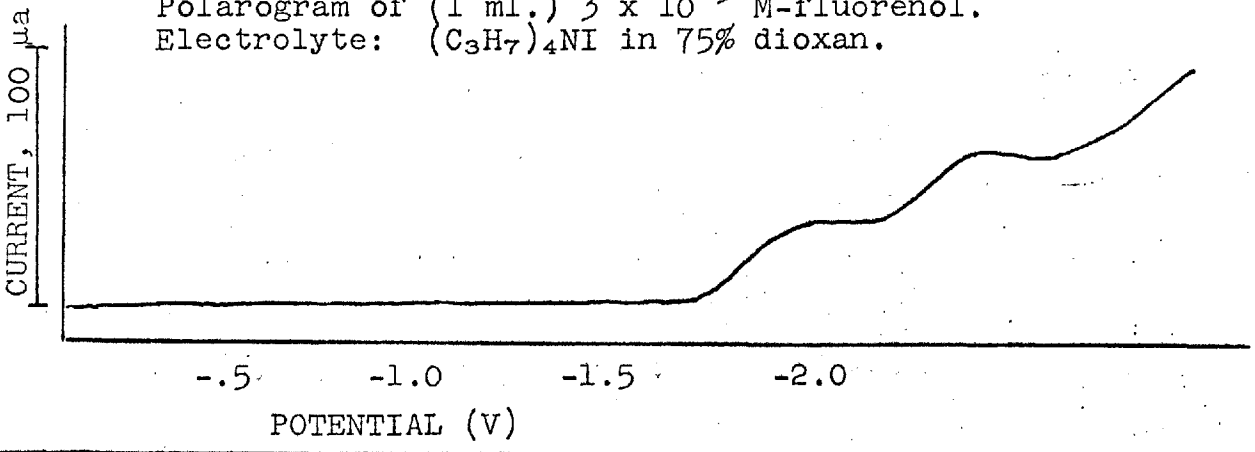
Polarogram of (4 ml.) 3 x 10^{-3} M-acetone
Electrolyte: $(C_3H_7)_4NI$ in 75% dioxan.



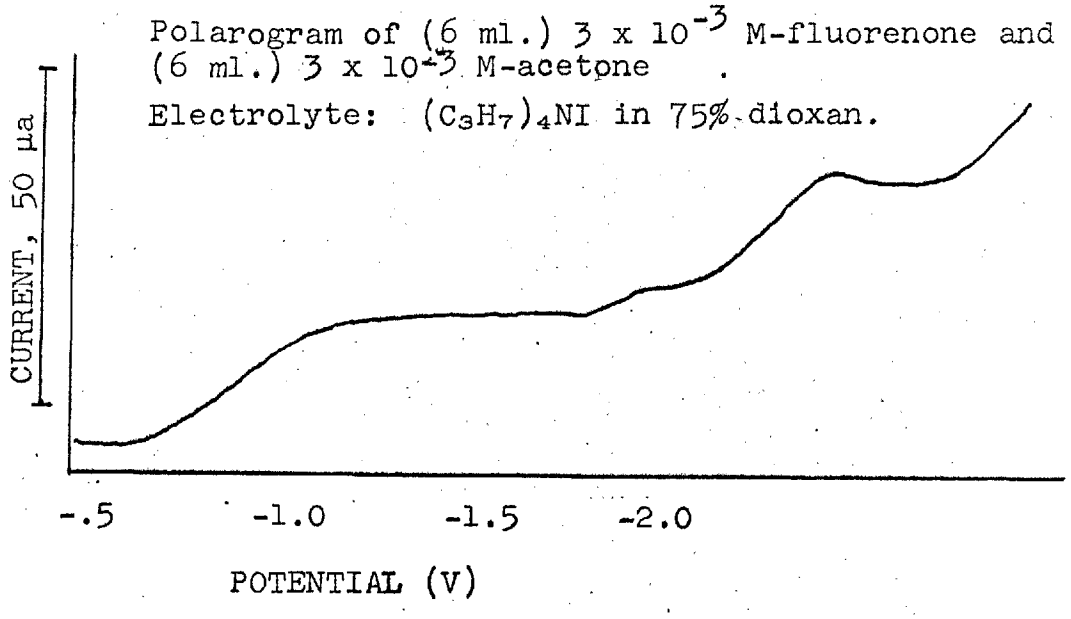
Polarogram of (6 ml.) 3 x10^{-3} M-acetone.
Electrolyte: $(C_3H_7)_4NI$ in 75% dioxan.



Polarogram of (1 ml.) 3 x 10^{-3} M-fluorenol.
Electrolyte: $(C_3H_7)_4NI$ in 75% dioxan.



Polarogram of (6 ml.) 3 x 10^{-3} M-fluorenone and (6 ml.) 3 x 10^{-3} M-acetone.
Electrolyte: $(C_3H_7)_4NI$ in 75% dioxan.



II. HEATS OF HYDROGENATION

In this study the heats of hydrogenation of some aliphatic carbonyl compounds were derived from the measured heats of combustion of the ketones and their corresponding carbinols. These quantities have already been determined directly by Lawlor but owing to their importance it was desirable to obtain them by an entirely independent method.

An account will be given here of the thermochemically studied reduction reactions and an agreement will be shown in many cases between the results obtained and those from combustion calorimetry. Studies were initiated by Kistiakowsky[18] and his co-workers on direct reduction by hydrogen gas. These were extended to hydrogenations in the liquid-phase by Williams[19] and later by Turner[20] and Skinner.[21] The successful application of metal hydrides as a source of hydrogen in thermochemical studies was first achieved by Jackman.[22]

Combustion calorimetry has occupied a predominant position in thermochemistry and its techniques have now been developed to a high standard. Until very recently the combustion method has provided most of the numerical values for the heats of formation of chemical compounds. It is most useful in the study of hydrocarbons; of compounds containing carbon, hydrogen, and nitrogen. The application of the combustion method to compounds containing other elements is in

progress or up till now uninvestigated.

Heats of hydrogenation can be calculated from heats of combustion but the direct measurement of heats of hydrogenation has a manifold advantage in potential accuracy, since it involves the experimental error of a single process and not the cumulative errors of several processes. However, in some cases indirect determination of heats of hydrogenation from heats of combustion was regarded as more reliable. The power of the combustion method or proceedure depends on its firmly established stoichiometry and the simplicity of the products that have well-established values of heats of formation.

Each of the combustion and the hydrogenation methods possesses an area of advantage between which there is a large tract of common ground. In fact the most important source of error in all measurements is inadequate purification of the materials.

Direct gas-phase hydrogenation:

The technique of this type of reaction was perfected by Kistiakowsky and his co-workers in a series of investigations starting in 1935. They measured a large number of heats of hydrogenation at 82° on unsaturated hydrocarbons, alcohols, ketones, aldehydes, and ethers.

The method adopted is suitable for the study of catalytic hydrogenations in the vapour phase at atmospheric pressure

and temperatures below 150°C. The standard calorimetric procedure of observing the temperature of the calorimeter in the fore-and-after periods and correcting the observed temperature change was regarded as unsuitable. Instead, the temperature rise over a period during which the catalyst is in a steady state was observed. This minimizes errors due to irreversible absorption of material on the surface of the catalyst and avoids the difficulty of correcting for thermal effects in the slow processes of absorption and desorption of the reactants and products. A mixture of excess hydrogen and the unsaturated substance was passed over the catalyst (copper, platinum or cobalt-nickel) contained in an adiabatic calorimeter. When the calorimeter has reached a state of steady change the quantity of gases that gave the desired temperature rise was measured. The calorimeter was then calibrated electrically and the heat of the reaction was calculated. Results obtained were shown to be precise to nearly 0.1%.

The calorimeter was a gold-plated cylindrical copper can suspended in a gold-plated calorimeter jacket. The calorimeter liquid, stirred mechanically, was diethylene glycol. It met the need for operating the calorimeter at elevated temperatures up to 150°C in a satisfactory way.

The completeness of the reaction was tested by reacting a known volume of the reacting gases, after passing over

the catalyst, with a weighed amount of bromine. Potassium iodine solution was added and the liberated iodide titrated. The hydrogenation of ethylene was found to be complete by this method. The amount of reaction was found by burning the effluent gases during a run and determining carbon dioxide gravimetrically. The materials for hydrogenation were purified by fractional distillation using a special still head. A freezing point apparatus was employed to check the purity of the substances.

This original work by Kistiakowsky and his associates led to very important results. It emphasized the fact that steric interactions are the major source of the one K cal. difference between the heats of hydrogenation of cis- and trans- butene. Also the lower heat of hydrogenation of cyclopentene than that of cyclohexene, is attributed to the eclipsing of hydrogens in cyclopentane despite the presence of greater strain in the cyclopentene than in the cyclohexene double bond. Angle strain is not the predominate factor in this case.

The same result, that the 5-membered ring compound has a lower heat of hydrogenation than the corresponding 6-membered ring compound, applies to cyclopentadiene, cyclohexadiene, hydrindene, and o-xylene. The differences for the above pairs of compounds are 1.7, 4.5 and 1.5 K.cal. respectively.

It was found that the heats of hydrogenation of propylene, 1-butene, iso-propylethylene and tert-butyl--ethylene are nearly identical. Consequently, the net result is independent of the nature of the alkyl substitution, except for the neopentyl group.

Another point of interest is the evaluation of resonance energies. Except for benzene (36 K.cal.) and furan (17.2 K.cal.) the increase in stability due to conjugation never exceeded 4 K.cal. as in the many cases studied.

Among the most important results obtained is the decrease in the heats of hydrogenation with the increase of alkyl substitution of the double bond. The difference between the heats of hydrogenation of ethylene and tetramethyl-ethylene is 6.2 K.cal./mole. This is the case also in benzene, ethylbenzene and mesitylene. Their heats of hydrogenation are -49.8, -48.9 and -47.6 K.cal./mole respectively. The heats calculated for the reactions acetylene $\longrightarrow$ ethylene (-42.2 K.cal./mole), propyne $\longrightarrow$ propylene (-39.6 K.cal./mole), and 2-butyne $\longrightarrow$ trans butene (-38.0 K.cal./mole), confirm this trend which can be explained on the basis of hyperconjugation.

Calculated heats of hydrogenation based on combustion data confirmed the results of Kistiakowsky especially in the case of easily purified compounds. The required quantities are obtained by difference from the heats of formation of

olefins and those of their corresponding paraffins.

Direct liquid-phase hydrogenation:

The first successful attempt to apply the catalytic hydrogenation method to reactions in the liquid phase was achieved by Williams in 1942. No restriction holds here as for the appreciable volatility of substances at a certain temperature. The reactions studied were of the type

$$X \text{ (liquid or solid)} + H_2 \text{ (gas)} \longrightarrow Y \text{ (in solution)}$$

corrections were applied to get values for the completely gaseous reactions.

$$X \text{ (gas)} + H_2 \text{ (gas)} \longrightarrow Y \text{ (gas)}$$

The method used to get heats of hydrogenation and of solution depended on measuring the temperature change of the calorimeter and its contents due to hydrogenation or solution. The energy equivalent of the calorimeter was determined electrically over the same range of temperature and the quantity of heat produced by a certain amount of material computed from these data.

The standard calorimetric proceedure was employed to correct for the observed temperature change. The correction was calculated from a knowledge of the rate of cooling (or heating) of the calorimeter and contents due only to heat exchange with the surroundings at two different temperatures.

The calorimeter vessel was a spherically shaped Dewar flask of about 500 c.c. capacity. The solvent, stirred mechanically, was glacial acetic acid and the catalyst was hydrated platinum oxide or palladium oxide.

The completeness of the reaction as well as the percentage purity of the materials was checked from the volume of hydrogen used and the theoretical volume required.

The test of the calorimeter was provided by the determination of the heat of hydrogenation of n-heptene-1. The value obtained ($-30.195 \pm .285$ K.cal./mole in the gas state at 355.1° K) is close to the value given by Kistiakowsky at the same temperature ($-30.137 \pm .037$ K.cal./mole).

In a comparison between the results achieved by his method and that of Kistiakowsky, Williams was able to demonstrate the good agreement between them. His values were all corrected to the gas state and at 82°.

The heat of hydrogenation of diethyl maleate (-34.0 K.cal./mole) is greater than that of ethylene (-32.8 K.cal./mole) which confirmed the view, already stated by Kistiakowsky, that there is conjugation in groups of the type C = C - O - but not in C = C - C - O -. Values were obtained for the resonance energies of 1,2 dihydronaphthalene (3.0 K.cal.), methyl trans cinnamate (3.5 K.cal.), stilbene (7.0 K.cal.), and finally for 1,4 diphenylbutadiene-1,3 (10.7 K.cal.).

The values for the last two compounds did not fall into line with those previously observed by Kistiakowsky, The reason for this is that the presence of a second phenyl group which can conjugate with the double bonds in a chain greatly increases the stability.

Also from this work, it was evident that the heat of hydrogenation of the 5-membered ring is less than that of the 6-membered ring to the extent of 2 K.cal. The calculated heat of complete hydrogenation of dihydronaphthalene to decalin is -71.9 K.cal., while that for indene, known before, is -69.9 K.cal.

From the measured heats of hydrogenation, values were obtained for the molar heats of isomerization of 1,4 dihydronaphthalene $\longrightarrow$ 1,2 dihydronaphthalene, of methyl cis cinnamate $\longleftrightarrow$ methyl trans cinnamate, of diethyl maleate $\longrightarrow$ diethyl fumarate, and of i-stilbene $\longrightarrow$ stilbene.

Liquid-phase hydrogenations by Skinner:

In a series of studies commencing in 1957, Skinner and his associates obtained the heats of hydrogenation in solution of several olefinic and acetylenic compounds. The calorimeter was similar to that of Williams, using ethanol or acetic acid as solvent and reduced platinum oxide or palladium oxide as a catalyst. A Pyrex reaction vessel was immersed in water in a Dewar flask and attached to a mechanical 'vibro--shaker' by an arm through the calorimeter lid.

The idea of shaking the reaction vessel was based on a study by Watt and Walling[23] of catalytic hydrogenation of olefins in the liquid phase. They found that mechanical shaking of the reaction mixture was more effective than rotary stirring. Accordingly, the reaction vessel was agitated at rates from 700 to 1000 osc./min. by the vibro--shaker and in this way a hydrogenation experiment could be completed in 10 - 15 min. In the William calorimeter a hydrogenation run took several hours to complete and excessive heat of stirring was produced.

The calorimeter was calibrated electrically with an accuracy of $\pm$.5% and it was thought that better performance could be attained by using a constant speed vibro-shaker instead of the variable speed type used. In a later paper, it was reported that the design was modified and the performance improved. The accuracy was limited by the nature of the hydrogenation process and the difficulty of determining the end point of the reaction. Heats of hydrogenation were computed from the volume of hydrogen used rather than on the mass of the material hydrogenated.

The work of Skinner and his associates reveals certain interesting aspects besides the support it gives to the reliability of the hydrogenation method when the results are cross-checked with those obtained from the combustion method.

The measured heats of hydrogenation by Skinner of octa-1:7--diyne ($\Delta H = -139.7 \pm 1.2$ K.cal./mole) and of dodeca-3:9--diyne ($\Delta H = -131.15 \pm .5$ K.cal./mole) are close to the calculated values, from heats of formation,[24] of heats of hydrogenation of two moles of 1-butyne (139.26 K.cal./mole) and of two moles of 3-hexyne (131.6 K.cal./mole). A difference of 3.9 K.cal./mole was observed between the heats of hydrogenation of dodeca-3:9-diyne and dodeca-5:7-diyne.

By comparison with theoretical calculations by Mulliken, Rieke and Brown and others,[25,26,27] which indicated that the hyper-conjugation energy in R - C ≡ C - R is twice that in R - C ≡ C - H, the net stabilization from hyperconjugation in the -5:7-isomer was taken to be half of that in the -3:9--diyne i.e. 6 - 6.5 K.cal./mole. The value of 6 - 6.5 K.cal./mole was obtained by Mulliken, Rieke and Brown as the empirical hyperconjugation energy in dialkyl acetylenes, R C ≡ C R, by a formula which enables conjugation energies to be empirically determined from experimentally observed heats of combustion. Therefore, to account for the observed difference in the heats of hydrogenation, the overall conjugation energy of the - C ≡ C - C ≡ C - system in the -5:7 diyne is of the order of 10 K.cal./mole. Skinner calculated the conjugation energy in diacetylenes, by the use of an improved method of calculation of conjugation and hyperconjugation energies described by Coulson and Crawford,

and the agreement between the calculated and the empirical value of 10 K.cal./mole was found satisfactory.

The heats of hydrogenation obtained by Skinner, of crystalline fumaric acid and of crystalline maleic acid to form succinic acid are -31.5± .3 K.cal./mole and -36.61 ± .4 K.cal./mole respectively. When compared with those calculated from the measured heats of combustion, by Huffman and Fox,[28] of crystalline maleic, fumaric and succinic acids i.e. -30.78 K.cal./mole and -36.21 K.cal./mole respectively the agreement is obviously good. However, the agreement between the value for the heat of isomerization of fumaric acid into maleic acid, 5.46 K.cal./mole, and that of Huffman and Fox, 5.43 K.cal./mole, is excellent. The reduction in the heats of hydrogenation of a vinyl, phenyl, or methyl substituted acetylene relative to the parent hydrocarbon, similar to the olefins, is also satisfactorily interpreted in terms of conjugation[29] and hyperconjugation.[30] Theoretical calculations supported this view when applied in some cases to account for the observed stability relationships. The following table shows the reduction in heats of hydrogenation brought about by substitution in both acetylenes and olefins.

Heats of hydrogenation of acetylenes and olefins

Substituent	Acetylenes			Ethylenes		
Phenyl	HC ≡ CH	74.4	3.7	$H_2C = CH_2$	32.8	4.2
	ØC ≡ CH(L.)	70.7	6.6	HØC = CH_2	28.6	8.0
	ØC ≡ CØ(C.)	64.1		ØHC = CØH(trans)	20.6	
Vinyl	HC ≡ CBu	69.5	6.2	H_2C = CHBu	30.1	6.2
Vinyl	C ≡ CBu(L.)	63.3		Vinyl HC = CHBu	23.9	
Methyl	HC ≡ CH	74.4	5.3	$H_2C = CH_2$	32.8	2.7
	MeC ≡ CH	69.1	4.0	MeCH = CH_2	30.1	2.5
	MeC ≡ CMe	65.1		MeCH = CHMe(trans)	27.6	

Substitution into acetylene of -COOH, -COOMe, and $-CONH_2$ increased the heats of hydrogenation relative to the unsubstituted acetylene as was observed also in the case of olefins.

In the following table some heats of hydrogenation measured by Skinner and his co-workers are compared with those derived from combustion to demonstrate the good agreement that exists.

Compound	Calc. -ΔH(K cal./mole)		Obs. -ΔH(K cal./mole
$C_4H_2O_4$ (C.)	86.3	28,31	86.8 ± 1.1
$C_6H_5C \equiv C.C_6H_5$ (C.)	62.8	32,33	64.1 ± 1.1
$C_6H_5C \equiv CH$ (liq.)	69.8	34,35	70.7 ± 1.0

The difference of 3.7 K cal./mole between the heats of hydrogenation of acetylene dicarboxylic acid and its dihydrate agrees with the measured heat of hydration of the anhydrous acid. It must be emphasised that heats of hydrogenation of some acetylenic compounds would differ from those in the gaseous state depending on the difference in the heats of vaporization of the acetylenic compound and its reduction product.

The measured heat of hydrogenation of hexene -1 (liq.) (ΔH = -30.1 ± .4 K cal./mole) is in good agreement with the value in the gaseous state as calculated from the difference between the heats of formation[24] of hexane (ΔH_f°, g= -39.96 K cal./mole) and of hexene -1 (ΔH_f°, g = -9.96 K cal./mole). Better agreement was shown when determined later (ΔH = -30.25 ± .2 K cal./mole) after the performance of the calorimeter had been improved. Also the heat of hydrogenation of maleic acid was re-determined and the new value reported (ΔH = -36.29 ± .2 K cal./mole) is closer

to the value calculated from the difference in the heats of formation of crystalline maleic acid and succinic acid.

The most interesting result obtained by Skinner and his associates is that the cis-isomers of the dec-en-ynes and the pent-en-ynes are possibly slightly more stable than the trans isomers. This is in contrast to the case of butene-2 where the trans isomer was shown by Kistiakowsky to be more stable, by ca. 1 K cal./mole than the cis-isomer and the relative instability of the cis-isomer being attributed to steric repulsion between the cis-disposed $-CH_3$ groups. The reversed trend in the cis and trans-pent-en-ynes and dec-en--ynes was explained on the basis that the -C=CH group is necessarily less sterically hindered than is the methyl group.

Liquid-phase hydrogenation reactions by Turner:

Liquid-phase catalytic hydrogenations in acetic acid at 25° were studied by R.B. Turner and his co-workers starting in 1957. Their method was a continuation to that of Williams and the calorimeter was also based on the Williams design. However, hydrogenation of the catalyst and the material under investigation occurred in the same time during a hydrogenation run. The heat of hydrogenation was calculated from the total heat evolved and the heat associated with the reduction of the catalyst, the latter quantity being determined separately.

The standard calorimetric procedure was used to correct the observed temperature change. The calorimeter was calibrated electrically with an error of ± .23%. The amount of reaction was calculated from the volume of hydrogen used. As a test for the calorimeter, the heat of hydrogenation of diethyl fumarate was determined and the value obtained ($\Delta H = -28.94 \pm .05$ K cal./mole) agreed with that of Williams for the same substance ($\Delta H = -29.08 \pm .15$ K cal./mole) within experimental error.

Many important results were obtained by Turner and his associates. From the heats of hydrogenation of several potentially aromatic substances e.g. cyclooctatetraene, 1, 3, 5-cyclooctatriene, azulene, heptafulvene, heptafulvalene and tropone, resonance energies were estimated by comparison with heats calculated for reasonable models. The resonance energy calculated for cyclooctatetraene is 2.4 K cal./mole a result which agrees reasonably well with the lower values derived from combustion data. The value of 4.8 K cal./mole was recently derived by Springall[36] from heat of combustion data.

A quantitative investigation of the existence or absence of homoallylic[37] stabilization in certain organic substances was carried out. It was shown that within experimental error bicycloheptadiene is devoid of homoallylic stabilization

which if present in this system must be small since the orientation of the π-orbitals involved is not favourable for efficient overlap. Also it was concluded from experimental evidence that stabilization of this sort is minimal in bicyclooctadiene.

Stability relationships were investigated among olefins possessing double bonds at various positions in a fused ring system and in a number of isomer pairs possessing endocyclic and exocyclic double bonds. The heats of hydrogenation of cholest-1-ene, cholest-2-ene, cholest-3-ene, cholest-5-ene, cholest-6-ene and of 3 -hydroxy-Δ^{11}-cholenic acid were determined and correlated with conformational properties of these molecules. The observed stability order was $-\Delta^{2} \simeq 5\rangle \Delta^{1} \simeq \Delta^{6}\rangle \Delta^{3}\rangle \Delta^{11}-$. The heats of hydrogenation (K cal./mole) have been measured by Turner for the following compounds, methylenecyclopentane (-26.9), 1-methylcyclopentene (-23.0); methylenecycloheptane (-26.3), 1-methylcycloheptene (-24.0); methylcyclohexane (-27.8), 1-methylcyclohexene (-25.4); ethylidenecyclopentane (-24.9), 1-ethylcyclopentene (-23.6); ethylidenecyclohexane (-26.3), 1-ethylcyclohexene (-25.1). It was concluded that in all these cases the endocyclic modification possesses the lower heat of hydrogenation and hence the greater stability.

Much evidence for the existence and magnitude of steric effects and steric interactions in certain organic molecules were provided. The measured heat of hydrogenation of bicyclooctadiene is almost 5 K cal. lower than that of bicycloheptadiene, a result that is opposite to what was expected. With respect to bicycloheptene and bicyclooctene the same number of hydrogen-hydrogen interactions are introduced in the hydrogenation of both olefins. Only bicyclooctane and probably also bicyclooctene can twist off from the position of maximum eclipsing and steric factors would hence be expected to raise the heat of hydrogenation of bicyclooctene relative to that of bicycloheptene. The difference between the heats of hydrogenation of the two olefins was therefore attributed to angle strain in bicycloheptene which is more severe than in the case of cycloheptene owing to geometric requirements of the bridged system.

A difference of .9 K cal./mole^{-1} was observed between the heats of hydrogenation of 4-methyl-cis-2-pentene and 4-methyl-trans-2-pentene which is identical with that recorded for the cis- and trans-butenes by Kistiakowsky (1.0 K cal./mole^{-1}). This was considered to lend further support to the idea that in compounds of this type the preferred conformations are those in which the isopropyl group is sterically equivalent to methyl.

The heat of hydrogenation obtained by Turner for cis-di-t-butylethylene is -36.2 K cal./mole and that for cis-cyclodecene is -20.7 K cal./mole. The difference of 15.5 K cal./mole between these two figures may in large part be due to steric phenomena.

Hydrogenation reactions in solution by Jackman:

Until recently no data were available for any attempts to extend the hydrogenation method to nitrogen compounds. In 1957, the first successful attempt to use metal hydrides as a source of hydrogen in a thermo-chemical study of this kind was reported by Jackman.

The heat of reaction of an aldimine and that of the corresponding amine with lithium aluminium hydride were measured. The latter heat of reaction was subtracted from the former to give the heat of hydrogenation of the liquid aldimine. These heats of hydrogenation were then corrected to the gaseous state.

The reaction vessels of the calorimeter were silvered vacuum jackets protected against moisture. In a hydrogenation run a solution of lithium aluminium hydride in diethylene glycol diethyl ether was pipetted into the calorimeter through the filling tube. The standard

calorimetric method was used to correct for the observed temperature change. The calorimeter was calibrated electrically.

As a test for the calorimeter Packham measured the heat of neutralization of .1 N sulphuric acid with .1 N potassium hydroxide and comparing his results with the literature data he was able to conclude that his measurement was accurate to $\pm$ .1 K cal./mole.

The heat of hydrogenation of the carbon-nitrogen double bond has been determined for a number of aldimines. The value for the resonance energy of acridine (84 K cal./mole) determined by reaction with lithium aluminium hydride is in good agreement with the latest figures for the resonance energy of anthracene. There appears to be indirect[38] evidence to suggest that the resonance energy of benzene and pyridine should be approximately the same. This reasoning may be applied to the case of acridine and anthracene. From a careful study of the heat of combustion of anthracene, Magnus and Becker[39] have determined the resonance energy of anthracene as 96.4 K cal./mole. Braude, Jackman and Linstead[40] obtained it as 87 K cal./mole by measuring the heat of dehydrogenation of 9:10-dihydroanthracene. Thus it is apparent that the resonance energy of anthracene

is considerably lower than the original figure proposed by Pauling as 105 K cal./mole.

The stoichiometry of the reduction of imines with lithium aluminium hydride was studied. It is well known that the imines may be readily hydrolysed, particularly in acid solution, to give primary amine and the aldehyde. Determination of the aldehyde present in the hydrolysed reaction mixture would therefore give a suitable method for estimating the extent of reduction. A more convenient method for estimation of the aldehyde was to titrate the acid liberated by reaction of the aldehyde with a neutral solution of hydroxylamine hydrochloride. This method proved to be sufficiently accurate as well as convenient.

The first successful extension of the metal hydride indirect hydrogenation method to the measurement of the heats of hydrogenation of carbonyl compounds was achieved by Jackman and Lawlor. Catalytic hydrogenation using catalysts available at present is unsatisfactory for these carbonyl compounds, because of the slowness of the reduction and of side reactions such as hydrogenation of aromatic groups.

The reactions of carbonyl compounds and alcohols with a large excess of lithium aluminium hydride were written as follows:-

(1) $R_1CO.R_2 + LiAlH_4 \longrightarrow R_1CH.R_2$ (O, $-AlH_3$ Li^+) $+ \Delta H_1$

(2) $R_1CHOH.R_2 + LiAlH_4 \longrightarrow R_1CH.R_2$ (O, $-AlH_3$ Li^+) $+ H_2 + \Delta H_2$

Subtraction of (2) from (1) gives the equation for the hydrogenation of $R_1CO.R_2$:-

$$R_1CO.R_2 + H_2 \longrightarrow R_1CHOH.R_2 + \Delta H_1 - \Delta H_2$$

There can be little doubt that the stoichiometries of reactions (1) and (2) are as shown in the equations,[41] and that the products are alkoxides.

The ideal method of proving the stoichiometry of the reduction is the isolation of the pure product. No techniques for the quantitative determination of alcohols are yet available. However, some evidence was provided to prove the stoichiometry of the reduction. The reactions carried out in the calorimeter were very rapid. The reaction was normally completed within one minute as judged by the temperature rise, but because of the high thermometer lag the reaction might have been completed within a much shorter period. Therefore, no carbonyl material was

expected to remain and in fact alcohols prepared in Jackman's laboratory by the lithium aluminium hydride reduction of ketones have contained no carbonyl material.

In the case of the carbonyl compounds there was the possibility that a part of each ketone reacted as the enol. However, the enol contents of the materials studied were very low and the rapidity of the reduction prevented appreciable quantities of ketone from tautomerising. Significant hydrogen evolution during the reaction of dry ketones in the calorimeter was not observed (1% of material reacting as the enol would certainly have been noticed). This fact indicates that no appreciable condensation occurs during reaction.

The only side reaction of simple ketones and aldehydes with lithium aluminium hydride reported in the literature is that of hydrogenolysis. All the cases so far recorded concern aromatic carbonyl compounds and all required high reagent concentration and heating over prolonged periods. Hochstein reduced a number of carbonyl compounds with lithium aluminium hydride in either dibutyl ether or N-ethyl-morpholine (10 g./l.) and he observed that for simple carbonyl compounds, the consumption of the hydride corresponded to the amount required to produce the alkoxides.

Lawlor's calorimeter was the one used in the earlier investigation by Jackman and Packham with some minor modifications made. The electric calibrations were generally

reproducible within .5% and showed no systematic dependence on the currents passed through the heater. The lowest standard error was given as $\pm$ .2 K cal./mole.

Kistiakowsky measured the heats of hydrogenation of acetone, butan-2-one and acetaldehyde at 355°K in the gas state. His values were -13.4 $\pm$ .1 K cal./mole and -13.2$\pm$ .1 K cal./mole for acetone and butan-2-one respectively. Extrapolation of these values to lower temperature would yield hydrogenation enthalpies of lesser magnitude. Lawlor's results for these ketones at 299°K were -13.2$\pm$.2 K cal./mole and -13.7$\pm$.2 K cal./mole for acetone and butan-2-one respectively.

The method Jackman and Lawlor have employed to measure the heats of hydrogenation of ketones should be applicable to most saturated aliphatic ketones and aldehydes though some procedural modifications would have to be made in some cases to avoid precipitate formation e.g. cyclopentanone and cyclohexanone and in the case of low boiling primary alcohols to reduce the vigour of the reduction. Carbonyl compounds having an appreciable enol content would yield imprecise heats of hydrogenation because of the necessity of estimating the heat of reaction of the enol and of determining the amount of material that has reacted as the enol. Measurements carried out on solid materials may give results of poor

reproducibility because of the possibility of more than one crystalline form being present. The fusion of a part of the material during ampoule-sealing could have produced a different crystalline form. The main disadvantage of the method is that other groups within the molecule may also be reduced but may not react completely. This means that a large number of interesting heats of hydrogenation (e.g. of α:β-unsaturated carbonyl compounds) cannot be accurately determined by this method.

PART B

I. EXPERIMENTAL

(1) Materials; preparation and purification.

The purity of butan-2-one, 3-methyl-butan-2-one, 3-methyl-butan-2-ol, 3:3-dimethyl-butan-2-one, 3:3-dimethyl--butan-2-ol, pentan-3-one, pentan-3-ol, trimethylacetaldehyde, and trimethylethanol was demonstrated by means of gas-liquid chromatography, which is probably a more reliable criterion of purity than constancy of boiling point or refractive index. Boiling points and melting points were usually employed merely to identify the substances studied. The literature values of physical properties were taken from Timmerman's 'Physico-chemical constants of pure organic compounds', the 'Dictionary of organic compounds' of Heilbron and Bunbury, and the Elsevier 'Encyclopaedia of organic chemistry'. These references will be abbreviated to T, H and B and E respectively.

The method of analysis is the same as described before. The chromatogram of solid trimethylethanol was made by melting the sample and warming the micro-pipette with a hot-air blower then the sample was injected onto the column at 40°C.

Butan-2-one. - Butan-2-one (Hopkins and Williams) was purified in the same manner as before (cf. p.18). The

material b.p 80° (T: -79.6) was shown to be pure by gas--liquid chromatography.

3-Methyl-butan-2-one. - 3-Methyl-butan-2-one (B.D.H.) was distilled through a short column. The product, b.p. 93.5°, gave a chromatogram showing an impurity which had been eluted just before the 3-methyl-butan-2-one. The impurity was not removed by careful redistillation of the ketone. It was necessary to resort to crystallisation of the semicarbazone derivative.

3-Methyl-butan-2-one (50 g.) was shaken with a solution of semicarbazide hydrochloride (100 g.) and sodium acetate (anhydrous, 150 g.) in water (500 ml.) and the mixture allowed to stand for 3 hours. The precipitated semicarbazone was filtered off, washed with a little cold water, and dried overnight in a vacuum desiccator. Yield 74 g., m.p. 111.5--112.5°. This product was recrystallised from warm water (<60°) to give semicarbazone, m.p. 113.5 - 114.5°, (28 g.). The mother liquor deposited more semicarbazone, m.p. 114-115°, (9 g.), after standing at 2° overnight. The combined product (37 g.) was recrystallised from warm water to give semicarbazone, m.p. 114-116° (32 g.), H and B:- m.p. 114°. Recrystallisation of a portion of this crop gave a product of identical melting point. The semicarbazone was decomposed by refluxing with phthalic acid in water, and the liberated

ketone distilled out in steam. The steam distillate was saturated with potassium carbonate and extracted with ether (3 x 20 ml.). The ether extract was dried over potassium carbonate and distilled through a short column yielding the ketone b.p. 93.5°, (14 g.); H and B:- 93 - 4°/753 mm. Isolation of the ketone was completed by fractional distillation through a micro spinning-band column. The product (10 g.) gave only one band on chromatography on the 'Argon Chromatograph'.

3-Methyl-butan-2-ol. - 3-Methyl-butan-2-one (B.D.H.), with about 1% of low boiling impurity, (30 g.), dissolved in sodium-dried ether (100 ml.) was added slowly with stirring to lithium aluminium hydride (5 g.) in dry ether (200 ml.). When the addition had been completed the mixture was refluxed for half an hour. The hydrides were decomposed by the dropwise addition, with stirring, of water. The inorganic precipitate was dissolved by the addition of dilute sulphuric acid. The ether solution of alcohol was separated and the aqueous layer extracted with ether (3 x 50 ml.). Concentrated aqueous potassium carbonate was used to remove acid from the combined ether solutions which, after a preliminary drying with potassium carbonate, were dried over anhydrous magnesium sulphate. The alcohol was isolated by fractional distillation through an 8" Dufton column.

The first fraction, b.p. 113-113.5°, n_D^{22} 1.4071, (4 g.) was rejected. The second fraction, distilling at 113.5° (760 mm.) (H and B:- b.p. 113.4°), was collected, n_D^{22} 1.4082, (23 g. 76%). The third fraction which distilled at 113.5--114°, n_D^{22} 1.4083, (1 g.) was rejected.

3:3-Dimethyl-butan-2-one. - 3:3-Dimethyl-butan-2-one was prepared in the same manner as before (cf. p.20) from pinacol hydrate (430 g.). Fractional distillation of the crude product through an 8" column of Fenske helices gave (110 g.) of ketone b.p. 105-5.5° (H and B:- 106°). The ketone was found to be pure by gas-liquid chromatography.

3:3-Dimethyl-butan-2-ol. - 3:3-Dimethyl-butan-2-ol prepared from stored pure pinacolone in the same manner as before (cf. p.21) was found to contain a very slight pre--peak. The impurity was not removed by repeated fractional distillation and was thought of as an alkene formed by dehydration on the column. Infra-red examination did not show that the alcohol contained any alkene. It was necessary to resort to crystallisation of the ester derivative.[42]

The hydrogen phthalate ester was prepared by heating the alcohol (50 g.) with phthalic anhydride (80 g.) for twelve hours at 110° in a metal bath. The products were

dissolved in ether and the ether solution extracted with aqueous sodium carbonate (4 l.; 2% solution). The extract was acidified with hydrochloric acid and the liberated ester extracted with benzene. After complete removal of the benzene, at first on a steam bath and finally under reduced pressure, the ester crystallised. Yield 80 g. (65%). The ester was recrystallised from petroleum ether (b.p. 60--80°) to constant melting point (66-67°). Yield 65 g. It was then hydrolysed by aqueous sodium hydroxide (300 ml., 10% solution) and the liberated alcohol distilled out in steam. The steam distillate was continuously extracted with 'Analar' petroleum ether. The solvent was evaporated at the pump. Fractional distillation of the crude product through an 8'' column of Fenske helices gave 15 g. alcohol b.p. 120°. The material was shown to be pure by gas-liquid chromatography.

Pentan-3-one. - Pentan-3-one (B.D.H.) was fractionally distilled and the sample of the main fraction retained gave only one band on chromatography.

Pentan-3-ol.- Pentan-3-one (B.D.H.) (43 g.) was reduced with lithium aluminium hydride (10 g.). The procedure was the same as for 3-methyl-butan-2-ol. The pentan-3-ol

obtained (35 g., 80%), b.p. 115° (754 mm.), was found to be pure by gas-liquid chromatography. The forerun (4 g.,b.p. 114-5°) and the residue measured approximately 5 ml. To ensure the complete removal of ether, the alcohol was re-fractionated (b.p. 115.5°-, 20 g.). T: - b.p. 116.2°/760 mm.

Trimethylacetaldehyde. - Trimethylacetaldehyde (Aldrich Chemical Co.) was fractionally distilled, under nitrogen, through an 8" column of Fenske helices. The main fraction, b.p. 73.5°, H and B: - b.p. 74-6°, gave only one band on chromatography. The aldehyde was always kept under nitrogen at 0°.

2:2:2-Trimethylethanol[43]. - Trimethylacetic acid (B.D.H.) (30 g.) was reduced with lithium aluminium hydride (6 g.). The proceedure was the same as for 3-methyl-butan-2-ol. The white crystalline solid obtained was recrystallised from 'Analar' petroleum ether to constant melting point and the solvent completely removed under reduced pressure. Yield 15 g. (60%), m.p. 49°, H and B:- m.p. 48° and 52-3°).

Drying samples and bag container filling.

The drying of materials for calorimetry is a very important phase of the purification if the amount of substance entered into reaction is directly determined by weighing

the quantity of material used. Because water has a relatively low molecular weight the errors introduced by its presence are large. There are many techniques[44,45,46] for filling thin-walled glass ampoules with volatile liquids using precaution to exclude air and water. In lawlor's method the materials for calorimetry were vacuum distilled from calcium hydride into 'Pyrex' ampoules. A modified Karl Fischer method, developed by Turner[47] in this Department, was used to demonstrate the effectiveness of the drying agent. The maximum concentration of water in the alcohol samples was shown to be .03% which would have produced a negligible increase in the heats of reaction. Lawlor was unable to estimate the water content of ketones by the Karl Fischer method.

In the calorimetric combustion experiments, the amount of reaction was determined from the mass of carbon dioxide produced. With this procedure it became unnecessary to determine[48] and correct for the amount of air and water that might be dissolved in the materials. However, the liquid substances for combustion were kept over type 4A molecular sieve (B.D.H.) using $^{1}/_{16}$ inch diameter pellets. The molecular sieve[49] action of some dehydrated crystalline zeolites is due to their structure. The molecular sieves are useful in the drying of liquids for 3 reasons:-

(a) They have a high absorption capacity for water from liquids containing only traces of water.

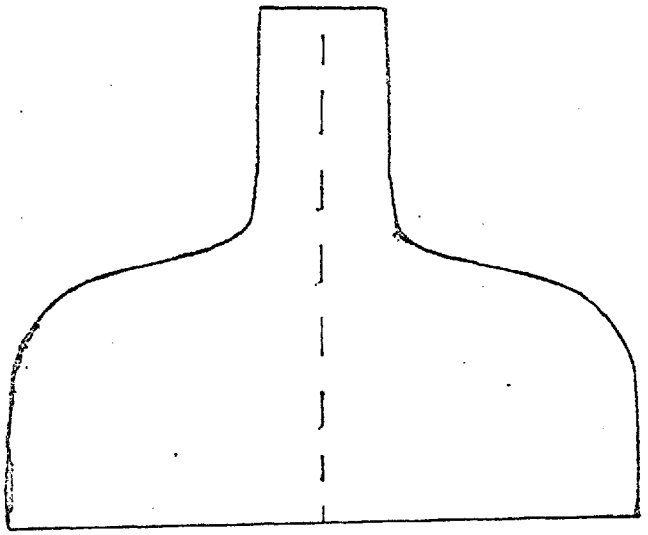
(b) They give very dry liquids.

(c) They can effectively dry polar liquids.

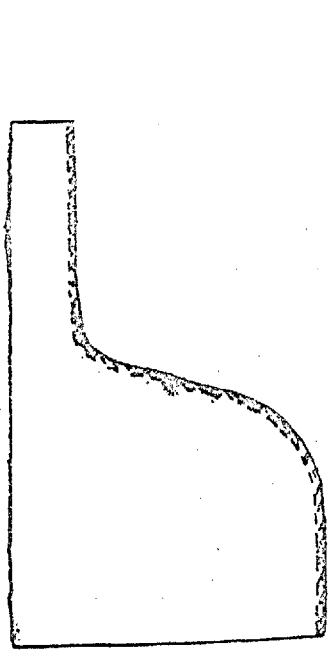
Their unique liquid drying properties are due to their very high selectivity for water and the fact that the molecules of the main component too large for the pores are prevented from competing for absorption surface. They have been used for drying acetone, methanol, ethanol and many other liquids. Types 4A and 5A sieves give higher water loadings at lower equilibrium water concentrations than either activated alumina or silica gel. Before carrying out the combustion experiments the purity of the materials was checked again by gas-liquid chromatography. In all cases the materials were found to retain their purity.

The only solid compound studied, namely 2:2:2-trimethyl-ethanol was stored for several days over phosphorus pentoxide in a desiccator.

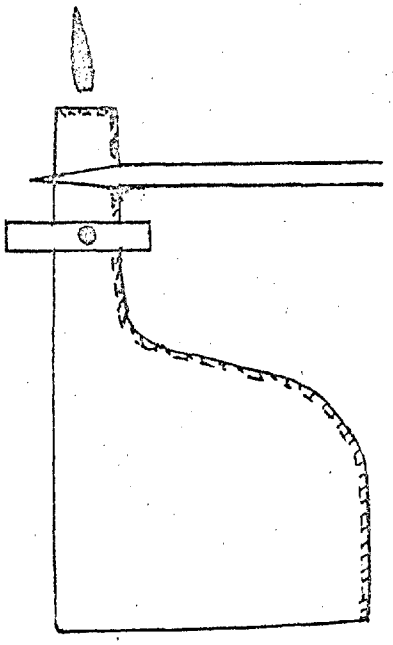
The sample containers were polyester bags made from terylene film (Melinex, .001 in. thickness) in a similar method of that described by Good and Scott.[50] The bag was made from a flat piece of film cut as shown in 'a' (Figure 1).



"a"



"b"



"c"

FIG. 1

This flat piece was folded and heat sealed to make the empty bag shown in 'b'. The heat sealing was done with a small thin Bunsen flame but never touching the edges of the piece which was held (with the edges extending approximately $^{1}/_{16}$ inch) between aluminium metal templates. The empty bags were kept in a desiccator over phosphorus pentoxide. The sample was transferred from the clear liquid over the molecular sieve to the bag with a hypodermic syringe. The syringe, after being used, was cleaned and kept again in a desiccator over phosphorus pentoxide. The air space in the bag was reduced as much as possible. The neck of the bag was then sealed with a special screw clamp the sealing being provided by two small pieces of neoprene. The liquid was removed from the neck (outside the clamp) by swabbing it with a filter paper. After the neck was thoroughly dry, the tip was held with tweezers and sealed as in 'c'. The dry empty bag was weighed in a dry weighing bottle. The filled bag was rolled and placed inside the platinum crucible used in the combustion experiments and re-weighed. All these operations of sample preparation were performed with the hands covered by thin cotton gloves to protect the film from contamination.

Solid 2:2:2-trimethylethanol was packed into the bag. The neck was sealed more easily than with the volatile liquids.

(2) Oxygen

Commercial oxygen containing a small amount of nitrogen was used. Before being admitted to the bomb the oxygen was passed through a tube containing cupric oxide heated to a temperature of about 600°C in order to burn out any combustible impurities which might be present. The apparatus used in purifying oxygen consisted of the cylinder containing the oxygen under pressure to which was attached a pressure gauge. A steel tube which was electrically heated to about 600°C, as measured with a thermocouple, contained the cupric oxide. This was followed by a coil immersed in cold water to cool the oxygen issuing from the oxidising tube. Another steel tube contained Carbosorb and anhydrous magnesium perchlorate to remove carbon dioxide and water from the oxygen before passing into the bomb. The connecting tubings in the apparatus were made of copper and the connecting fittings of brass. This apparatus was constructed in the College Workshop.

(3) Carbon dioxide analysis.

The absorbers were made of soft glass with ground glass stoppers and when in use the stoppers were lubricated with Apiezon grease. They were 20 cm. long, with cross section of about 3 $cm.^2$ and an internal volume of about 60 $cm.^3$

For use in the absorption of carbon dioxide each of three tubes was freshly filled with carbosorb (B.D.H. micro-analytical reagent, 14-22 Mesh) and with one cm. layers of Anhydrone (anhydrous magnesium perchlorate, B.D.H. micro-analytical reagent 14-22 Mesh) and phosphorus pentoxide at the entrance and exit ends respectively. Layers of asbestos fibre bounded the Anhydrone, the Carbosorb and the phosphorus pentoxide. The combustion gases or the oxygen for flushing were passed first in a tube containing Anhydron and phosphorus pentoxide to remove water. A guard tube containing in sequence phosphorus pentoxide, Anhydrone and Carbosorb followed the three absorption tubes to prevent back diffusion of water vapour or carbon dioxide. A flow meter discharging to the air of the room was connected to the guard tube. All the connecting tubings were of special rubber used in the College Micro-Analytical Laboratory and all connections were wired.

The analytical train was flushed for about one hour with dry, pure oxygen before the combustion gases were permitted in. After a calorimetric combustion experiment an adaptor for connecting the bomb to the analytical train was put in position. The gaseous products were passed at a rate of flow adjusted so that they took about one and a half hours to cease. The bomb was then charged twice to 150 lb/in^2 with pure oxygen and the gas passed through the system.

The mass of carbon dioxide collected was near 3 g. Absorption was mostly in the first and second tubes and the change in weight of the third one was usually zero within ± .00010 g. The precautions of handling the absorption tubes were followed as recommended by Rossini.[51] To obtain weights in vacuo, the factor 1.00045 was applied as recommended also by Rossini.[52]

Jessup[53] and Rossini[45] have found that no significant amount of nitric acid was removed from solution in the water in the bomb by about the same quantity of gas issuing from the bomb. The reliability of this method was shown by combustion tests with thermochemically standard benzoic acid e.g. in two experiments the percentage of carbon dioxide observed to calculated was 99.95 and 99.98.

(4) Examination of completeness of combustion.

Tests were made occasionally for carbon monoxide in the bomb gases after combustion but did not give any indication of incomplete combustion. The detection of carbon monoxide was carried out by the iodine pentoxide method.[54] Iodine pentoxide (B.D.H.) was dried at 250°C before use. A U-tube containing (25 g.) was immersed in an oil bath heated at 125-150°C. It was connected to the last carbon dioxide absorber in the analytical train. The liberated iodine passed to a trap containing about (1 g.) of potassium

iodide in 10 c.c. water and was titrated against .005 N sodium thiosulphate solution using starch as indicator. In calibration experiments with benzoic acid the potassium iodide solution remained colourless or very faintly blue requiring only one drop of sodium thiosulphate and that would produce a negligible correction. The technique of burning samples in polyester containers previously tried by Skinner[55] was very successful. The reaction was in most cases very clean and no carbon monoxide or soot were detected. In calibration experiments the minute amount of soot found inside the crucible was corrected for by determining its quantity as the difference between the dried and glowed crucible.

(5) Correction for the amount of nitric acid formed.

When the bomb was opened the interior was inspected for soot. If soot was found anywhere outside the crucible the experiment was rejected. If no soot was found the internal surface of the bomb was washed out with distilled water and the amount of nitric acid in the washings was determined by titration against .1 N sodium hydroxide solution using methyl orange as indicator. The use of an indicator that is practically insensitive to carbon dioxide such as methyl orange was recommended by Jessup.[56] The sodium hydroxide

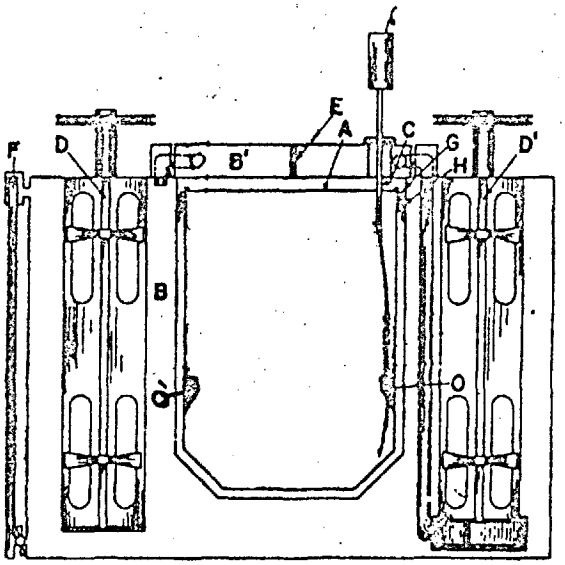
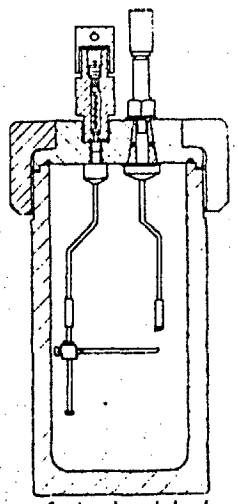


Figure 2. Sectional view of calorimetric system with bomb and rotating mechanism in place in calorimeter.

FIG. 3



Section through bomb

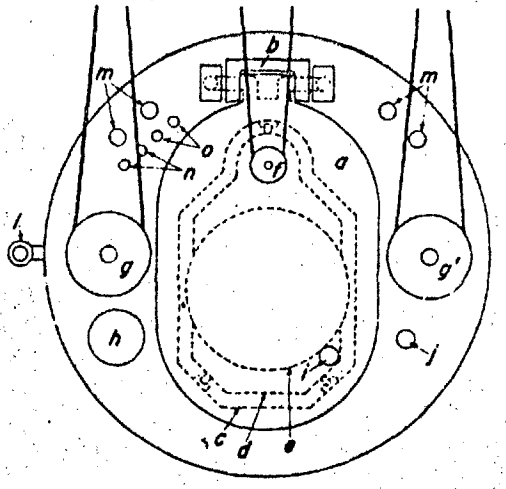


Figure 4. Top view of calorimetric system.

solution, standardised against .1 N constant boiling hydrochloric acid,[57] was kept in a polyethylene aspirator protected by a soda lime guard tube. The normality was checked from time to time and found to remain nearly constant.

(6) Calorimetry.

The apparatus used was a rotating bomb calorimeter built in the College Workshop according to a design by the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines, Bartlesville, Okla.[58] However, the bomb rotating mechanism did not need to be in action for our purpose. The calorimetric system is of the constant temperature jacket type. Figure 2 shows a diagramatic sectional view of the apparatus which consists of the conventional parts (i.e., calorimeter A, constant temperature jacket B and B'. and

a partition E in the lid into the other side of the jacket lid, and then back into the jacket tank through the other side of the hinge. The temperature of the jacket water was kept at 28°C regulated to $\pm$ .002° by balancing a small constant flow of cold water from a refrigeration machine against an intermittent heat input supplied by a 100-watt tubular heater. Excess water escaped through the tube F and returned to the refrigeration machine.

The calorimeter A was suspended in the jacket well. Three pegs G near the top of the calorimeter walls rest in V-grooves in corresponding lucite blocks H. The shape of the calorimeter and the walls of the well were such that an air gap 10 mm. thick separates them on all sides. The only objects in this space were the three supports H, a part of the thermometer C, and four electrical leads which are not shown.

The rotating bomb tried first (internal volume, .343 litre) was made of stainless steel and was lined with platinum (.01 in. thick). The sealing gasket, $^1/_{16}$ in. thick was made of fine gold. Several months were spent to get this bomb sealed but without success. A Gallenkamp calorimeter bomb (Figure 3) was used instead. The bomb had a capacity of 300 ml. and was of three piece construction comprising a body and a cap which were machined from solid rolled

stainless steel bar and a retaining nut which was machined from rolled aluminium bronze bar. The sealing gasket was a rubber 'O'-ring situated in a groove in the cap. The bomb cap was tightened by hand only. With hand tightening the metal to metal contact was achieved between the bomb cap and body. Two inconel electrodes were fitted to the bomb cap. One has a ring shaped support for the platinum crucible and was electrically connected to the cap and the other was insulated by a tapered fibre bush protected under the lid by a mica washer. There was a socket at the upper end of the insulated electrode and a plug was supplied for connecting it to the firing circuit. The return current path was normally via the calorimeter vessel and the water jacket. A hole and a sleeve were provided on each electrode stem for fastening the firing wire. The bomb was certified in the National Physical Laboratory as capable of standing a hydraulic Pressure of 300 atmospheres. It was suspended in the calorimeter vessel by a copper ring support that rested in positioning grooves in copper blocks O and O'.

A top view of the calorimetric system is given in Figure 4. This shows the cylindrical form of the outside jacket, the shape of the jacket lid, a, and its hinge, b. The dotted lines in the hinge show the opening through which the jacket water is pumped into and out of the lid. The

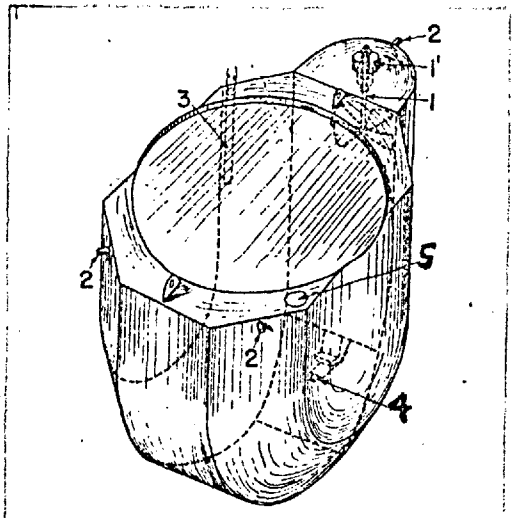


Figure 5. Perspective view of calorimeter can.

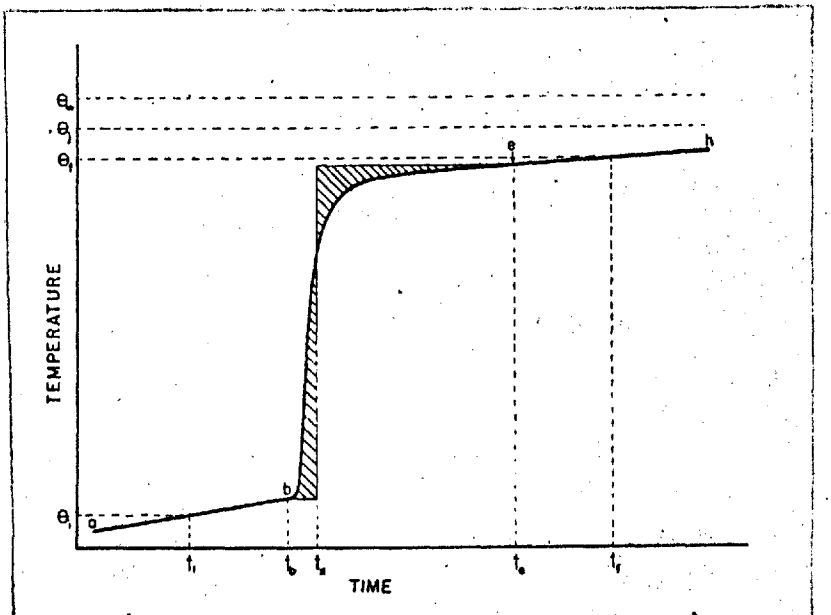


Figure 6. Time-temperature curve for a bomb-calorimetric experiment.

dotted lines c, d and e show the shape and position of the well, calorimeter, and calorimeter lid respectively. Pulley f, which is driven by a synchronous motor, is the end of a spring collet that drives a stirrer in the calorimeter. Pulleys g and g' drive the jacket stirrers. Ports h, i, and j are for the jacket thermoregulator, the calorimeter thermometer and the jacket thermometer respectively. The sketch also shows the overflow pipe l, the jacket heater terminals m, the calorimeter heater terminals n, and the terminals o for the electrical ignition circuit.

A perspective view of the calorimeter vessel is shown in Figure 5. Shown in the drawing are: 1 and 1', the stirrer for circulating water in the calorimeter vessel and an oil seal through which passes the stirrer shaft; 2, the pegs for suspending the calorimeter in the jacket well; 3, the calorimeter heater that raises the temperature to the desired starting value; 4, bomb positioning device; and 5, the opening in which the calorimeter thermometer is placed.

Temperature measurements were made with a calorimetric platinum resistance thermometer, hermetically sealed in a silver sheath, manufactured by Cambridge Instrument Company, in conjunction with an F.E. Smith's difference bridge and a sensitive d'Arsonnal galvanometer manufactured by the same firm. A rubber bushing on the shaft of the thermometer closed port 5 in the calorimeter when the system was

assembled. The thermometer was always kept at a certain depth in the calorimeter.

The temperature of the room was controlled at 23 $\pm$ .2°.

(7) Determination of the corrected temperature rise.[59]

The time - temperature curve shown in Figure 6 is typical of those obtained by us in both calibration and combustion experiments. The temperature is expressed here in ohms. Parts ab, be, and eh of the curve represent the relation between the temperature, θ, of the calorimeter and time, t, in the initial, main, and final periods, respectively. The horizontal lines at the top represent the temperature of the jacket θj, and the convergence temperature, θ^{∞}, of the calorimeter, that is, the temperature which the calorimeter would attain in an infinite time if θj and the rate of stirring remained constant. The length of the initial and final periods was 20 min. each, and during these periods measurements of temperature were made at equal time intervals of 2 min. The length of the main period which depends upon the lag of the bomb in a combustion experiment was 10 min. The final steady rate of change of temperature was attained at the end of this period. To obtain sufficient accuracy temperatures in the main period were obtained by interpolation at intervals of 15 sec.

The observed temperature rise of the calorimeter, (θe - θb) was corrected for the heat of stirring and thermal leakage

using the proceedure recommended by Coops based on the Regnault-Pfaundler formula. According to this proceedure, in brief, the correction is calculated from the time-temperature curve, on the assumption that the rate, U, of the temperature rise of the calorimeter due to heat of stirring is constant, and the rate of temperature rise due to thermal leakage is proportional to the difference between the temperatures of the calorimeter and jacket (Newton's law of cooling). The total rate of temperature rise due to heat of stirring and thermal leakage is then given by

$$d\theta / dt = U + k (\theta j - \theta) \qquad (1)$$

where k is the 'cooling constant' of the calorimeter. Since $d\theta/dt = \theta$ when $\theta = \theta\mathscr{o}$, then from equation 1

$$\theta j = \theta\mathscr{o} - U/k$$

substituting this expression for θj in equation 1 gives

$$d\theta/dt = k (\theta\mathscr{o} - \theta) \qquad (2)$$

The constants U, $\theta\mathscr{o}$, and k can be calculated from the data of the initial and final periods. Thus if gi and gf represent the values of $d\theta/dt$ at the mean temperatures θi and θf of the initial and final periods, respectively

$$k = \frac{gi - gf}{\theta f - \theta i} \qquad (3)$$

$$\theta\mathscr{o} = \frac{gi\theta f - gf\theta i}{gi - gf} \qquad (4)$$

The correction, $\Delta\theta$, which must be added to the observed temperature rise, $(\theta e - \theta b)$, to eliminate the effect of heat of stirring and thermal leakage can be obtained by integration of any one of equations 1 and 2. One of the resulting expressions for $\Delta\theta$ and which was used is

$$\Delta\theta = -k \int_{tb}^{te} (\theta\mathscr{o} - \theta)\, dt$$

$$= -k\,(\theta\mathscr{o} - \theta m)\quad (te - tb) \qquad (5)$$

In this expression θm represents the average temperature of the wall of the calorimeter in the main period. The Regnault--Pfaundler method is used in finding the value of θm when n temperatures, θr, are obtained by interpolation between observed values at equal time intervals, 15 sec., during the main period. The average temperature is then given by

$$\theta m = \left\{ \sum_{r=2}^{n-1} \theta + \frac{\theta b + \theta e}{2} \right\} \frac{1}{n-1} \qquad (6)$$

The corrected temperature rise is given by

$$\Delta\theta \text{ corr.} = \theta e - \theta b + \Delta\theta \qquad (7)$$

Corrected values of θb and θe can be obtained by the method of least squares. Thus, to the extent that the curves of

θ versus t of the initial and final periods can be considered linear, the corrected values are calculated from the relation

$$\theta \text{ corr.} = {}^{1}/_{n} \sum_{r=1}^{n} \theta r \pm \left[(n-1)/2\right] g, \quad (8)$$

where θr represents the r^{th} temperature reading of the initial (or final) period, made in a series of n observations at equally spaced times, 2 min., and g represents the average change in temperature per interval for that period calculated from

$$g = 6 \frac{(n-1)\ (\theta n - \theta 1) + (n-3)\ (\theta n - 1 - \theta 2)}{n\ (n^2 - 1)} \quad (9)$$

The plus sign before the last term in equation (8) is used in calculating θb from the data of the initial period while the minus sign is used in calculating θe from the data of the final period.

(8) Determination of the energy equivalent with benzoic acid.

If the heat of combustion is referred to $\theta b = 25^{\circ}C$ then the energy equivalent of the calorimetric system is defined by

$$\epsilon_f = \frac{ms\left[-\Delta EB_{(\theta b)}\right] + q_i + q_n - q_c}{\Delta\theta \text{ corr.}} \quad (10)$$

where ms is the mass in grams of benzoic acid burnt, $\Delta EB_{(\theta b)}$

represents the heat of combustion per gram of benzoic acid at the temperature θb, and under the conditions of the actual bomb process, q_i is the energy used to ignite the charge, q_n is the energy produced by the formation of nitric acid in the bomb at the temperature θb, and q_c is the quantity of heat which would have been produced by the combustion in the bomb of any soot found in the crucible at the end of the experiment. However, the results of determinations of energy equivalent are to be reduced to the basis of a standard calorimeter system which does not involve benzoic acid or its products.

ϵsf may be taken as the energy equivalent of the system with a specified mass of water in the calorimeter vessel, and with the bomb empty. Then if ϵ_f represents the energy equivalent of the final system as determined with benzoic acid, the energy equivalent of the standard final calorimetric system would be given by

$$\epsilon_{sf} = \epsilon_f - \epsilon_{cf} \quad ,$$

where ϵ_{cf} would be calculated from the heat capacities of the crucible, oxygen, carbon dioxide, and water in the bomb at the end of the experiment with benzoic acid, and the specific heats and differences in mass of any other materials present in different amounts in the standard calorimeter system and the system as actually used.

Benzoic acid is now well established as the most convenient standard substance for calibrating bomb calorimeters. Benzoic acid of a high degree of purity, in tablets, with a moisture content not exceeding 0.001% is especially prepared for this work in the B.D.H. laboratories and submitted for certification to the National Physical Laboratory. The tablets weighing approximately .2 g. each, are supplied in sealed tubes containing 20 g., the certified value on the label of the package used was 26439.0 absolute joules per gram mass (standard error of 3.1 j/g). The standard conditions for combustion are as follows:

a) The combustion reaction is referred to 25°C.

b) Absolute pressure of oxygen in the bomb before combustion = 30 atmospheres at 25°C.

c) Weight of benzoic acid burnt: 3 g. per litre capacity of the bomb.

d) Volume of water in the bomb before combustion 3 ml. per litre capacity of the bomb.

The heat of combustion of the standard sample benzoic acid under conditions differing by small amounts from the standard conditions specified by (a), (b), (c), and (d) above will be obtained by multiplying the value given above by the factor[60,61]

$$f = 1 + 10^{-6} [20\,(P - 30) + 42\,(ms/v - 3) + 30\,(mw/v - 3) - 45\,(\theta - 25)] \quad (11)$$

Where P is the initial pressure in atmospheres of the oxygen at the temperature θ, to which the reaction is referred, ms is the mass in grams of the sample burnt, mw is the mass in grams of water placed in the bomb, and V is the internal volume of the bomb in litres.

(9) Experimental proceedure.

In the preparation for a calibration with benzoic acid or the combustion of a sample identical proceedure was adopted.

The platinum crucible was weighed, charged with benzoic acid or a rolled polyester sample container and reweighed. The benzoic acid (about 1.5 g.) was weighed to 0.01 mg. The tablets of benzoic acid were transferred with a clean dry forceps, from their tube container left open in a desiccator over phosphorus pentoxide, to the crucible and heaped over each other. A piece of platinum fuse wire (.1 mm. in diameter, 3 in. long) was stretched between the bomb electrodes and made into a small loop in the middle. A 3 in. long piece of dry cotton thread was weighed and tied around the wire in the loop. The bomb cap was placed on a stand. With the ring support swung to one side, the

crucible with the sample, was placed in position. The crucible was swung into position, the ring clamped and the ends of the cotton were arranged to be under the sample (in case of benzoic acid by a gentle knock at the crucible the heaped tablets fell on the cotton). 1 ml. of distilled water was introduced into the body of the bomb before sealing. The toroidal sealing ring was replaced if the bomb had failed to seal and another ring of the same weight to the nearest mg used in the meantime.

The air present in the bomb was removed by filling the bomb with pure oxygen to 450 Lb/in.^{2} and releasing the pressure using a special cap on the bomb inlet tube. The pillar inside this would depress the valve and release the residual gas. This operation was repeated. The bomb was finally charged to 450 Lb/in.^{2}, at room temperature, equivalent to about 30 atmospheres. The oxygen was introduced to the bomb by a filling tube (with a hand tightening union) attached to the oxygen purifying apparatus. After filling, a sealing cap which had a fixed tommy bar was used to seal the inlet tube of the bomb. To test for leaks the bomb was immersed in water for 30 min. The bomb was then carefully dried, and with the firing lead attached, was put in place in the dry calorimeter vessel. 2 ml. of light lubricating oil were introduced into the oil seal in the

calorimeter vessel through which the stirrer shaft passed. The thermometer hole and the small opening through which the firing lead passes were sealed with rubber stoppers. The calorimeter lid was placed in position.

3 Kg. of distilled water with a slight excess and sufficient to submerge the bomb were weighed to $\pm$ .01 g. into the calorimeter vessel. The excess amount of water was removed via the thermometer hole with a fine dropper. The calorimeter vessel was suspended in the jacket well and the firing leads and the heating leads were connected to their terminals. The calorimeter thermometer was put in place and the jacket lid put on.

The stirrer for circulating the water in the calorimeter vessel was started. The calorimeter vessel and contents were heated to slightly below the starting temperature by means of the calorimeter heater. When a steady state has been attained, and the standard starting temperature was reached, the observations of resistance and time of the initial period were made. On the 20th min. the charge was fired at the resistance value corresponding to 25^{o}C. The electric current for firing was taken from a transformer with a secondary voltage of 10 as measured by a voltmeter. After firing the observations of resistance and time of the

main period were begun immediately. These were made by observing the times to the nearest second at which previously selected values of resistance were reached. The resistances were so spaced as to permit accurate evaluation of the correction, $\Delta\theta$, in accordance with the method outlined before. On the 30th min. when a steady rate of change of temperature has again been attained the observation of the resistance and time of the final period were made. The carbon dioxide analysis was carried out and then the titration of nitric acid formed as described before.

The way in which a heat of combustion was computed from the experimental data is illustrated for butan-2-one below:-

Calibration.

(i) Corrected values of resistance proportional to the temperatures θb and θe were obtained from the data of the initial and final periods respectively by means of equation (8), using the values of gi and gf determined as described under (ii) below. These were 27.51197 and 27.77721 ohm respectively. The difference = .26524 ohm was proportional to the observed temperature rise ($\theta e - \theta b$).

(ii) Values of the initial and final rates gi and gf were calculated by means of equation (9). These were .00163 and .00019 ohm/2 min. interval respectively. Values of the constants k and θ_ρ were calculated by means of equations (3) and (4) and found to be .00525 ohm min^{-1} and 27.81250 ohm respectively. The resistance proportional to the mean temperature, θm, during the main period was obtained by graphical integration of the resistance - time curve during this period, by means of equation (6). The value obtained was θm = 28.42157 ohm. The correction, $\Delta\theta$, for thermal leakage and heat of stirring was calculated by means of equation (5).

$$\Delta\theta = .00084 \text{ ohm.}$$

The overall change in resistance of the platinum resistance thermometer, proportional to the corrected temperature rise, $\Delta\theta$ corr., was given by equation (7).

$$\Delta Rc = .26524 + .00084 = .26608 \text{ ohm.}$$

(iv) The factor, f, was calculated by inserting in equation (11) the values of P, ms/v, mw/v and the temperature to which the reaction was referred i.e. 30.62056, 1.50047/.3, .90665/.3 and 25°C respectively. The value for the heat of combustion of benzoic acid to be used for this experiment was then obtained by

multiplying the value which was applicable under the standard conditions by the value for the factor f for this experiment = 26439 x 1.000097 =26441.6 j/g.

(v)With the above data the value of ϵ_f resulting from the experiment was calculated by means of equation (10)

$$\epsilon_f = \frac{1.50047\ (26441.6)+60.4+24.3-8.3}{.26608} = \frac{39.768}{.26608} = 149.459 \text{ Kj/ohm}$$

where 1.50047 g., and 26441.6, 60.4, 24.3 and 8.3 joule were the values for ms, $-\Delta EB_{(25)}$, q_i, q_n and q_c as defined previously.

The value of ϵ_{sf} was calculated by means of the equation

$$\epsilon_{sf} = \epsilon_f - \epsilon_{cf} = 149.459 - .183 = 149.276 \text{ kj/ohm}$$

$$= \epsilon_f - 10^{-3}\ D[21.0\ nO_2 + 4.18\ mw + 2.28\ ms + .136\ mpt]$$

where D = 10.17915 = number of degrees centigrade equivalent to one unit of the temperature scale used,

nO_2 = 0.39176 = number of moles of oxygen initially present in the bomb (from the equation of State),

ms = 1.50047 = mass of benzoic acid in grams,

mpt= 18.32816= mass of platinum crucible in grams,

mw = .90665 = mass of water initially present in bomb in grams.

Six calibration experiments were performed and the arithmetic mean was taken as the energy equivalent of the standard final

calorimeter system. In this case ϵ_{sf} = 149.220 ± .027 Kj/ohm.

Combustion of butan-2-one.

The combustion of .12543 g. melinex bag containing about 1.09630 g. butan-2-one and of .00358 g. cotton thread gave ΔR_c = .26835 ohm. The heat generated in the combustion reaction was therefore

.26835 x 149.220 = 40.043 Kj

q_M = 2.872 Kj = the heat liberated from the combustion of .12543 g. melinex.

q_i = .058 Kj

q_n = .030 Kj

The heat of combustion of 1.09365 g. butan-2-one (calculated from the mass of CO_2 found) was given by 40.043 - (.058 + .030 + 2.872) = 37.093 Kj

The heat of combustion/g. mass $(-\Delta U^\circ_c/M) = \frac{37.093}{1.09365}$ = 33.917 Kj

The arithmetic mean of six acceptable experiments was taken and the value obtained was 33.901 ± .006 Kj/g. for the heat of combustion per gram mass.

The heat of combustion per mole of the actual bomb process $= \frac{33.901}{4.184}$ x 72.104 = -584.223 K cal/mole.

The total correction for reduction to standard states was

calculated by means of equation (82) derived by Washburn.[62]

(per cent. corr.) total = -.041

$-\Delta U^{o}c$ (decrease in intrinsic energy for the pure chemical reaction under standard conditions and at 25°C)

= 583.983 K cal./mole

by adding the work quantity $\Delta nRT = -1.5 \times 1.98718 \times 298.16$

= -.888 K cal. to $-\Delta U^{o}c$ the heat of the isobaric reaction at 1 atmosphere is given by $-\Delta H^{o}c$ = 584.87 K cal./mole.

The overall standard deviation to be applied to $-\Delta H^{o}c$ was calculated by the precision error method of Rossini[63] i.e.

$$\bar{S} = \sqrt{(\bar{S}E)^2 + (\bar{S}B)^2 + (\bar{S}\Delta U^{o}c)^2} = 0.05\%$$

where $\bar{S}E$ = .036% = standard deviation of the energy equivalent

$\bar{S}B$ = .012% = standard deviation of the heat of combustion of benzoic acid

$\bar{S}\Delta U^{o}c$ = .034% = standard deviation in $\Delta U^{o}c$

$\therefore -\Delta H^{o}c = 584.87 \pm .29$ K cal./mole

(10) Units and auxiliary quantities.

The heats of combustion are given in joules and derived heats of formation in thermochemical calories defined by 1 cal ≡ 4.1840 absolute joule.

The correction for the heat produced by the formation of nitric acid in the bomb at 25°C is calculated using the value of 59 Kj per mole of nitric acid formed. The corrections for the ignition energy due to combustion of the cotton fuse were based on the recommended value of 16.24 Kj/g. of cotton used. The corrections for the energy of combustion of the Melinex polyester containers were based on the heat of combustion measured by Skinner and Snelson i.e. $-\Delta U^{\circ}c$ = 22.902 $\pm$ .005 Kj/g true mass of Melinex. To correct weighings in air to mass in vacuo the density of Melinex (g/ml.) at 20°C was taken as 1.38.

Heats of formation $\Delta H^{\circ}f$ were calculated from the measured heats of combustion $\Delta H^{\circ}c$, assuming the values recommended in Cir. 500 (Nat. Bur. Stand., Washington, 1952) for $\Delta H^{\circ}f$ (CO_2, g.)
= -94.0518 K cal./mole, and $\Delta H^{\circ}f$ (H_2O, liq.) = -68.3174 K cal./mole.

The equation of state of oxygen was taken as

$$n_{O_2} = [PV/.08206T]\,[1 + (890 - 11.3\,\theta)\,10^{-6}\,P]$$

where P = Pressure in atmospheres

T = temperature in degrees Kelvin

θ = temperature in degrees centigrade (celsius)

V = volume in litres

n_{O_2} = number of moles of oxygen

The heat of combustion of carbon was based on the value of 33 Kj/g.

(11) Results.

The energy equivalent was redetermined following any change in the calorimeter system. The only large change made was the replacement of the insulated electrode of the bomb by one in which the mica was protected from underneath by a steel ring. Before acquiring the analytical balance the required constant amount of water in the calorimeter vessel was taken by volume. Although this method is not recommended for accurate work it was the only means at the time and it was thought that the error involved would be small because of the large amount of water used. However, six successive calibration experiments with benzoic acid in this way were precise to $\pm$ .06% and this was short of the precision aimed at. A considerable improvement occurred when the quantity of water was weighed to the nearest .01g. together with some other modifications. The bridge readings were corrected for. The tube containing the benzoic acid was kept in a dry atmosphere once it was opened because the relative humidity prevailing in the room was usually high. The results of six successive calibration experiments were then precise to $\pm$ .018% and was later improved with the acquired experience. The error in computing ΔRc was less than .01%. The lid of the calorimeter vessel was found to cause irregularities in the initial and final rates. This

was shown by a change in the fourth decimal in the resistance/ interval values of g_i and g_f. The lid has to be kept in position firmly to eliminate this factor which was due to loss of water by evaporation.

The carbon dioxide analysis of the bomb gases from Melinex combustions reported by Skinner was that 2.28620 g. carbon dioxide were produced per gram mass of the Melinex burnt. This figure was used in all the calculations and it corresponds to 99.824% purity of Melinex sample relative to the ideal formula $C_{10}H_8O_4$. Part of the deficit (.176%) was thought to be due to water retained by the Melinex film used and part due to deviation from the ideal formula. The mass of the compound burnt in each experiment was determined from the mass of carbon dioxide produced on combustion. This was usually slightly less than the weight of the compound introduced into the bomb as determined by direct rough weighing, the difference being due to pick up of water vapour during the process of filling and sealing the Melinex bag. The dry Melinex bag was accurately weighed in a dry weighing bottle. The filled bag was rolled and weighed directly and roughly in the crucible because it tended to leak in a large number of cases by many handlings. No attempt was made to dry the materials completely as when the amount of reaction is determined by weighing the quantity of

material used. However, the rough ratio of CO_2 produced to calculated was always as high as to indicate that the reaction was complete and the material was pure. This was also shown by the fact that the reactions were very clean witn no soot or carbon monoxide. The analytical method for determining CO_2 was shown to be reliable in experiments with benzoic acid.

The heats of combustion and of formation of the materials studied are represented in the tables below. The error limits concerning the heats of formation ($\pm$ .4 K cal./mole) include the standard errors in $-\Delta H^{\circ}c$ ($\pm$ .3 K cal./mole) and an error of $\pm$ .1 K cal./mole in the heats of vaporisation as determined by Lawlor. The following are the heats of vaporisation used in the calculations.

Compound	Heat of vaporisation at 25° (K cal. mole^{-1})
Butan-2-one	8.45
3-Methyl-butan-2-one	8.95
3-Methyl-butan-2-ol	12.65
3:3-Dimethyl-butan-2-one	9.25
3:3-Dimethyl-butan-2-ol	12.05
Pentan-3-one	9.2
Pentan-3-ol	12.7
Trimethylacetaldehyde	7.75
2:2:2-Trimethylethanol	13.35

The above heats of vaporisation were determined from the variation of Vapour-pressure with temperature by means of the integrated form of the Clapeyron-Clausius equation.

TABLE 1.

Determination of the energy equivalent of the standard calorimeter system.

Expt.		(1)	(2)	(3)	(4)	(5)	(6)
$ms/-\Delta EB(25)/$	(Kj)	39.6748	39.6196	39.7277	39.431	39.7194	39.5695
q_i	(Kj)	.0604	.0590	.0518	.0555	.0581	.0562
q_n	(Kj)	.0243	.0249	.0247	.0251	.0265	.0249
q_c	(Kj)	.0083	.0066	.0036	.0102	.0083	.0089
ΔRc	(ohm)	.26608	.26571	.26632	.26467	.26649	.26558
ϵ_f	Kj/ohm	149.459	149.449	149.474	149.326	149.394	149.334
ϵ_{sf}	Kj/ohm	149.276	149.263	149.288	149.143	149.205	149.145
ϵ_{sf}	mean	$149.220 \pm .027$ Kj/ohm					

TABLE 2

Butan-2-one

$CH_3\ CO\ CH_2\ CH_3$: m. w. = 72.104

ϵ_{sf} = 149.220 ± .027 Kj/ohm

Expt.	(1)	(2)	(3)	(4)	(5)	(6)
wt. of ketone (g)	1.09630	1.11785	1.06019	1.10441	1.12517	1.08009
q_M (Kj)	2.872	2.522	2.909	2.772	2.511	2.884
q_n (Kj)	.030	.030	.032	.036	.030	.027
q_i (Kj)	.058	.054	.058	.054	.048	.053
ΔR_c (ohm)	.26835	.26938	.25758	.26923	.27126	.26476
mass from CO_2 (g)	1.09365	1.10854	1.04511	1.10083	1.11799	1.07827
$-\Delta U^\circ_c/M$ (Kj/g)	33.917	33.910	33.907	33.895	33.889	33.890

$-\Delta U^\circ_c/M$ mean = 33.901 ± .006 (Kj/g

$\bar{S}E$ = 0.036%

$\bar{S}B$ = .012%

$\bar{S}_{\Delta U^\circ_c}$ = .034%

$\bar{S}$ = .05%

$-\Delta U^\circ_c$ = 583.98 ± .29 K cal./mole

Table 2 (cont.)

$-\Delta_n RT$	=	.89 K cal
$-\Delta H^\circ c$	=	584.87 ± .29 K cal./mole
$\Delta H^\circ f(CH_3COCH_2CH_3, liq.)$	=	- 64.60 ± .29 K cal./mole
$\Delta H_{vap.}$ (25°C)	=	8.45 K cal./mole
$\Delta H^\circ f(CH_3COCH_2CH_3, gas)$	=	- 56.15 ± .39 K cal./mole

TABLE 3

Determination of the energy equivalent of the standard calorimeter system.

Expt.		(1)	(2)	(3)
$\dot{m}s[-\Delta EB(25)]$	(Kj)	40.082	40.367	40.015
q_i	(Kj)	.058	.051	.055
q_n	(Kj)	.003	.013	.012
q_c	(Kj)	.004	.007	.010
ΔRc	(ohm)	.26833	.27028	.26789
ϵ_f	Kj/ohm	149.618	149.615	149.658
ϵS_f	Kj/ohm	149.432	149.429	149.472
ϵS_f	mean	$149.444 \pm .013$ Kj/ohm		

TABLE 4

Pentan - 3 - one

$CH_3\ CH_2\ CO\ CH_2\ CH_3$; m. w. = 86.13

$\epsilon S_f = 149.444 \pm .013$ Kj/ohm

Expt.	(1)	(2)	(3)	(4)
Wt of ketone (g)	1.04680	1.02954	1.04345	1.03355
q_M (Kj)	2.644	2.890	3.042	3.047
q_n (Kj)	.014	.015	.012	.014
q_i (Kj)	.058	.063	.057	.054
ΔR_c (ohm)	.26810	.26665	.27061	.26877
mass from CO_2 (g)	1.03816	1.02471	1.03846	1.02962
$-\Delta U^\circ c/M$ (Kj/g)	35.977	35.992	35.947	35.985

$-\Delta U^\circ c/M$ mean $= 35.975 \pm .010$ Kj/g

$\bar{S}E = .017\%$

$\bar{S}B = .012\%$

$\bar{S}\Delta U^\circ c = .054\%$

$\bar{S} = .058\%$

$-\Delta U^\circ c = 740.26 \pm .43$ K cal./mole

Table 4 (cont.)

$-\Delta nRT$	= 1.18 K cal
$-\Delta H^{\circ}c$	= 741.44 ± .43 K cal./mole
$\Delta H^{\circ}f$ ($CH_3CH_2COCH_2CH_3$, liq.)	= - 70.41 ± .43 K cal./mole
ΔH vap. (25°c)	= 9.2 K cal./mole
$\Delta H^{\circ}f$ (gas)	= -61.21 ± .53 K cal./mole

TABLE 5

Pentan-3-ol

$CH_3\ CH_2\ CH(OH)\ CH_2\ CH_3$; m. w. = 88.146

$\epsilon S_f = 149.444 \pm .013$ Kj/ohm

Expt.	(1)	(2)	(3)	(4)	(5)
Wt. of carbinol (g)	.99749	.99841	.99011	.98673	.98444
q_M (Kj)	2.951	2.860	2.931	2.972	2.912
q_n (Kj)	.012	.012	.012	.013	.012
q_i (Kj)	.051	.053	.056	.056	.057
ΔR_c (ohm)	.26904	.26862	.26742	.26706	.26592
mass from CO_2 (g)	.98934	.98996	.98344	.98018	.97710
$-\Delta U^\circ_c/M$ (Kj/g)	37.593	37.596	37.587	37.616	37.621

$-\Delta U^\circ_c/M$ mean $= 37.603 \pm .007$ Kj/g

$\bar{S}E = .017\%$

$\bar{S}B = .012\%$

$\bar{S}\Delta U^\circ_c = .036\%$

Table 5 (cont.)

$\bar{S}$	= .042%
$-\Delta U^{\circ}c$	= 791.96 ± .33 K cal./mole
$-\Delta nRT$	= 1.48 K cal.
$-\Delta H^{\circ}c$	= 793.44 ± .33 K cal./mole
$\Delta H^{\circ}f(CH_3CH_2CH(OH)CH_2CH_3,liq.)$	= -86.72 ± .33 K cal./mole
ΔH vap. (25°C)	= 12.7
$\Delta H^{\circ}f$ (gas)	= -74.02 ± .43 K cal./mole

TABLE 6

3:3-Dimethyl-butan-2-one

$C(CH_3)_3\ COCH_3$; m. w. = 100.156

ϵS_f = 149.444 ± .013 Kj/ohm

Expt.	(1)	(2)	(3)	(4)	(5)
Wt. of ketone (g)	.98283	.98029	.97909	.98471	.98258
q_M (Kj)	3.038	2.931	2.713	3.041	2.940
q_n (Kj)	.012	.012	.012	.012	.012
q_i (Kj)	.054	.055	.056	.059	.054
ΔR_c (ohm)	.26615	.26495	.26284	.26681	.26522
mass from CO_2 (g)	.98129	.97967	.97694	.98322	.97995
$-\Delta U^\circ c/M$ (Kj/g)	37.370	37.356	37.360	37.388	37.379

$-\Delta U^\circ c/M$ (mean) 37.371 ± .006 Kj/g

$\tilde{S}E$ = .017%

$\tilde{S}B$ = .012%

$\tilde{S}\Delta U^\circ c$ = .03%

$\tilde{S}$ = .037%

Table 6 (cont.)

$-\Delta U^{\circ}c$	= 894.25 ± .33 K cal./mole
$-\Delta nRT$	= 1.48 K cal
$-\Delta H^{\circ}c$	= 895.73 ± .33 K cal./mole
$\Delta H^{\circ}f$ ($C(CH_3)_3COCH_3$, liq.)	= -78.49 ± .33 K cal./mole
ΔH vap. (25°C)	= 9.25
$\Delta H^{\circ}f$ (gas)	= -69.24 ± .43 K cal./mole

TABLE 7

3:3-Dimethyl-butan-2-ol

$C(CH_3)_3 CHOH) CH_3$; m. w. = 102.172

$\epsilon S_f = 149.444 \pm .013$ Kj/ohm

Expt.	(1)	(2)	(3)	(4)	(5)
Wt. of carbinol(g)	.92683	.92389	.95005	.92867	.94066
q_M (Kj)	3.024	2.980	2.911	2.827	2.639
q_n (Kj)	.011	.011	.012	.012	.012
q_i (Kj)	.053	.056	.056	.058	.058
ΔR_c (ohm)	.25953	.25735	.26436	.25855	.26031
mass from CO_2 (g)	.92317	.91581	.94496	.92417	.93554
$-\Delta U^\circ c/M$ (Kj/g)	38.668	38.667	38.656	38.675	38.687

$-\Delta U^\circ c/M$ mean $38.671 \pm .005$ (Kj/g

$\bar{S}E = .017\%$

$\bar{S}B = .012\%$

$\bar{S}\Delta U^\circ c = .026\%$

Table 7 (cont.)

$\bar{S}$	= .033%
$-\Delta U^{\circ}c$	= 944.05 ± .31 K cal./mole
$-\Delta nRT$	= 1.78 K cal
$-\Delta H^{\circ}c$	= 945.83 ± .31 K cal./mole
$\Delta H^{\circ}f$ ($C(CH_3)_3CH(OH)CH_3$, liq.)	= -96.71 ± .31 K cal./mole
ΔH vap. (25°C)	= 12.05 K cal./mole
$\Delta H^{\circ}f$ (gas)	= -84.66 ± .41 K cal./mole

TABLE 8

3-Methyl-butan-2-one

$CH(CH_3)_2\ CO\ CH_3$; m. w. = 86.13

ϵS_f = 149.444 ± .013 Kj/ohm.

Expt.	(1)	(2)	(3)	(4)	(5)
Wt. of ketone (g)	.99357	1.00218	.99007	.99644	1.00388
q_M (Kj)	2.832	3.027	2.653	2.842	2.679
q_n (Kj)	.012	.012	.012	.011	.012
q_i (Kj)	.053	.057	.052	.054	.051
ΔR_c (ohm)	.25767	.26065	.25538	.25723	.25721
mass from CO_2 (g)	.99218	.99927	.98866	.99076	.99508
$-\Delta U^\circ_c/M$ (Kj/g)	35.891	35.883	35.855	35.865	35.872

$-\Delta U^\circ_c/M$ mean = 35.873 ± .006 Kj/g

$\bar{S}E$ = .017%

$\bar{S}B$ = .012%

$\bar{S}\Delta U^\circ_c$ = .036%

Table 8 (cont.)

$\bar{S}$	= .042%
$-\Delta U^{\circ}c$	= 738.16 ± .31 K cal./mole
$-\Delta nRT$	= 1.18 K cal
$-\Delta H^{\circ}c$	= 739.34 ± .31 K cal./mole
$\Delta H^{\circ}f$ ($CH(CH_3)_2COCH_3$, liq.)	= -72.51 ± .31 K cal./mole
ΔH vap. (25°C)	= 8.95 K cal./mole
$\Delta H^{\circ}f$ (gas)	= -63.56 ± .41 K cal./mole

TABLE 9

3-Methyl-butan-2-ol

$CH(CH_3)_2 CH(OH) CH_3$; m.w. = 88.146

$\epsilon S_f = 149.444 \pm .013$ Kj/ohm.

Expt.	(1)	(2)	(3)	(4)	(5)	(6)
Wt. of carbinol(g)	.98462	.97706	.99231	.98079	.98516	.99090
q_M (Kj)	2.964	3.008	3.075	2.922	2.937	3.009
q_n (Kj)	.011	.011	.011	.012	.011	.012
q_i (Kj)	.058	.052	.049	.058	.056	.050
ΔR_c (ohm)	.26643	.26494	.26909	.26535	.26650	.26811
mass from CO_2(g)	.98339	.97628	.99051	.97954	.98411	.98815
$-\Delta U^\circ c/M$ (Kj/g)	37.404	37.410	37.434	37.429	37.418	37.440

$-\Delta U^\circ c/M$ mean $= 37.423 \pm .006$ Kj/g

$\bar{S}E = .017\%$

$\bar{S}B = .012\%$

$\bar{S}\Delta U^\circ c = .03\%$

$\bar{S} = .037\%$

Table 9 (cont.)

$-\Delta U^{\circ}c$	= 788.17 ± .29 K cal./mole
$-\Delta nRT$	= 1.48 K cal
$-\Delta H^{\circ}c$	= 789.65 ± .29 K cal./mole
$\Delta H^{\circ}f$ ($CH(CH_3)_2CH(OH)CH_3$, liq.)	= -90.51 ± .29 K cal./mole
ΔH vap. (25°C)	= 12.65 K cal./mole
$\Delta H^{\circ}f$ (gas)	= -77.86 ± .39 K cal./mole

TABLE 10

Determination of the energy equivalent of the standard calorimeter system.

Expt.	(1)	(2)	(3)	(4)
$ms[-\Delta E_B(25)]$ (Kj)	39.879	38.784	39.294	39.012
q_i (Kj)	.060	.056	.051	.065
q_n (Kj)	.010	.009	.010	.009
q_c (Kj)	.006	.004	.006	.008
ΔRc (ohm)	.26699	.25961	.26293	.26130
ϵ_f Kj/ohm	149.650	149.659	149.701	149.613
ϵS_f Kj/ohm	149.464	149.473	149.515	149.427
ϵS_f mean	149.470 $\pm$ .018 Kj/ohm			

TABLE 11

2:2:2-Trimethylethanol

$C(CH_3)_3 CH_2 OH$; m. w. = 88.146

ϵS_f = 149.470 ± .018 Kj/ohm

Expt.	(1)	(2)	(3)	(4)
Wt. of carbinol (g)	.99935	.99582	1.00877	1.01152
q_M (Kj)	2.622	2.571	2.277	2.528
q_n (Kj)	.015	.010	.012	.014
q_i (Kj)	.058	.059	.058	.056
ΔRc (ohm)	.26734	.26635	.26780	.27027
mass from CO_2 (g)	.99537	.99247	1.00674	1.00912
$-\Delta U^\circ c/M$ (Kj/g)	37.437	37.453	37.429	37.457

$-\Delta U^\circ c/M$ mean 37.444 ± .007 Kj/g

$\bar{S}E$ = .024%

$\bar{S}B$ = .012%

$\bar{S}\Delta U^\circ c$ = .036%

Table 11 (cont.)

$\bar{S}$	= .045%
$-\Delta U^{\circ}c$	= 788.61 ± .35 K cal./mole
$-\Delta nRT$	= 1.48 K cal
$-\Delta H^{\circ}c$	= 790.09 ± .35 K cal./mole
$\Delta H^{\circ}f$ ($C(CH_3)_3CH_2OH$, Solid)	= -90.07 ± .35 K cal./mole
ΔH vap. (25°C)	= 13.35 K cal./mole
$\Delta H^{\circ}f$ (gas)	= -76.72 ± .45 K cal./mole

TABLE 12

Trimethylacetaldehyde

$C(CH_3)_3 C HO$; m. w. = 86.13

ϵS_f = 149.470 ± .018 Kj/ohm

Expt.	(1)	(2)	(3)	(4)	(5)
Wt. of aldehyde (g)	.94346	.98758	.97660	.99704	.98611
q_M (Kj)	3.158	3.091	3.048	2.951	3.124
q_r (Kj)	.013	.014	.012	.014	.054
q_i (Kj)	.049	.056	.053	.055	.063
ΔR_c (ohm)	.25196	.26177	.25899	.26337	.26183
mass from CO_2 (g)	.94293	.98541	.97501	.99499	.98295
$-\Delta U^\circ_c/M$ (Kj/g)	36.524	36.499	36.510	36.531	36.518

$-\Delta U^\circ_c/M$ mean = 36.516 + .006 Kj/g

$\bar{S}E$ = .024%

$\bar{S}B$ = .012%

$\bar{S}\Delta U^\circ_c$ = .032%

$\bar{S}$ = .042%

Table 12 (cont.)

$-\Delta U^{\circ}c$	= 751.40 ± .32 K cal./mole
$-\Delta nRT$	= 1.184 K cal
$-\Delta H^{\circ}c$	= 752.58 ± .32 K cal./mole
$\Delta H^{\circ}f$ ($C(CH_3)_3CHO$, liq.)	= -59.26 ± .32 K cal./mole
ΔH vap. (25°C)	= 7.75 K cal./mole
$\Delta H^{\circ}f$ (gas)	= -51.51 ± .43 K cal./mole

PART B.

II. DISCUSSION.

Our main interest is in the derived heats of hydrogenation of the studied carbonyl compounds from the measured heats of combustion. Substituent effects in heats of hydrogenation will be considered in some detail. However, bond energy terms and the deviation from additivity of the heats of combustion of alcohols and carbonyl compounds are first compared with the literature values.

(1) The heats of combustion of some alcohols and carbonyl compounds.

The heats of combustion of ketones, aldehydes and alcohols that have been reported in the literature are frequently unreliable. Some of the more recent work has been done with great care and reliable values are available.

The mean bond energy term, $\bar{E}$ (C : O), in each of the studied carbonyl compounds was derived by using -

(a) the $-\Delta H^{o}f$ terms, CO_2 94.05 and H_2O 68.32 K cal./mole,

(b) the heats of atomisation ΔHa, graphite 171.7, $\frac{1}{2}$ H_2 (g) 52.09, $\frac{1}{2}$ O_2(g) 59.16 K cal./g. atom

(these are the currently accepted 'best' values see e.g. 'Selected values of chemical thermodynamic properties' Nat. Bur. Stand. Cir. 500, Washington, 1952), and

(c) the mean bond energy terms $\bar{E}$, C - C 83.1, C - H 98.85 K. cal.

The results obtained are represented in Table 1.

TABLE 1

Energy term (in K cal./mole)

Compound.	$-\Delta H^{o}c$	$-\Delta H^{o}f$	ΔHvap.	$\bar{E}$(C:O)
Butan-2-one	584.87	64.60	8.45	178.7
3-Methyl-butan-2-one	739.34	72.51	8.95	181.2
3:3-Dimethyl-butan-2-one	895.73	78.49	9.25	182.0
Pentan-3-one	741.44	70.41	9.20	178.9
Trimethylacetaldehyde	752.58	59.26	7.75	169.2

The mean value of the $\bar{E}$ (C:O) terms for the mono-ketonic compounds is 180.2 k cal.

Springall and White[64] derived the mean bond energy term, $\bar{E}$ (C:O), for the carbonyl system in certain ketones.

The above-mentioned quantities necessary for the derivation were used. The mean value obtained, 179.6 K cal./mole, was considered reasonably concordant with Pauling's value. The recent values given by Pauling[65] for the $\bar{E}$ (C:O) are as follows:

164 K cal. in formaldehyde, 171 K cal. in other aldehydes and 174 K cal. in ketones.

Our mean value of the $\bar{E}$ (C:O) terms is in agreement with Springall's [e]. The $\bar{E}$ (C:O) term in trimethylacetaldehyde is very reasonably concordant with Pauling's value for aldehydes.

The derived mean bond energy terms, $\bar{E}$ (O - H), in the studied carbinols are summarised in Table 2.

The same quantities as before were used in driving $\bar{E}$ (O - H) terms together with Coat[e]'s value for $\bar{E}$ (C - O). Coats[ef] and Sutton[66] gave a value of $\bar{E}$ (C - O) = 85.5 K cal. using the heats of atomisation ΔHa, C 171.6, H 51.71 and O 58.9 K cal./g-atom. This value gave the best fit to the values for the heats of formation of alcohols[67] using the mean bond energy terms $\bar{E}$, C-C 83.0, C-H 98.45 and O-H 110.0 K cal. $\bar{E}$(O-H) = 110.0 K cal. is based on the low value of the heat of atomisation ΔHa, graphite 126.3 K cal./g-atom.

TABLE 2.

Compound.	$-\Delta H^{o}c$	$-\Delta H^{o}f$	ΔHvap.	$\bar{E}$(O-H)K cal.
Butan-2-ol	635.91	81.88	11.82	112.5
3-Methyl-butan-2-ol	789.65	90.51	12.65	115.4
3:3-Dimethyl-butan-2-ol	945.83	96.71	12.05	117.2
Pentan-2-ol	793.44	86.72	12.70	111.5
2:2:2-Trimethylethanol	790.09	90.07	13.35	114.2

The general agreement among the $\bar{E}$ (O-H) terms is reasonably good and the mean value, 114.2 K cal., agrees with the values derived from heats of formation of alcohols by Rossini and Skinner. The heats of formation and vaporisation for butan-2-ol are those given by Skinner.

The deviation from additivity of the heats of combustion of alcohols and carbonyl compounds determined in this study is represented in Table 3.

The same heats of vaporisation used in previous calculations were used to obtain the heats of combustion of the compounds, H, in the gas state.

The values for the heats of combustion in the gas state of the corresponding paraffins, H_o, were taken from 'Selected values of properties of hydrocarbons (A.P.I. Research Project 44), 1952.'

TABLE 3

Compound	n	H	H_o	H_o - H	
Me CHOH Pr^i	2	802.30	843.24	40.94	mean 40.09
Me CHOH Bu^t	2	957.88	998.17	40.31	
Et CHOH Et	2	806.14	845.16	39.02	
$Me_3C.\ CH_2OH$	1	803.44	840.49	37.05	
Me CO Et	2	593.32	687.98	94.66	mean
Me CO Pr^i	2	748.29	843.24	94.95	

Table 3 (cont.)

Me CO Bu^t	2	904.98	998.17	93.19	94.33
Et CO Et	2	750.64	845.16	94.52	
Me_3C. CHO	1	760.33	840.49	80.16	

In Table 3 the values of H_o - H and n follow the same relation derived by Dewar and Pettit[68] for the apparent bond energy between carbon and a hetero-atom i.e. Ecx = (Ecx)o + nA. Where (Ecx)o is the value of Ecx for the methane derivative and n is the number of carbon atoms adjacent to the C-X bond. In the case of carbonyl compounds, the comparison will be between R_2 CO and R_2 CH_2. A is a measure of chain-branching in the corresponding paraffin. The branching factor is eliminated by comparing the heats of formation of the hetero-compounds with those of corresponding paraffins. In practice heats of combustion have been used in place of heats of formation, the differences between these will differ from ($\Delta H - \Delta H_o$) for a given series of compounds only by a constant term.

In case of alcohols the H_o - H values obtained by Dewar for n = 2 and n = 1 were 40.7 and 37.0 respectively. These values are in very close agreement with ours. However, the agreement is reasonably good in case of carbonyl compounds,

where Dewar's H_o - H values for n = 2 and n = 1 are 97.5 and 88.1 respectively and our values are 94.33 and 80.16 respectively. No references were given as to the source from which the heats of combustion used in Dewar's calculations were quoted. The heats of combustion of alcohols seem to have been taken from reliable sources,[67] but most of those of carbonyl compounds are probably unestablished or old values.

(2) Substituent effects in reaction energies

The reaction energy (heat of reaction, free-energy change, or activation free energy) is affected by inductive interactions, resonance stabilisation, and steric interactions of the substituents with reactant and with product functional groups (product ≡ transition state when activation energies are being considered).

Closely allied to each of the above potential energy effects is the influence of intramolecular kinetic energy (the kinetic effect). Part of the energy of a molecule lies in vibrational and rotational motions so that changes in the molecule which modify the restrictions of these motions alter the kinetic energy content of the molecule. It appears reasonable to suppose that a decrease in the degrees of freedom within the molecule diminishes both the

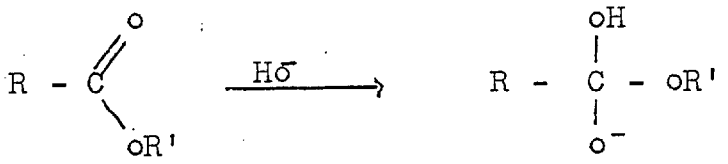
kinetic-energy content and the entropy of the molecule. For the purpose of this discussion the expression 'effect of the kinetic energy content' will be written as 'enthalpic effect'.

Another factor which influences the vibrational and rotational energy levels is the mass of the molecule. The conditions required for this ponderal substituent effect to be observed in a reaction energy[69] is that there must be large differences between the masses of reactant and product molecules, and between the masses of the substituents. The ponderal effect was found to have considerable importance in halide/alkyl halide exchange reactions in which the requisite mass differences are large.

a) Effect of kinetic-energy changes on reaction energies.

Consider a series of compounds with a common functional group. When the functional group undergoes a reaction the hindrances to intramolecular motions are altered. It is reasonable to suppose that these alterations cause a greater change in the hindrances to intramolecular motions of highly hindered molecules than in those molecules whose internal movements are relatively free.[70] This principle is the basis of the discussion of kinetic effects throughout the thesis.

As an example of the effect of kinetic energy we may consider alkaline ester hydrolysis. The rate-determining step is thought to be:-



The hindrance to internal motion is greater in the transition state than in the reactant because of the introduction of a group and the decrease in the bond angles. Therefore, if R is t-butyl the decrease in kinetic-energy content during the reaction is greater than the decrease in kinetic energy content when R is ethyl. Hence the free-energy of activation would be less positive when R is t-butyl than when R is ethyl, if no other kinetic effect were operating. When R is t-butyl the decrease in the entropy of reaction is greater than that when R is ethyl, so that the entropic effect tends to enlarge the free-energy of activation as the ability of the substituents to hinder the motions of the reaction centre increases.

In general it is not yet possible to calculate the magnitudes of the mutually opposing enthalpic and entropic effects, and only the entropy change is experimentally observable.

It is found that reactions, which lead to products having greater hindrances to intramolecular motions than the reactants, are retarded by substituents which can interfere with intramolecular motions at the reaction centre, even when there is no significant change in steric strain during the reaction.[8,71] Since enthalpic effects would cause an acceleration of the reaction with increasing substituent bulk, entropic effects must normally be greater than enthalpic effects.

b) Linear potential-energy relationships.

The inability to deduce reaction energies mathematically has obliged chemists to attempt the empirical correlation of substituent effects with energies of reaction. In order to establish general systems for the correlation and prediction of reaction energies the available experimental reaction energies must be broken down into components which may be attributed to the various substituent effects. The most successful correlations are based on the assumption that a substituent effect is the sum of independent inductive, resonance and steric effects.

The presence of four substituent effect variables makes the correlation of measurements, which are somewhat imprecise in the field of reaction energies, a complex and difficult proceedure. Initially, therefore, reaction series in which some of the substituent effects were to

be small were examined. Systems in which steric and kinetic substituent effects would be small are the reactions of functional groups whose substituents are p- and m- substituted phenyl groups; and it was with these systems that the earliest of the successful correlations were achieved. This type of reaction series is made all the more suitable for study by the absence of neighbouring group effects and by the constancy of reaction mechanism within a reaction series.

i) The Hammett Equation.

The Hammett inductive substituent effects, σ values, referred to previously usually contain contributions from resonance effects because most substituents in the para position undergo resonance with the reaction centre. The Hammett equation frequently fails to correlate reaction energies because the resonance effects and hence the effective σ values may vary markedly according to the nature of the reaction. The use of the p-NO_2 σ value obtained from the ionisation of benzoic acids leads to the failure of Hammett's equation to correlate the free energy of protonation of p-nitraniline with those of other anilines.[72]

The rates of hydrolysis of aliphatic esters and of O-substituted benzoic esters are not correlated by Hammett's method using σ values derived from the ionisation constants

of the carboxylic acids.[73,74] This failure is due to non-constant steric and kinetic energy differences between reactant and product (transition state) throughout the reaction series and the failure of these differences to parallel the inductive substituent effect.

ii) The Taft Equation.

Taft's way to isolate quantitative measures of inductive effects of substituents by a method in which the effects of resonance, steric strain, and kinetic energy were cancelled was referred to before. This method is based on the assumption that resonance and steric effects are virtually the same in both acid and base catalysed ester hydrolysis.[75]

Substituent effects which have been found by empirical correlations, such as Taft's and attributed to particular potential energy interactions should not be dogmatically accepted as evidence, or measures, of particular potential--energy substituent effects[76] until the possibility that they might have arisen from other sources has been discounted.

Taft has developed two methods of isolating resonance effects of p-substituents in the reactions of p- and m-substituted phenyl derivatives.[77] Both methods derive from his equation.

Resonance substituent effect, $R = \log(kP/ko) - \sigma^* \rho^*$ (1)

$$R = (1-\alpha)^{-1} . \log(kP/km) \quad (2)$$

kP, km, and kO refer to the rates of reaction of p-substituted, m-substituted, and unsubstituted phenyl derivatives respectively. The reduction of the resonance effect when a substituent is moved from the para to the meta position is represented by α which is constant for a given reaction series. Equation (2) is based on the assumption that σ^* is essentially the same in both para and meta positions.[78]

Taft and Lewis have analysed the rate data of twenty-nine reaction series of p- and m-alkyl substituted phenyl derivatives.[77] For each reaction series the substituent resonance effects (R values) were isolated. Since hyperconjugation was the only resonance effect of which the alkyl groups were capable the R values were taken as a measure of the change in the net hydrogen and carbon hyper conjugation of the alkyl group with the reaction centre during reaction. It was found that the R values were correlated by the relationship.

$$R = n_H h_H + n_c h_c \quad (3)$$

Where h_H and h_c were the magnitudes of the hyper conjugation effects of an α-hydrogen atom and of a β-carbon atom respectively, and n_H and n_c the numbers of α-hydrogen

atoms and of β-carbon atoms respectively. The ratio of h_H to h_c was found to be 1.3 ± 0.1 and represented the relative conjugative capacities of C - H and C - C bonds in p-alkyl groups.

Adkins' carbonyl-carbinol equilibrium constants are of particular interest since they yield free energies of hydrogenation of a number of the ketones in which we are interested. The results for unconjugated carbonyl compounds were analysed by Taft's technique[79] and they were correlated by the equation.

$$\Delta G^{\circ} - \Delta G^{\circ}_{o} = (-6.0 \pm .5).\ (\sigma^*) + n_H\, h_H + n_c\, h_c$$

The data correlated by the equation were inaccurate ($\Delta G^{\circ} - \Delta G^{\circ}_{o}$ being known to $\pm$ .4 K cal./mole). Consequently the parameters of the correlation were uncertain. The results for $\alpha:\beta$-unsaturated and aryl-carbonyl compounds have also been analysed and the relationships of R values to structure are those expected from resonance theory.[80] However, it has been shown before that Adkins' method was unsound.

(3) The heats of hydrogenation of six carbonyl compounds.

TABLE 4

Compound	$-\Delta H$ (K cal./mole^{-1}) calculated	Gas state at 25°C observed (Lawlor)
Acetone	13.35	13.2
Butan-2-one	13.95	13.7
3-Methyl-butan-2-one	14.30	14.0
3:3-Dimethyl-butan-2-one	15.42	15.4
Pentan-3-one	12.81	13.1
Trimethylacetaldehyde	25.21	16.7

The heats of hydrogenation in the second column of Table 4 were calculated as the difference between the heats of formation in the gas state at 25°C of the carbinols and the corresponding carbonyl compounds.

The value for acetone was derived from accepted values for the heats of formation of acetone and isopropanol.

The heat of combustion of acetone vapour, measured at 25°C in a flame calorimeter by Miles and Hunt[81] corresponds[82] to $\Delta H^{\circ}f$ (acetone, gas) = -51.72 K cal./mole.

Skinner measured the heat of combustion of isopropanol and his value together with ΔH vap. (calculated from heat of vaporisation data by Harrison and Williams[83]) leads finally to $\Delta H^{\circ}f$ (isopropanol, gas) = -65.07 K cal./mole.

Therefore, $\Delta H = -65.07 - (-51.72) = -13.35$ K cal./mole for the reaction.

$$\text{Me Co Me}_{(g)} + H_{2(g)} \longrightarrow \text{MeCHOH Me}_{(g)}$$

with the reactants and product at 25°C in the gaseous state. The value for butan-2-one was derived from Skinner's reliable value of $\Delta H^{\circ}f$ (Sec-butanol, g) = -70.1 K cal./mole and our value of $\Delta H^{\circ}f$ (Butan-2-one, g) = -56.15 K cal./mole.

(a) Comparison of Results with Literature Values.

Kistiakowsky[18e] measured the heats of hydrogenation of acetone, butan-2-one, and acetaldehyde at 82°C in the gas state, and his values for these compounds were $-13.41 \pm .1$, $-13.19 \pm .1$ and $16.75 \pm .1$ K cal./mole respectively.

Lawlor mentioned that extrapolation of his values for acetone and butan-2-one to lower temperature would yield hydrogenation enthalpies of lesser magnitude and therefore a substantial disagreement between his result for butan-2-one and that of Kistiakowsky. However, on correcting Kistiakowsky's observed heats of hydrogenation for acetone and butan-2-one at 82°C to 25°C using proper heat capacity data by Pennington and Kobe and by Dolliver et al. the results are -13.58 and -12.95 K cal. mole^{-1} respectively. It can be seen that Lawlor's value for butan-2-one is actually in better agreement with Kistiakowsky's one than his value for acetone. Our value

for butan-2-one is in excellent agreement with that of Kistiakowsky. This shows that all the three calorimeters give concordant result. There is a large disagreement between our derived heat of hydrogenation for trimethylacetaldehyde and that of Lawlor. However, the bond energy term $\bar{E}$ (C:O) in trimethylacetaldehyde agrees with the value for aldehydes as shown above. Lawlor's value for trimethylacetaldehyde is close to that of Kistiakowsky for acetaldehyde. A higher heat of hydrogenation of trimethylacetaldehyde than acetaldehyde should be expected if hyperconjugation is called upon to explain differences in the heats of hydrogenation of carbonyl compounds.

The heats of combustion of butanal and 2-ethyl--hexanal, together with those of the corresponding alcohols, have been recently determined.[48] The heats of hydrogenation in the liquid state, calculated from the heats of combustion, are 22.5 K cal.mole^{-1} and 20.1 K cal.mole^{-1} for butanal and 2-ethyl-hexanal respectively. Heat measurements with aliphatic aldehydes are notoriously difficult to carry out with precision because of the tendency of aldehydes to condense and to polymerise. In the absence of independent evidence we have no means of deciding whether Lawlor's or our result for trimethylacetaldehyde is the more correct.

(b) The pattern of the results.

There are some well-defined trends between the heats of hydrogenation and the corresponding carbon-atom contents of the molecules examined (cf. Table 4). The discussion applies also to the heats of combustion.

The methyl ketones fall into a group with an almost linear increase (within experimental error) in the heats of hydrogenation. The heat of hydrogenation of the ethyl ketone studied, namely pentan-3-one is considerably less exothermic than the isomeric methyl ketone.

The heats of hydrogenation of the ketones increase as the electronegativities of the substituents decrease. The heats of hydrogenation increase as the number of α-hydrogen atoms per molecule decrease.

(c) The qualitative analysis of the results.

An increase in the electronegativities of the substituents attached to a carbonyl group raises the energy of a carbonyl compound by withdrawing electrons from the highly electronegative carbonyl group. The corresponding increase in the energy of an alcohol is much less because the carbonyl group is more electronegative and polarisable than the carbinol group. Therefore the heats of hydrogenation of aldehydes and ketones should increase with increasing electron-withdrawing power of the substituents. Thus induction produces effects in the opposite direction to those observed.

Hyperconjugation reduces the energy of carbonyl compounds by releasing electrons to satisfy the electron demand of the carbonyl oxygen, and by delocalising electrons over the H-C-C = o system. No such mechanism is available to lower the energies of the corresponding alcohols. It follows that the heats of hydrogenation of carbonyl compounds should tend to decrease with an increase in the number of α-hydrogen atoms. The trend of the heats of hydrogenation is, qualitatively, the one expected from consideration of hyperconjugation.

Steric strain should increase with molecular weight in the series of ketones which we are discussing. The strain is more important in the alcohols than in the corresponding ketones (due to reduction in bond angles) so that the heats of hydrogenation of the ketones should be reduced as the molecular weight increases.

There is no evidence of appreciable steric strain in any of the molecules in which we are interested, or in the saturated hydrocarbons formally derived from our alcohols by replacing -oH by $-CH_3$.

If no kinetic effects occur in the energies of hydrogenation, Taft's equation would give the same correlation for the heats of reaction and the free-energies of reaction. The results of applying Taft's equation to the

prediction of our results are shown in Table 5. The parameters employed are those obtained from Adkins' results.[79] It will be seen from Table 5 that there is not the slightest agreement between our values and Taft's correlation of Adkins' results.

Although the numerical values of Adkins' measurements cannot be accepted with confidence, the differences between the effect of a substituent in a free-energy of hydrogenation and its effect in the corresponding heat of hydrogenation is thought to be significant.

The fact that $\Delta G^{\circ} - \Delta G^{\circ}_{o}$ is not generally equal to $\Delta H^{\circ} - \Delta H^{\circ}_{o}$ clearly demonstrates that kinetic substituent effects contribute to $\Delta G^{\circ} - \Delta G^{\circ}_{o}$ and/or $\Delta H^{\circ} - \Delta H^{\circ}_{o}$.

TABLE 5

Prediction of substituent effects in the heats of hydrogenation of R_1 CO. R_2 (Acetone standard)

R_1	R_2	a	b	c	(a + b + c)	$\Delta H^\circ - \Delta H_o^\circ$ expl.
		-6x6*	n_H=6x0.5	n_c x .2	$(\Delta H^\circ - \Delta H_o^\circ)$ calc.	
Me	Me	0.0	0.0	0.0	0.0	0.0
Et	Me	+ .6	- .5	+ .2	+ .3	- .60
i-Pr	Me	+1.1	-1.0	+ .4	+ .5	- .95
t-Bu	Me	+1.8	-1.5	+ .6	+ .9	- 2.07
Et	Et	+1.0	-1.0	+ .4	+ .6	+ .54
t-Bu	H	-1.1	-3.0	- .6	-3.5	-11.86

TABLE 6

Entropic effects in the relative free-energies of hydrogenation of R_1 CO. R_2. (Acetone standard).

R_1	R_2	$\Delta G^\circ - \Delta G_o^{\circ(i)}$	$\Delta H^\circ - \Delta H_o^\circ$	$-T(\Delta S^\circ - \Delta S_o^\circ)$
Me	Me	0.0	0.0	0.0
Et	Me	+ .3	- .6 ± .52	+ .9
i-Pr	Me	+ .3	- .95 ± .56	+ 1.25
t-Bu	Me	+ .4	- 2.07 ± .59	+ 2.47
Et	Et	+ .9	+ .54 ± .68	+ .36
t-Bu	H	- 3.8	-11.86 ± .62	+ 8.06

(i) From a Table of Reference 80 P.4011

In view of the doubts expressed concerning Adkins's free-energy data, only the magnitudes of $-T(\Delta S^\circ - \Delta S_o^\circ)$ are considered to be significant. Nothing is known about the magnitude of the enthalpic effect except that it is probably less than the entropic effect.

An increase in the exothermicity of the heats of hydrogenation with an increasing number of methyl groups attached to the α-carbon atoms can be readily explained in terms of kinetic effects. The hindrances to intramolecular motions are greater in the alcohols than in the ketones,

(1) because the bond angles about the carbinol carbon atom are less than those about the carbonyl carbon atom, and

(2) because there is one more hydrogen atom on the carbinol-carbon atom than on the carbonyl-carbon atom.

This means that the kinetic - energy content of an alcohol is more sensitive to α-substitution than that of the corresponding ketone. Therefore the decrease in kinetic-energy during the hydrogenation becomes greater with increasing α-substitution of the ketones. Since the decrease in kinetic--energy content is largest for the hydrogenation of carbonyl compounds with the highest degree of α-substitution, the heats of hydrogenation tend to be greatest for the highly-branched ketones.

If the experimental substituent effects are the products of kinetic factors alone, $\Delta G^{\circ} - \Delta G^{\circ}_{o}$ should be of opposite sign to $\Delta H^{\circ} - \Delta H^{\circ}_{o}$ and it would be expected that the magnitude of $\Delta G^{\circ} - \Delta G^{\circ}_{o}$ should be approximately proportional to the magnitude of $\Delta H^{\circ} - \Delta H^{\circ}_{o}$. In the case of pentan-3-one the sign of $\Delta G^{\circ} - \Delta G^{\circ}_{o}$ is probably the same as that of $\Delta H^{\circ} - \Delta H^{\circ}_{o}$. This would indicate that appreciable potential energy factors are involved in determining the overall substituent effects.

The evidence considered in this section shows that it is highly probable that potential-energy effects and kinetic-

energy effects contribute to the observed effects of substituents upon the energies of hydrogenation. At the present time no conclusions can be drawn concerning the relative importance of the effects discussed above.

One of the interesting features of our results is the existence of large differences between the heats of hydrogenation of isomeric carbonyl compounds which are not readily attributed to potential-energy effects alone.

If the inductive effect were to be employed to account for an appreciable difference between the heats of hydrogenation of ketone isomers, Taft's ρ^* value would have to be of the order of -10 to -20 K cal.mole^{-1}, and to account for the whole isomer difference ρ^* would have to be of the order of -60 to -70 K cal.mole^{-1}. The highest ρ^* value that Taft has observed is less in magnitude than -8 K cal.mole^{-1}. It is therefore highly improbable that the inductive effect plays any part in determining the isomer differences.

Steric interaction in the product lowers the enthalpy change for a hydrogenation process. Steric strain would be more important in a methyl ketone series than in ethyl ketone series. Therefore, steric strain would produce an isomer difference opposite to that obtained i.e. a reduced heat of hydrogenation for the methyl ketone.

The differences between the heats of hydrogenation of isomeric carbonyl compounds are most easily explained on the basis of enthalpic effects. Restriction of intra--molecular motions by non-bonded interactions is expected to be greater in a methyl ketone than in an isomeric ethyl ketone. Hence the change in kinetic-energy content during the hydrogenation of a methyl ketone exceeds the corresponding change which occurs during the hydrogenation of the isomeric ethyl ketone. The fact that the heats of combustion of branched hydrocarbons are considerably less than those of the straight chain isomers, the 'Rossini effect',[84] provides excellent support for the enthalpic interpretation of our isomer differences.

The kinetic effects have been discussed here only in terms of hindrances to intramolecular vibrations and rotations. There are substantial changes in the force constants of the molecules during hydrogenation which may bring about an appreciable difference between the vibrational energies of the reactant and product molecules.

A substituent effect is generated if this vibrational--energy difference is not constant from compound to compound. It is not known whether such a substituent effect augments or reduces the effect of hindrances to intramolecular motions.

The heats of hydrogenation of aldehydes are normally greater than those of ketones, and this is probably due to the inductive effect of the hydrogen atom attached to the carbonyl carbon.

(4) CONCLUSIONS

It was emphasised that induction and hyperconjugation both play a part in determining substituent effects in the heats of hydrogenation of aldehydes and ketones. The directions of the potential-energy effects were indicated. The application of Taft's parameters, derived from Adkins' results, to the prediction of our results led to complete disagreement. The enthalpic effect was considered the most important of all substituent effects in the heats of hydrogenation of ketones.

There can be little doubt that Adkins' equilibration method is unsound. The effect of varying the catalyst concentration on the carbonyl-carbinol equilibrium constants was investigated in more detail.

The determination of the relative importance of the substituent effects is not even qualitatively possible at present. Empirical correlations lead to dubious conclusions unless a large number of data are available to enable a meaningful statistical analysis to be carried out. So many effects may operate that some of the possibilities must be eliminated or estimated before our results can be fully analysed.

The derived heats of hydrogenation from the measured heats of combustion gave support to those accurately

determined either by catalytic hydrogenation in the vapour phase or by hydrogenation in solution using metal hydrides as a source of hydrogen. Bond energy terms and the deviation from additivity of the heats of combustion of alcohols and carbonyl compounds agreed with the literature values. The deviation from additivity of the heats of combustion was correlated by equations derived by modern mathematical treatment. The principle of additivity of bond energies cannot account for the observed difference between the heats of combustion of isomeric carbonyl compounds.

That bond energy terms are average quantities was clearly shown. The carbonyl bond has three different values corresponding to formaldehyde, other aldehydes and ketones.

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