SOME KINETIC STUDIES ON KETONE FORMATION

THESIS

submitted for the
Degree of Doctor of Philosophy
at
Glasgow University
by
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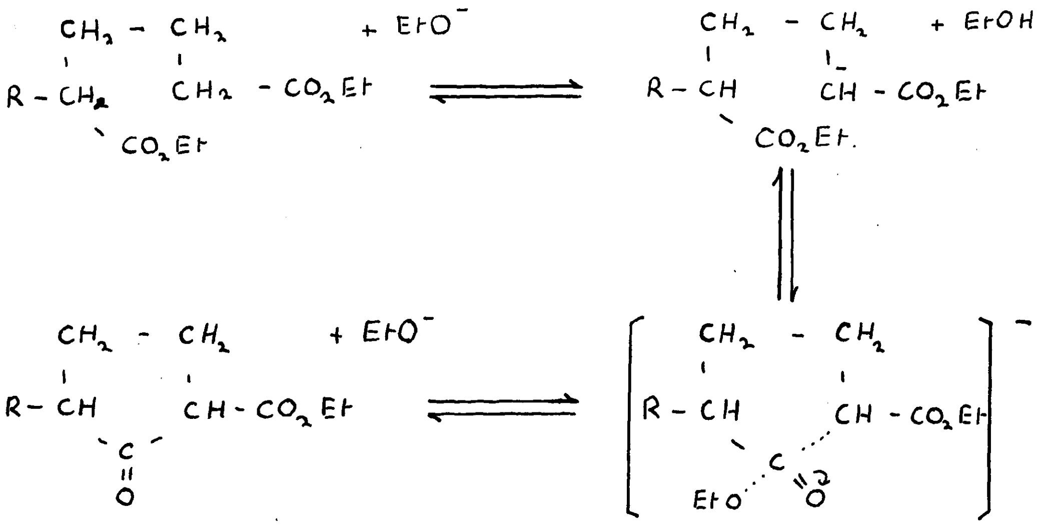
SUMMARY.

The thesis consists of two parts. In the first, a kinetic study was made of the Dieckmann ring closure of α- and β-alkyl-substituted esters of adipic acid. This may be considered as an intramolecular Claisen condensation, where the accepting carbonyl centre is influenced by the alkyl substituent R, while the attacking centre is non-substituted. The reaction has been studied for +I substituents, which, according to current theories, should decelerate nucleophilic substitution.

A reaction mechanism has been proposed, which requires that the rate determining process is the making or breaking of the relevant carbonyl carbon - carbon bond, or, regarding this reaction as a typical carbonyl addition, the slow step is the union of the anion produced by base extraction, with the carbonyl group.

This may be represented as follows -



R = H, CH_3, C_2H_5 and i-C_3H_7.

Part two is a kinetic study of the pyrolytic decomposition of sodium salts of adipic acid, β-methyladipic acid and acetic acid. The results show that the order of reaction in each case is integral, which indicates that the mechanism is ionic rather than free radical.

The decomposition of disodium adipate, has been considered to be an autocatalytic reaction of the first order, while that of β-methyladipic acid is unimolecular. Pyrolysis of sodium acetate to yield acetone, however is more complicated. For about 50% of its course, the pyrolysis obeys a second order rate equation, but as the reaction proceeds further, the order becomes complex. It was also noted that at higher temperatures - above 480°C. - the kinetics could not be resolved, which seems to indicate a change of mechanism.

As most measurements were made below 450°C., the results are discussed by means of an ionic mechanism, which seems fitted to explain the known data.

Part I

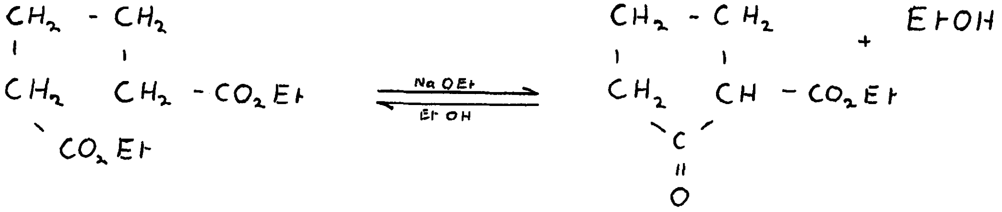
A Kinetic Study on the Dieckmann Ring Closure of Diethyl Adipate and its Alkyl Substituted Homologues.

HISTORICAL INTRODUCTION

The reaction bearing the name of Claisen was first carried out by Guether in 1863 (1, 2) but it was not until 1887 and later, that it was generalised and extended. Claisen then investigated the general chemistry of the condensation (3), and proposed a mechanism for the reaction.

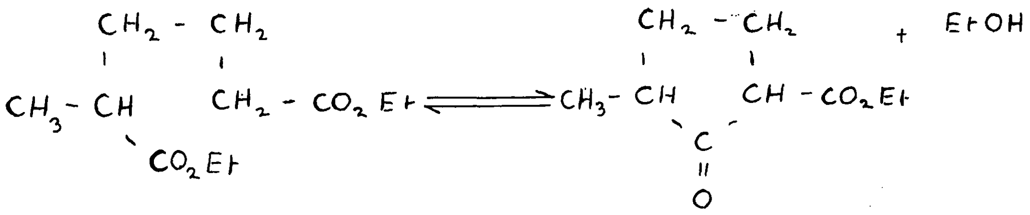
The Claisen condensation consists of reaction between a carboxylic ester, and an active methylene compound e.g. ester, nitrile, or carbonyl compound, containing at least one α-hydrogen atom. The product is a β-keto-compound, or in the case of formic ester a β-aldehydo-compound. The condensing agent is usually sodium ethoxide in anhydrous ethyl alcohol, or solid sodium ethoxide. Since the mechanism of this reaction has become more fully investigated, more powerful condensing agents have been discovered, e.g. sodamide, mesityl magnesium bromide and sodium triphenylmethylide.

Following the example of Claisen and others (4, 5, 6) Dieckmann (7) developed the use of this reaction for ring closure. The Dieckmann reaction is the intramolecular condensation of the esters of certain dicarboxylic acids, in the presence of sodium ethoxide to give cyclic 2-carbethoxy-ketonic compounds.
For example, diethyl adipate:-



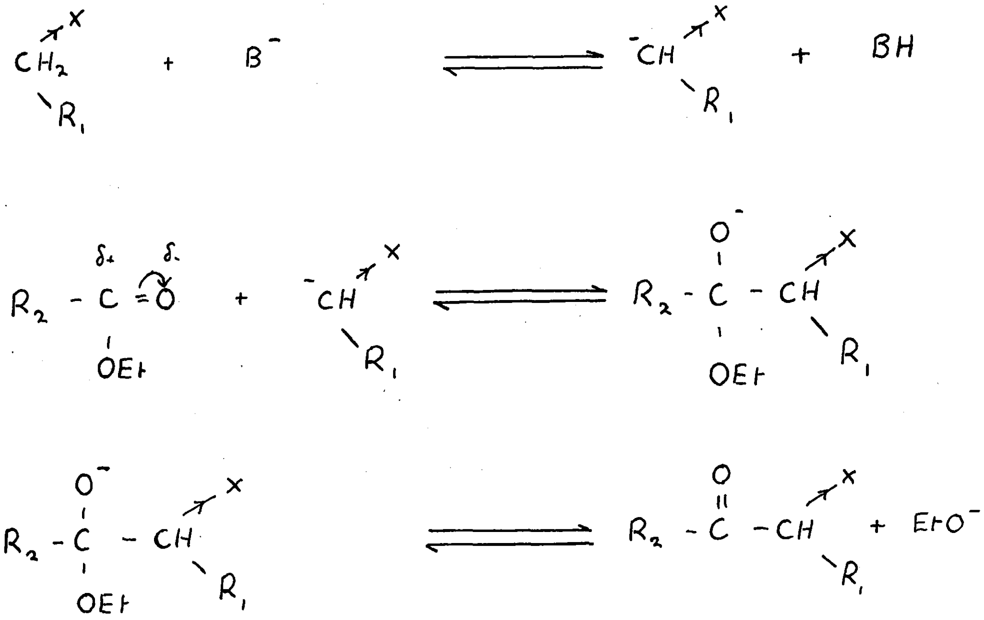
The results were as predicted, diethyl adipate ring closed easily and smoothly to give 2-carbethoxycyclopentanone, and diethyl pimelate gave 2-carbethoxycyclohexanone, though slightly less readily. Those homologues of diethyl adipate which would be expected to give 3 or 4 membered rings would not undergo intramolecular cyclisation, while diethyl suberate, the homologue one higher than diethyl pimelate, gave only a trace of ketonic product. Higher members of this series behaved even less favourably.

A more extensive and general survey of this reaction as a means of cyclisation of diethyl adipate, diethyl pimelate, and their α-methyl-substituted derivatives, was published in 1901 by Dieckmann (8). The ring closure of diethyl α-methyladipate was formulated according to the reaction mechanism proposed by Claisen (9).

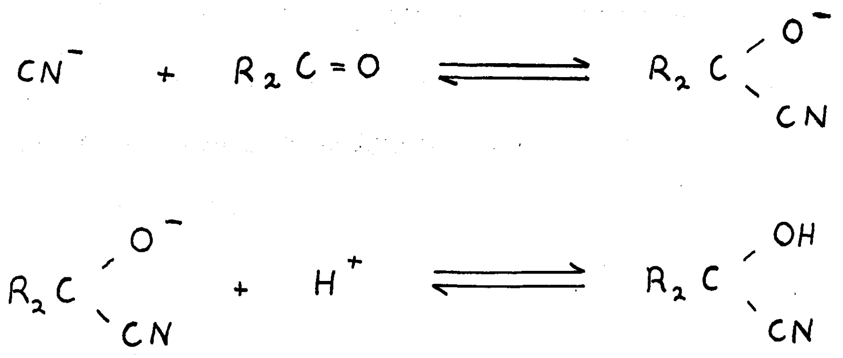


Lapworth proposed the generally accepted anion addition mechanism (10 , 11). It was postulated that the basic alkoxide ion reversibly removed a proton from the active methylene compound, to yield a carbanion, which combined reversibly with the carbonyl carbon atom to give ultimately a β-keto-compound. This may be written in a general form where

B = basic catalyst ion eg. EtO^- , Ph_3C^- etc.
X = the electron attracting substituent causing activation of the methylene group. This may be $-CO_2Et$, $-COR$, $-CN$, etc.

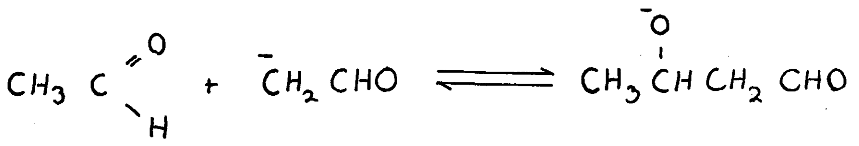


Kinetic studies on the cyanhydrin reaction (12, 13) show that the rate determining step is the addition of the cyanide ion to the carbonyl compound.



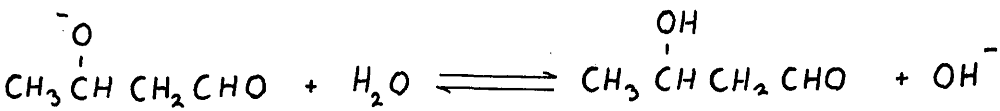
The analogous aldol reaction extensively studied by Bell (14, 15) is shown also to proceed in stages. The slow step is the extraction of a proton from one of the molecules of acetaldehyde involved, as follows

$$CH_3CHO + OH^- \rightleftharpoons \bar{C}H_2CHO + H_2O \qquad (a)$$



(b)

$$CH_3C(=O)H + \bar{C}H_2CHO \rightleftharpoons CH_3CH(O^-)CH_2CHO \qquad (b)$$

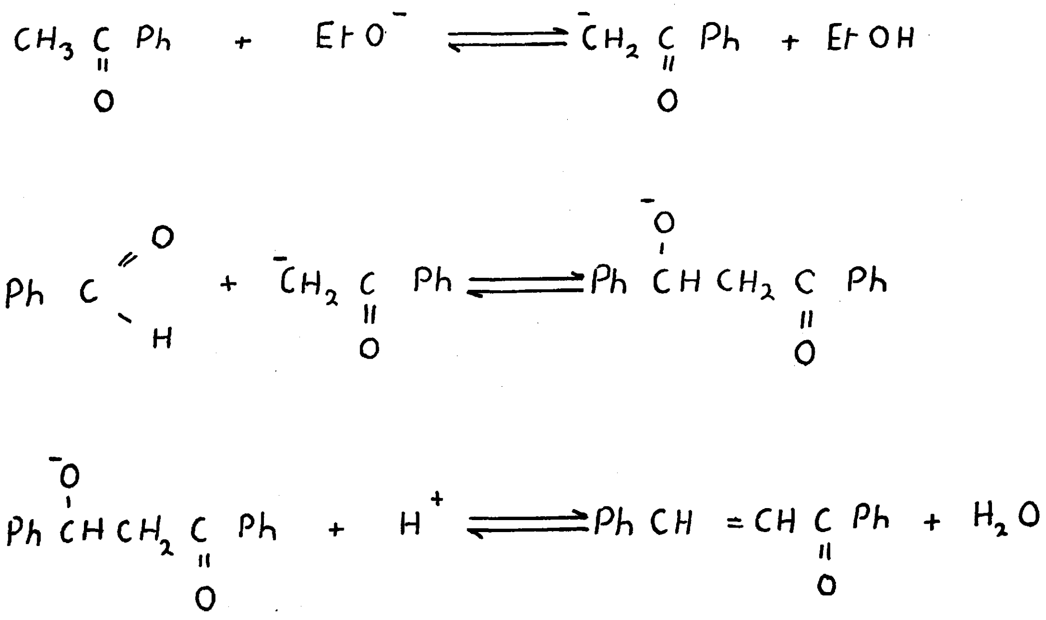


(c)

$$CH_3CH(O^-)CH_2CHO + H_2O \rightleftharpoons CH_3CH(OH)CH_2CHO + OH^- \qquad (c)$$

That the reverse stage (a) is slow and subsequent stages are fast is illustrated by isotopic studies (16). Since, when the reaction is conducted in presence of deuterium oxide, no deuterium becomes attached to carbon, the anion must react immediately with an acetaldehyde molecule.

The condensation of benzaldehyde and acetophenone in ethyl alcohol catalysed by sodium ethoxide has also been studied kinetically (17)



$$CH_3\underset{\underset{O}{\|}}{C}\,Ph + EtO^- \rightleftharpoons {}^-CH_2\underset{\underset{O}{\|}}{C}\,Ph + EtOH$$

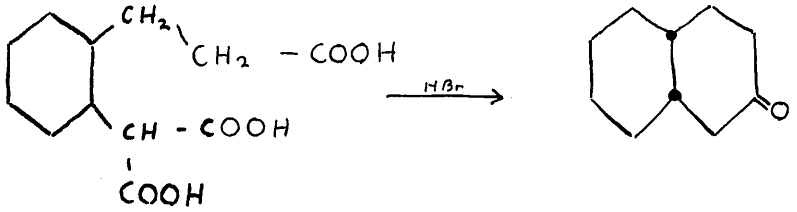
$$Ph\,C\begin{array}{l}\diagup\!\!\diagup O\\ \diagdown H\end{array} + {}^-CH_2\underset{\underset{O}{\|}}{C}\,Ph \rightleftharpoons Ph\,\overset{\overset{{}^-O}{|}}{C}H\,CH_2\underset{\underset{O}{\|}}{C}\,Ph$$

$$Ph\,\overset{\overset{{}^-O}{|}}{C}H\,CH_2\underset{\underset{O}{\|}}{C}\,Ph + H^+ \rightleftharpoons Ph\,CH=CH\underset{\underset{O}{\|}}{C}\,Ph + H_2O$$

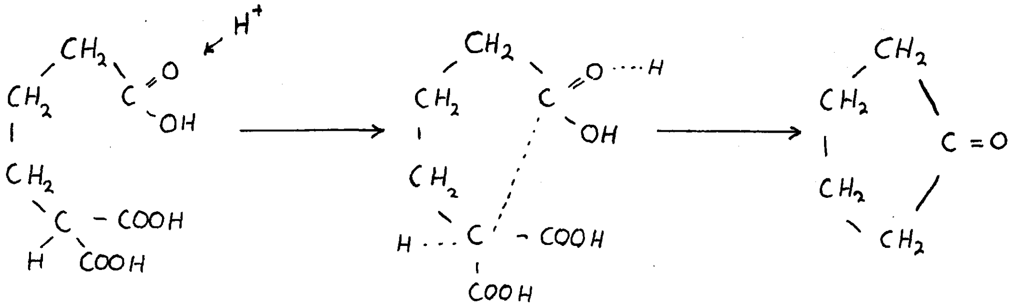
Anion formation is found to be the fast stage while the slow one is probably the addition of the anion to the carbonyl compound. This is in agreement with the work undertaken on the Dieckmann ring closure. The work of Coombs and Evans was however, not sufficiently extensive to provide a critical survey of the effect of constitutional changes within the reacting molecules, on the rates of the individual steps which constitute the overall reaction.

No detailed kinetic work has been published on acid catalysed addition reactions.

It has been found that α-carboxyadipic acids yield cyclopentanone under the influence of hydrobromic acid (18). The reaction appears to be specific for five membered ring compounds, which by general experience close with special facility, other than in the special case of cis-decalone.



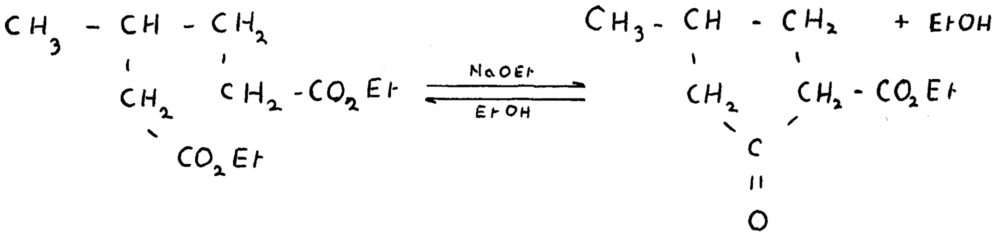
The reaction mechanism differs from that in base catalysed reactions, and that proposed by these authors is formulated below



The presence of an α-carboxylic acid group is essential.

Studies on the products of Dieckmann ring closure of β-substituted-adipic acids have been made by Chakravarti (19, 20) who found that alkyl substituents deactivate their neighbouring methylene groups, and that ring closures thus occur exclusively in one direction.

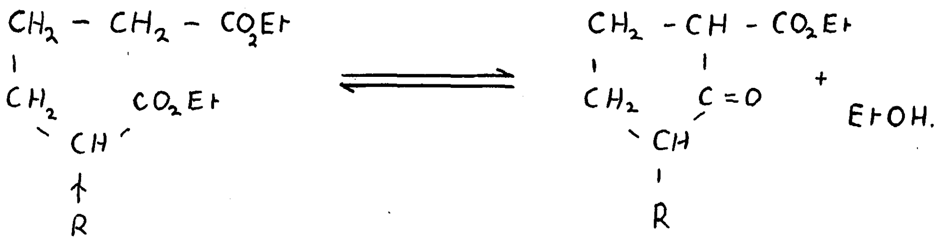
e.g. Diethyl β-methyladipate.



The effect of the +I substituent studied, as in β-carbethoxy-diethyladipate, is not so strong, and two products are formed.

No kinetic studies on the Dieckmann reaction have been recorded, and this investigation was undertaken to study the effect of constitutional changes within the molecule on the facility of ring closure of certain alkyl substituted diethyl adipates.

In an α-alkyl-substituted adipate, ring closure is as follows -



R = H, CH_3, C_2H_5 and i-C_3H_7.

The alkyl group influences the accepting carbonyl portion of the molecule, and is sufficiently far removed from the active methylene group to assume that it will have little effect upon the initial ionisation.

The rate of ring closure of the diethyl ester of β-methyladipic acid was also studied, and it was hoped that the results would prove less speculative than those of Coombs and Evans (17).

EXPERIMENTAL RESULTS AND MATHEMATICAL ANALYSIS.

The cyclisation of diethyladipate and its alkyl-substituted derivatives, was conducted in presence of a large excess of sodium ethoxide in anhydrous ethyl alcohol. The reaction is reversible, both forward and back reactions being of the first order.

This may be represented generally:-

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

where k_1 and k_{-1} are the rate constants of the forward and back reactions. Beginning the experiment with pure A of concentration a, then after time t the concentration of B is x, and that of A is (a-x).

$\therefore$ Rate of production of B is given by

$$\frac{dx}{dt} = k_1 (a-x) - k_{-1} x \qquad \text{---------------} \; 1)$$

At equilibrium the rate of the forward reaction equals that of the back reaction, (i.e. rate of production of B is zero). If the concentration of B at equilibrium is x_e then

$$k_1 (a-x_e) = k_{-1} x_e \qquad \text{---------------} \; 2)$$

$$\text{i.e. } k_{-1} = \frac{k_1 (a-x_e)}{x_e} \qquad \text{---------------} \; 3)$$

Substitution into (1) gives

$$\frac{dx}{dt} = k_1 (a - x) - k_1 x \frac{(a - x_e)}{x_e} \quad \text{---------} \; 4)$$

$$= \frac{k_1 a (x_e - x)}{x_e}$$

when $t = 0$, $x = 0$

Integrating we get

$$k_1 = \frac{x_e}{at} \ln \frac{x_e}{x_e - x} \quad \text{----------} \; 5)$$

at equilibrium, the rate of forward and back reactions are equal, hence

$$k_1 (a - x_e) = k_{-1} x_e$$

and on rearranging

$$\frac{x_e}{a} = \frac{k_1}{k_1 + k_{-1}}$$

Substitution for $\frac{x_e}{a}$ in equation 5 we get

$$k_1 + k_{-1} = \frac{1}{t} \ln \frac{x_e}{x_e - x} \quad \text{-----------} \; 6)$$

$(k_1 + k_{-1})$ gives the value of K, the overall reaction rate, which is analogous to that for a simple first order reaction. The plot of log $(x_e - x)$ against time t, gives a straight line. This is illustrated by

Fig. 1. **Diethylβ-methyladipate.**

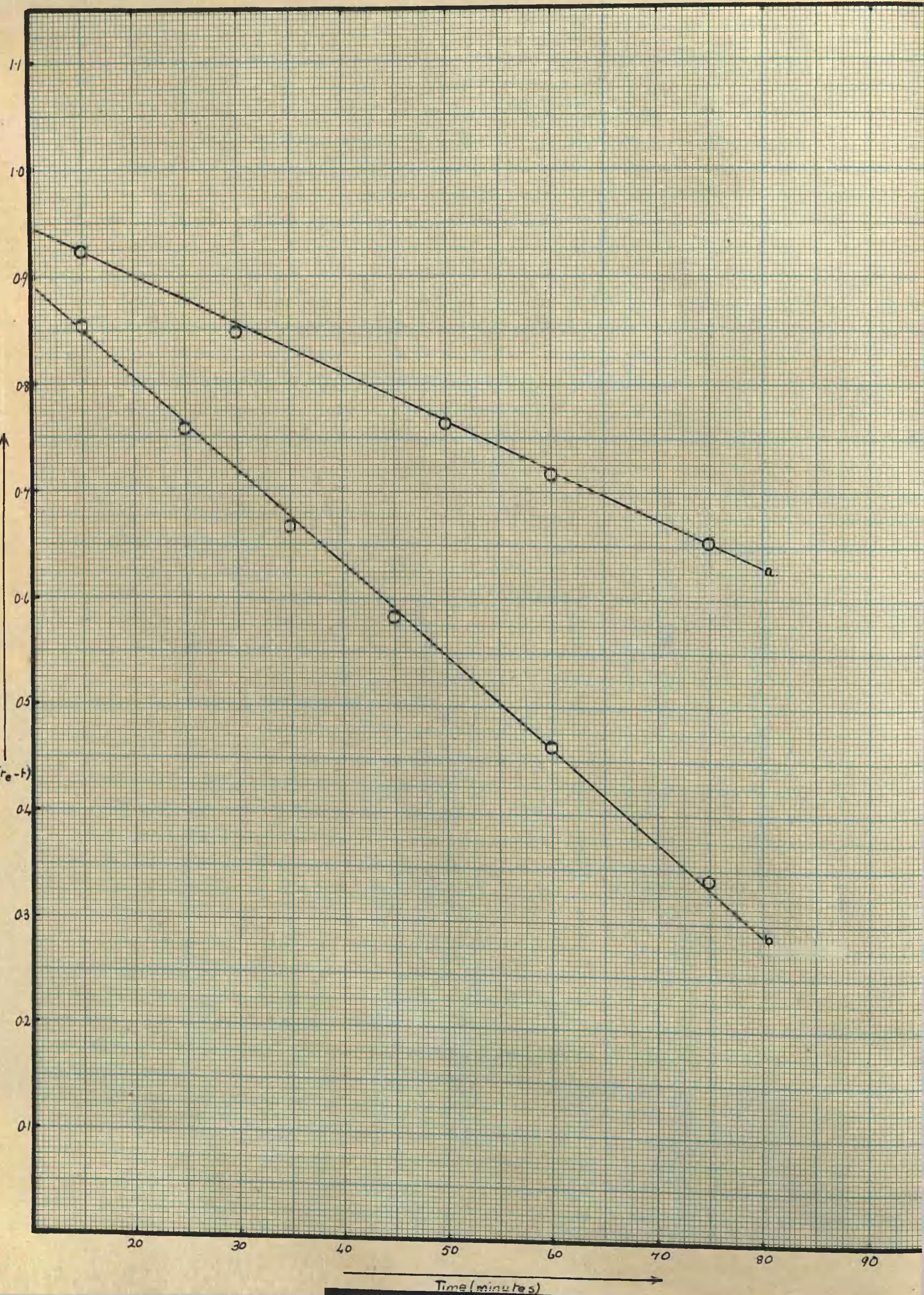
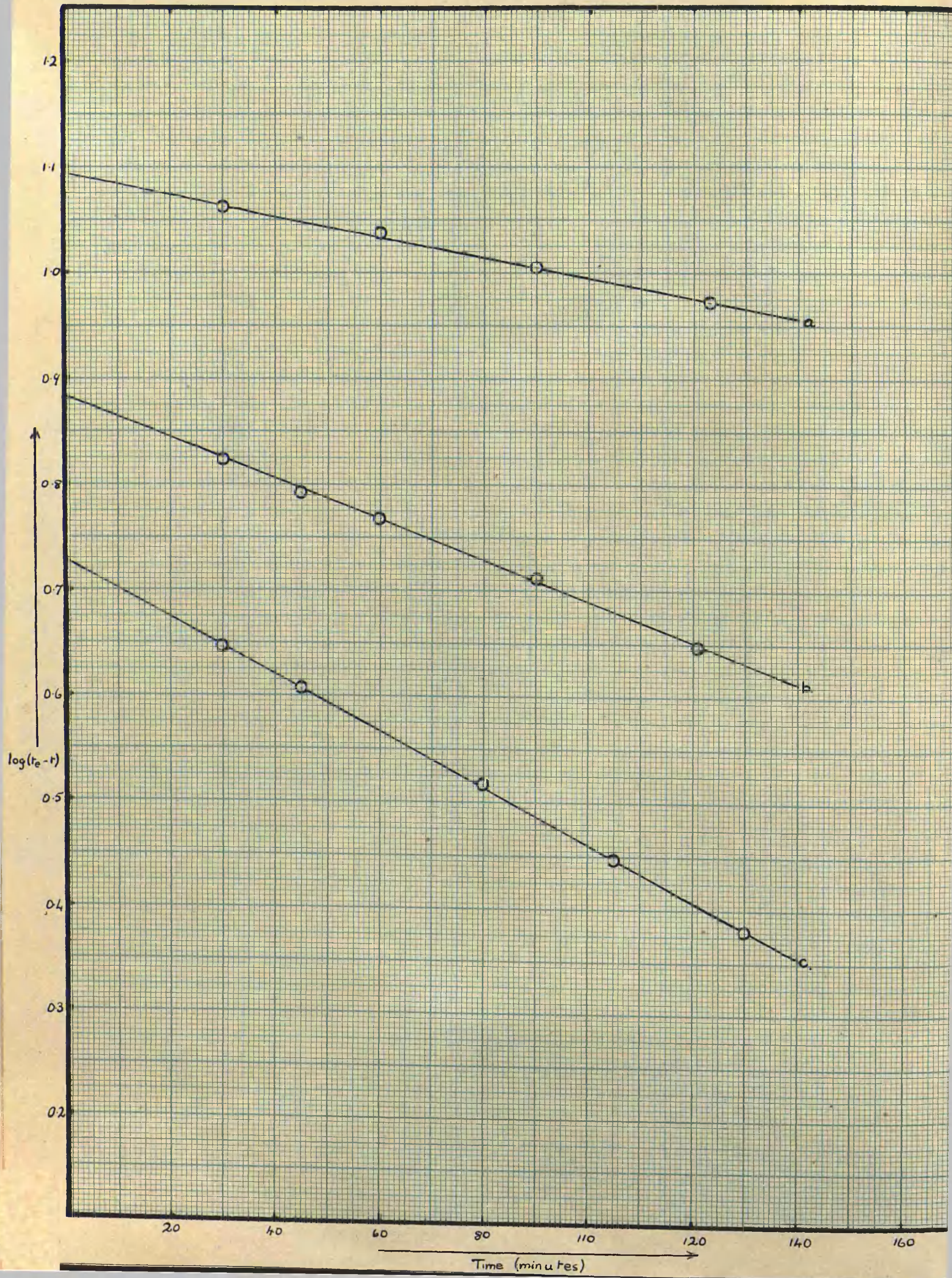


Fig. 2. Diethyl α-methyladipate.



Figs. 1 and 2. Fig. 1 is for diethyl β-methyladipate at a) 35°C. and b) 45°C, and Fig. 2, diethyl α-methyladipate at a) 35°C, b) 45°C and c) 50°C.

Values for the rate constants of forward and back reactions, are most readily obtained as follows -

$$K = k_1 + k_{-1} \qquad \text{------------------} \quad 7)$$

At equilibrium $k_1(a-x_e) = k_{-1}x_e$

$$k_{-1} = \frac{k_1}{x_e}(a-x_e)$$

Substituting into equation 7) we get

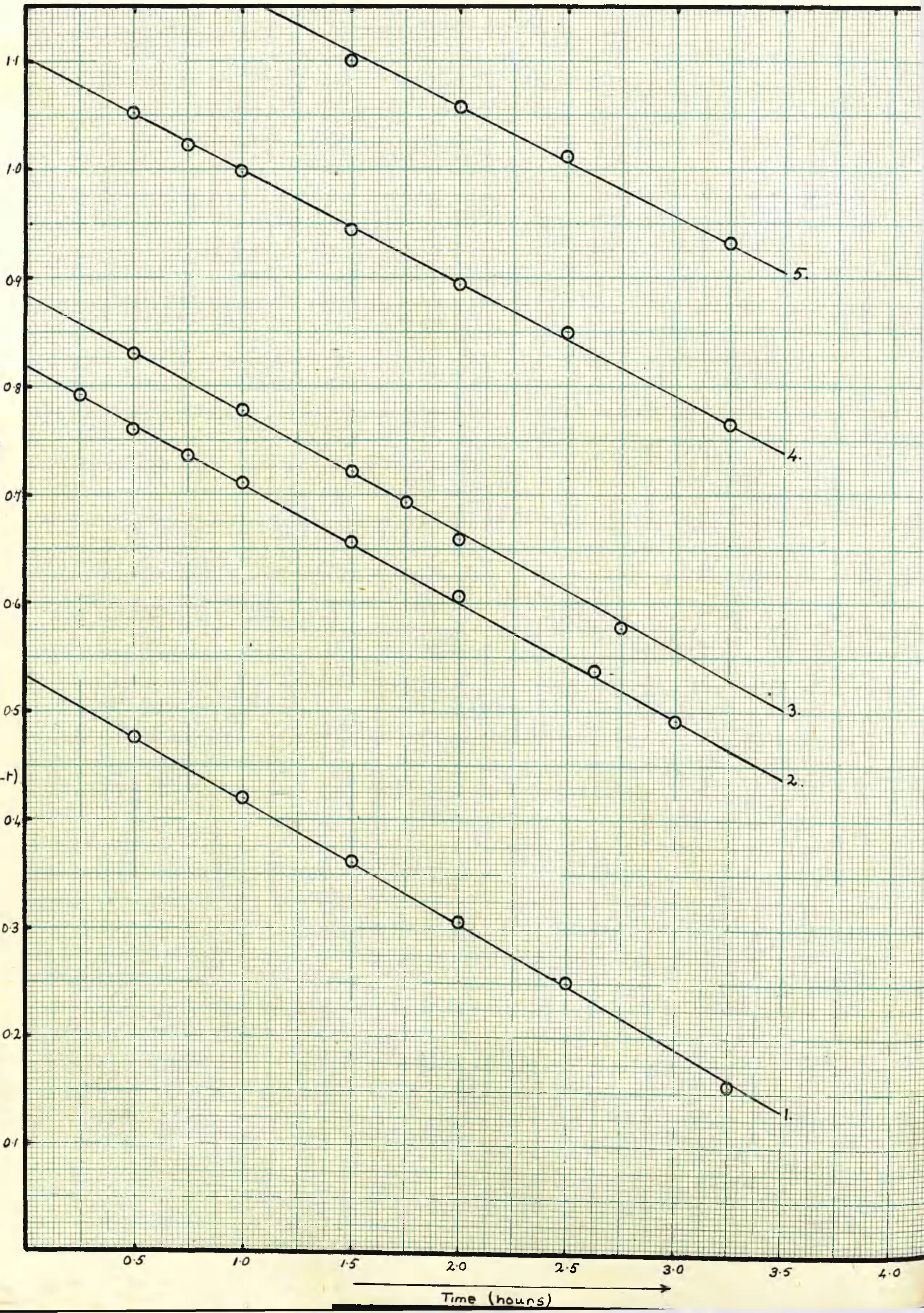
$$K = k_1 + \frac{k_1}{x_e}(a-x_e)$$

which rearranges to

$$K = k_1\frac{a}{x_e}$$

$$\text{i.e. } k_1 = K\,\frac{\text{concentration of products}}{\text{concentration of reactant + product.}}$$

Fig. 3. Diethyl Adipate at 40°C.



That the Dieckmann reaction does obey the kinetic equation for a first order equilibrium reaction under the experimental conditions employed, is shown numerically in table I which follows.

Table I. Ring Closure of Diethyl Adipate at 40°C. in(2.85 ± 0.05)M. Sodium Ethoxide.

Molecularity.	0.089	0.110	0.198	0.220
10^3K (mins.$^{-1}$)^a	4.34	4.23	4.31	4.37
10^3k_1(mins.$^{-1}$)^a	b	3.21	3.43	3.48
10^3k_{-1}(mins.$^{-1}$)^a	b	1.02	0.88	0.89
Graph number on Fig. 3 opposite.	1	2	4	5

a. K represents the overall velocity constant.
k_1 that for ring closure.
k_{-1} that for ring opening.

b. Equilibrium value rather small for accurate determination of k_1 and k_{-1}.

These results are illustrate graphically in Fig. 3.

Table II gives the measured first order velocity constants for the homologous series of diethyl esters of substituted adipic acids, in alcoholic sodium ethoxide solutions.

Table II. Velocity Constants measured in (2.85 ± 0.05) Molar Sodium Ethoxide Solution x 10^3 mins.$^{-1}$.

Temperature		35°C	40°C	45°C	50°C
Diethyl adipate	k_1	1.68	3.16, 3.44	5.34	13.10
	k_{-1}	0.48	1.00, 0.89	1.21	2.72
Diethyl α-methyl-adipate	k_1	1.61	2.36	3.83	-
	k_{-1}	1.01	2.15	2.46	-
Diethyl α-ethyl adipate	k_1	1.32	2.52	4.75	7.01
	k_{-1}	1.13	2.62	3.81	6.87
Diethyl α-i-propyl-adipate	k_1	-	Reaction too slow for measurement	1.26	-
	k_{-1}	-		1.11	-
Diethyl β-methyl-adipate	k_1	8.12	-	16.90	-
	k_{-1}	2.78	-	5.22	-

Preparation of the diethyl ester of β-methyl-adipic acid, and some preliminary work on this compound was done by R.S. Craig.

Table III gives the Activation Energies and Arrhenius Factors for those compounds on which sufficient measurements had been made to allow their calculation.

Table III

Compound	E_1 (K cals.)	E_{-1} (K cals.)	A_1 (mins.$^{-1}$)	A_{-1} (mins.$^{-1}$)
Diethyl adipate	24.0	23.9	4.9×10^{13}	3.0×10^{12}
Diethyl α-methyl-adipate	17.5	17.7	1.2×10^{9}	1.1×10^{9}
Diethyl α-ethyl-adipate	25.2	24.2	3.0×10^{14}	4.5×10^{13}

Comparison of Reaction Rates in Different Media

Experiments on methyl adipate in an anhydrous methyl alcohol, sodium methoxide solution at 40°C showed that the reaction did proceed, but very slowly.

Di-n-propyl adipate in anhydrous n-propyl alcohol, sodium n-propoxide solution under similar conditions reacted at a comparable rate to diethyl adipate in ethyl alcohol. Since a saturated solution of sodium n-propoxide in n-propyl alcohol is only 2.3 molar, while sodium ethoxide in ethyl alcohol is 2.8 molar, the numerical results are not accurately comparable.

Sodium is scarcely soluble in i-propyl alcohol, a saturated solution of sodium i-propoxide in alcohol being about 0.3 molar. Experiments on di-i-propyl adipate in i-propyl alcohol, sodium i-propoxide solution gave no noticeable product after four days at 40°C. This may be accounted for by the low concentration of i-propoxide ions in solution.

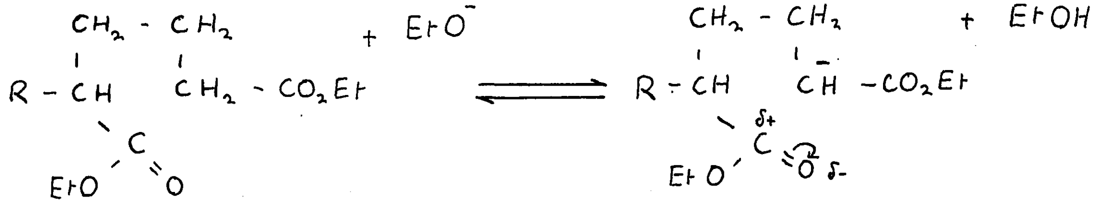
These qualitative results show that the reaction rate increases with increasing basic strength of the solution, the order being

$$\mathrm{Me\,O^-} < \mathrm{Et\,O^-} < n\text{-}\mathrm{PrO^-}$$

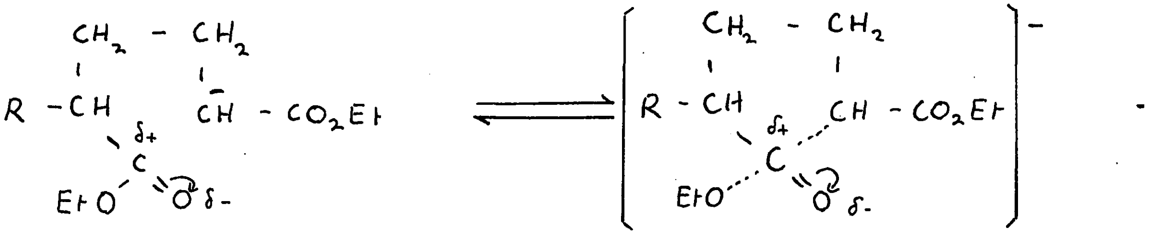
THEORETICAL INTERPRETATION of RESULTS

In accordance with the generally accepted mechanism for base catalysed condensation reactions (9), it is convenient to consider the overall reaction of α-alkyl-substituted adipates as composed of stages I - III.

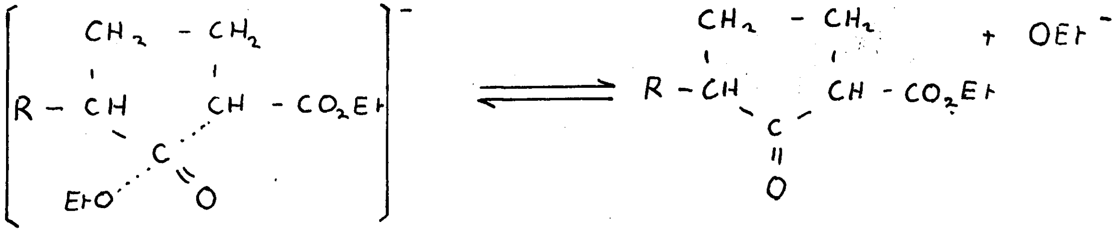
Stage 1.



Stage 11.

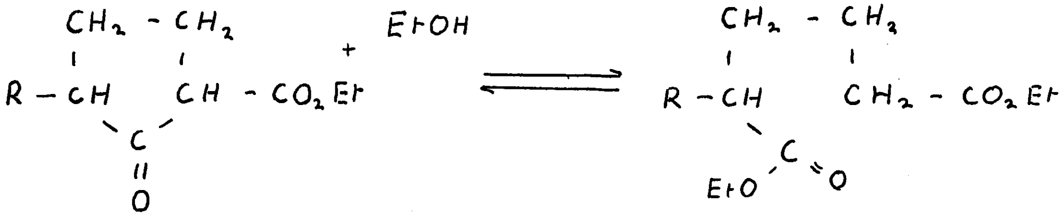


Stage 111.

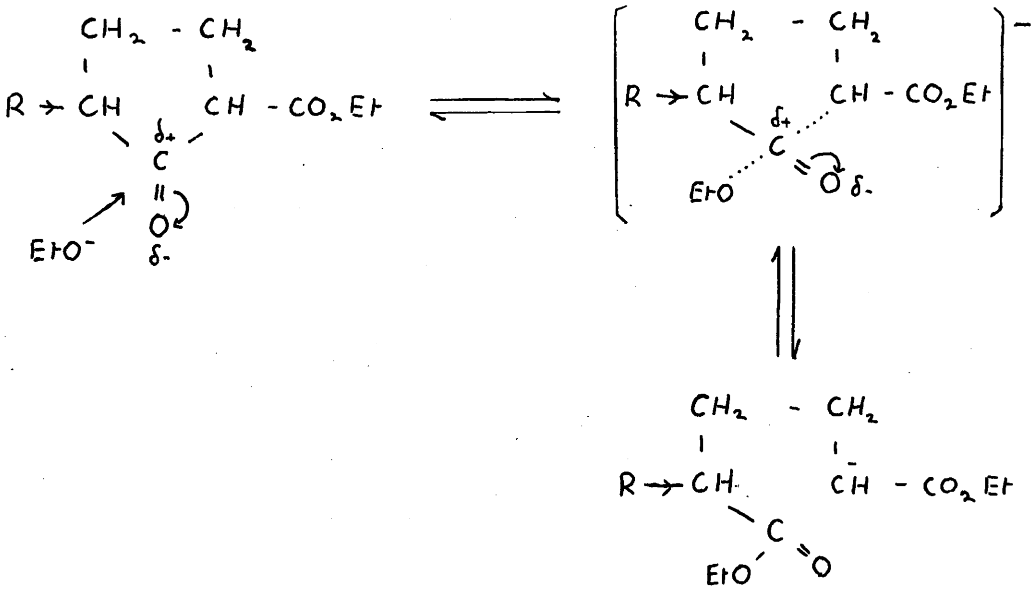


R = H, CH_3, C_2H_5 and C_3H_7.

Considering the reverse reaction, namely the cleavage of 5-alkyl-2-carbethoxycyclopentanone to yield the diethyl ester of an α-alkyladipic acid



Since the reactions took place in a medium of low dielectric constant, and high concentration of sodium ethoxide, ring cleavage may be considered as a nucleophilic bimolecular attack by an ethoxide ion on the carbonyl carbon atom



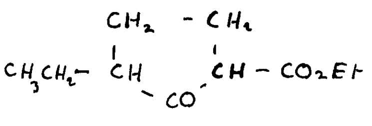
A.

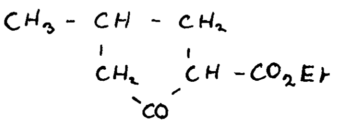
The presence of α-alkyl substituents should hinder the attack of the ethoxide group, but facilitate the breakdown of the carbon-carbon bond to give the anion A. The known electron releases of alkyl groups increase in the order H < Me < Et, and this would mean that alkyl groups increase the negativity around the carbonyl carbon atom hindering the ethoxide approach, but aiding the consequent breaking of the carbon-carbon bond.

The rate constants given in table II, page 20, show that the rates of ring opening increase H < Me < Et. With the α-i-propyl compound, however, the rate is decreased, and construction of scale models showed that increase in size of the α-substituent becomes sterically important in this latter case.

The variation in first order rate constants indicates that the rate determining step could be the breaking of the carbon-carbon bond.

That the steric factor becomes increasingly more important as the size of the substituent R in the α-position to the carbonyl group increases, was tested by comparing the rates of reaction of 2-carbethoxy-5-ethylcyclopentanone, and 2-carbethoxy-4-methylcyclopentanone. To a first approximation their electronic effects may be considered equal, the difference being their spatial atomic arrangement.

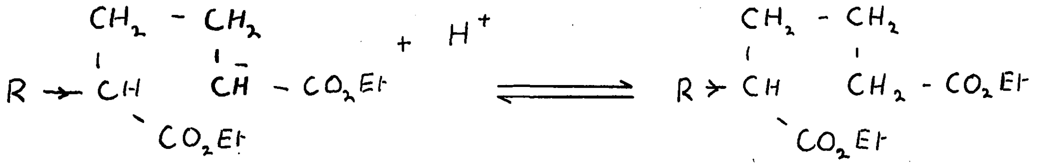




When the substituent is in the β-position to the carbonyl group, ring opening is faster by a factor of 1.4 than when it is in the α-position. This may be taken to show that the steric factor is not very large when the α-substituent is an ethyl group.

For the α-i-propyl compound, the steric effect would be expected to be greater, and this would account for the decrease in rate of ring fission for 2-carbethoxy-5-i-propylcyclopentanone.

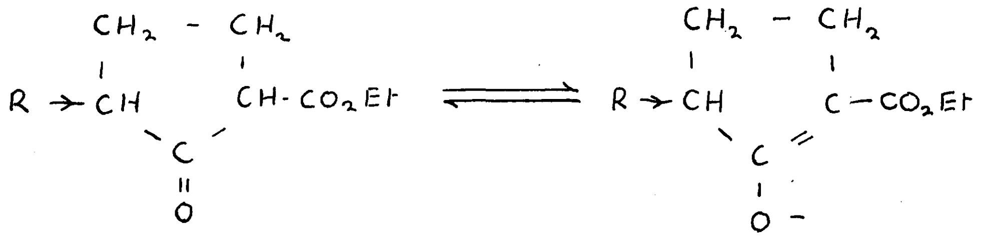
To complete reaction in the reverse direction, it remains for the anion produced to take up a hydrogen ion,



$$R \rightarrow CH(CO_2Et)-CH_2-CH_2-\bar{C}H-CO_2Et + H^+ \rightleftharpoons R \rightarrow CH(CO_2Et)-CH_2-CH_2-CH_2-CO_2Et$$

That this should be the rate determining step is unlikely as the electronic effect of an alkyl group is localised, and only considered effective when it is within three carbon atoms of the centre under discussion. Here the alkyl group R is four carbon atoms away from the active methylene group. Therefore, it would be expected to have little effect upon the rate of reaction, though if a variation in reaction rates were to be predicted it would be in the order H, < β-methyl, < α-ethyl, < α-methyl. Inspection of the table of results shows no such trend, as the rates of ring fission are in the opposite direction of ring formation. This step therefore cannot be considered to be rate determining.

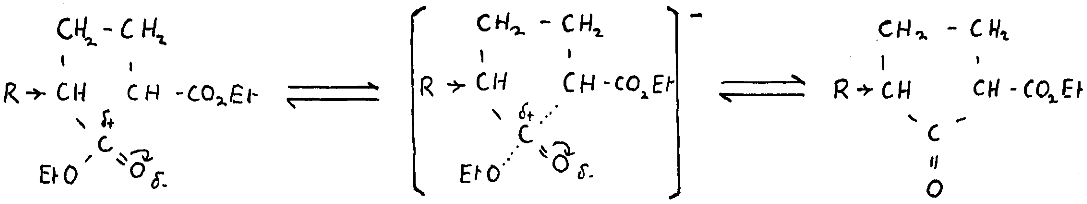
For the discussion of ring cleavage the reactant, 5-alkyl-2-carbethoxycyclopentanone, has been assumed to be present in the keto-form. Enolisation will be governed by the same electronic effects as reversible anion formation.



Were this rate determining, the rate constants recorded would again be expected to vary in the order H, β-methyl, α-ethyl, α-methyl.

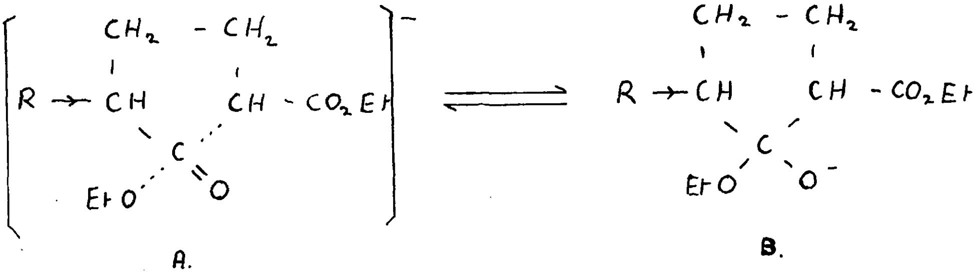
In ring cleavage, enolisation has been assumed to play little part since in the presence of a high concentration of ethoxide ions the amount of the keto-form of the molecule will be reduced to a low level, which has been assumed to be similar in each case. Enolisation might however disturb quantitative agreement of the reaction rates with theory.

Ring closure will occur by an S_N2 mechanism



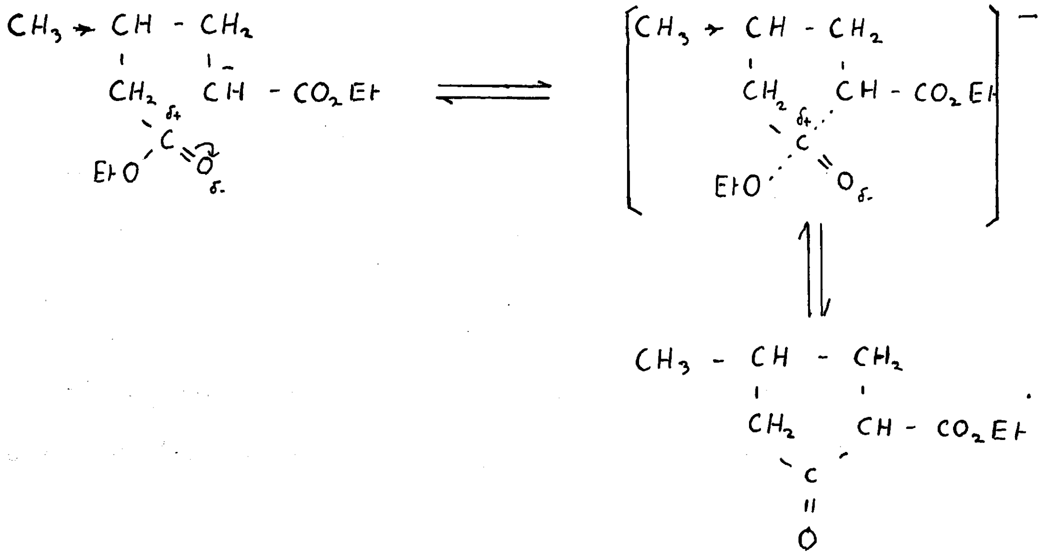
The presence of an α-alkyl substituent tends to decrease the positive character of the carbonyl carbon atom. This would decrease the rate of bond formation between the carbonyl carbon atom and the anionic centre, but increase the rate of loss of ethoxide ion. The results indicate that bond formation is the rate determining step, though the results do not vary in such a regular fashion as did those for the reverse reaction - ring fission. At each temperature the measured velocity constant for the unsubstituted compound is greater than either of those for the α-methyl, or α-ethyl-substituted compounds.

The overall process will be complicated by polarisation.



This will facilitate ring closure through the enolic form B, and ring fission with loss of an ethoxide ion through the keto-form A.

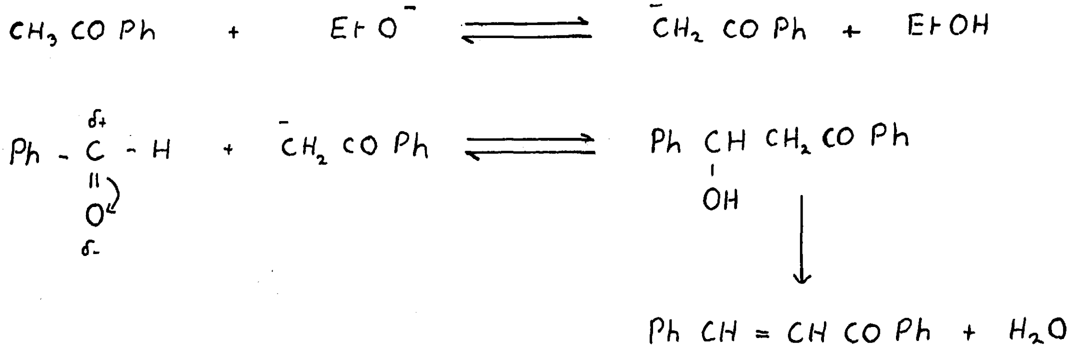
For β-methyl adipic ester the rate of ring closure is greatly enhanced, being three times that of any of the α-substituted compounds.



This is compatible with the statement that the rate determining step is bond formation, as the methyl group in this position will have less effect on the carbonyl carbon atom than does a substituent in the α-position, and it is sufficiently near to the anionic centre to enhance its negativity.

The acceleration is not wholly a polar effect, however, as the methyl group in the β-position will tend to force the ends of the molecule together, thus making reaction more probable.

Coombs and Evans (17) in their work on the condensation of benzaldehyde with acetophenone concluded also that anion formation is not the rate determining process.



$$CH_3COPh + EtO^- \rightleftharpoons {}^-CH_2COPh + EtOH$$

$$Ph-\overset{\delta+}{C}(=\overset{\delta-}{O})-H + {}^-CH_2COPh \rightleftharpoons PhCH(OH)CH_2COPh$$

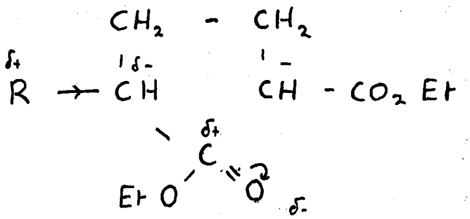
$$\downarrow$$

$$PhCH=CHCOPh + H_2O$$

The slow stage is most probably the addition of the anion to the carbonyl group, since the dehydration of the ketol to give the product isolated would be expected to be fairly fast.

This agrees with the results for the Dieckmann reaction where the rate determining step is the union of the anionic centre with the carbonyl group.

In the compounds studied, the +I substituents methyl, ethyl, and i-propyl influencing the accepting carbonyl portion of the molecule, were found to inhibit the nucleophilic addition of the anionic centre.



This has been predicted by Ingold (9).

KINETIC OBSERVATIONS

In order to find a suitable working temperature, and the best solvent and catalyst for kinetic observations, test experiments were carried out. The appropriate adipic ester - diethyladipate or dimethyladipate, was added to a solution of sodium alkoxide in anhydrous ethyl and methyl alcohols. Reaction was allowed to proceed at a variety of temperatures, and an estimate of the velocity of the reaction obtained by chemical analysis of the reaction mixture. The products of ring closure of adipic and pimelic esters, are keto-enol systems, from which it is possible to prepare many of the typical ketonic derivatives. In this case the 2:4-dinitrophenylhydrazone was used.

The reaction mixtures were prepared by adding 1.5 gms. of the appropriate ester to 50 mls. of a freshly prepared solution of sodium ethoxide or methoxide. Experiments were carried out at 18°C, 25°C and 40°C in solutions of sodium ethoxide and sodium methoxide.

Analysis of the Reaction Mixture:

5 ml. samples were withdrawn and added to an ice-cold solution of 3N hydrochloric acid. 100 mls. of cooled 2:4-dinitrophenylhydrazine hydrochloride solution were added, and the precipitate allowed to digest for 24 hours at room temperature.

The 2:4-dinitrophenylhydrazone was filtered off in a weighed No. 3 sintered glass crucible.

The results obtained may be summarised as in table IV which follows at the end of this section, p. 34.

Analysis of the reaction mixture by quantitative estimation of the 2:4-dinitrophenylhydrazone of 2-carbethoxycyclopentanone was found to be unreliable, as the derivative did not always come down in a crystalline form. Even when it did so, experiment showed that results obtained were too high. As a result no numerical data was obtained from these experiments, but the necessary information for carrying out observations by a more accurate method was obtained.

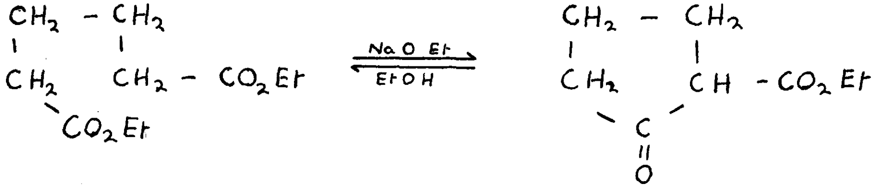
Physical methods thought to be suitable were (a) Dilatometry and (b) Colorimetry, and experiments were attempted at 40°C on diethyladipate in a saturated solution of sodium ethoxide in anhydrous ethyl alcohol. A saturated sodium ethoxide/ ethyl alcohol solution contains 2.8 - 2.9 gm. mols./ litre.

Table IV. Comparative Study of the Rates of Ring Closure in Methyl and Ethyl Alcohols at Different Alkoxide Concentrations.

Composition of Solution.	Observations at 18°C.	25°C.	40°C.
Dimethyladipate (0.1 M.) plus sodium methoxide (1.5M.) in methyl alcohol.	Imperceptible reaction after three days.	Imperceptible reaction after three days.	Imperceptible reaction after three days.
Dimethyladipate (0.1 M.) plus sodium methoxide (2.8M.) in methyl alcohol.	Imperceptible reaction.	Very slow reaction.	Slow reaction.
Diethyl adipate (0.1 M.) plus sodium ethoxide (1.5 M.) in ethyl alcohol.	Very slow reaction.	Slow but measurable reaction.	Measurable reaction.
Diethyl adipate (0.1 M.) plus sodium ethoxide (2.8 M.) in ethyl alcohol.	Slow but measurable reaction.	Measurable reaction.	Measurable reaction total time required being approx. 24 hrs.

DILATOMETRY

Since the reaction consists of a ring closure, it was thought that some volume change might be expected.



The method used was as given by Benford and Ingold (21).

Dilatometers of 25 ml. capacity having very long limbs of fine capillary tubing were constructed, so that the whole of the vessel containing reaction mixture could be submerged in the thermostat, and the volume change observed through glass windows in the tank.

The reaction mixtures prepared were about 0.1 M. with respect to diethyladipate and 2.8 M. with respect to sodium ethoxide - strict precautions being taken to exclude water, since if any water enters, there is practically instantaneous deposition of the disodium salt of adipic acid. Besides being very hygroscopic, sodium ethoxide solution of this concentration is very viscous - this renders the filling of the dilatometer very difficult, and makes drainage very slow. It was found that as a result of this, it was practically impossible to prevent blockages in the capillary side arms, which rendered results inaccurate.

A successful dilatometric run at 40°C gave results as follows:-

Molarity of solution w.r.t. sodium ethoxide = 2.873 .

Molarity of solution w.r.t. diethyladipate = 1.454 .

Time (hours)	h (cms.)	$K = \frac{2.303}{t} \log_{10} \frac{h_e}{(h_e - h)}$ (mins.$^{-1}$)
$1\frac{3}{4}$	20.737	4.39×10^{-3}
2	20.720	4.45×10^{-3}
$2\frac{1}{2}$	20.666	4.01×10^{-3}
3	20.607	4.03×10^{-3}
$3\frac{1}{2}$	20.548	4.29×10^{-3}
4	20.509	4.25×10^{-3}
$4\frac{1}{2}$	20.479	4.10×10^{-3}
5	20.431	3.96×10^{-3}
$5\frac{1}{2}$	20.412	4.13×10^{-3}
21	20.119	-
25	20.073	-
28	20.020	-
35	19.925	-

$K_{av.} = 4.19 \times 10^{-3}$ mins.$^{-1}$

$k_1 = 3.16 \times 10^{-3}$ mins.$^{-1}$

$k_{-1} = 1.03 \times 10^{-3}$ mins.$^{-1}$

These results show, that the overall partial molal volume change for this reaction is very small, the total volume change giving only about 0.5 cms. fall in the capillary tubes. Dilatometers of greater capacity were not favoured, as fluctuations in the level of liquid in the limb caused by small temperature variations in the thermostat became serious. Had the overall volume change been larger this would have been of less consequence. Thermostatic variation gave all readings a possible error of ± 0.01 cms.

Though every precaution had been taken to cut down evaporation losses, readings taken after reaction was complete, i.e. at 25, 28 and 35 hours show that evaporation was still appreciable. To reduce this loss the limbs of the dilatometer were constructed of the finest possible capillary tubing and made very long, so that at least six inches of tubing were left unoccupied by reaction mixture. Small glass caps, which diminished evaporation, without affecting the fall of the liquid in the dilatometer limbs were added, but even after this, the level in the dilatometer, fell at the rate of about 0.013 cms. per hour.

The dilatometric method gives accurate and dependable results, when mobile and less volatile liquids are used. Observations using dilatometry were discontinued for the following reasons:-

(a) The reaction mixture is too viscous making filling difficult, and causing blockages in the capillary tubes.

(b) Evaporation losses are large at the temperature required for measurable reaction, and measures which cut down evaporation aggravate the above difficulties.

(c) The partial molal volume change on reaction is very small.

COLORIMETRIC ESTIMATION

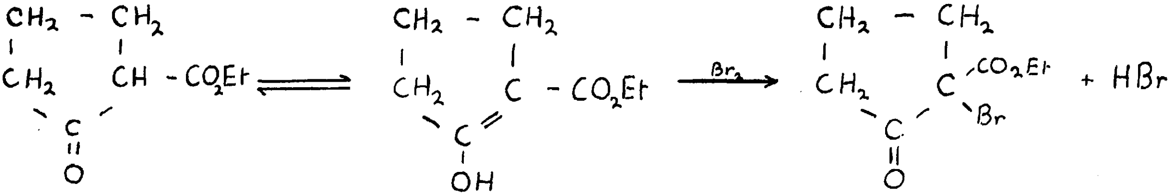
β-keto-esters in neutral solutions of aqueous alcoholic ferric chloride give deep violet or blue colourations caused by the formation of a complex (22).

It was proposed to use this colouration as a quantitative colorimetric analysis of the concentration of β-keto-esters produced. The success or failure of this as an estimation depended very largely on the pH of the solution, and under the required conditions it was found not to give dependable results.

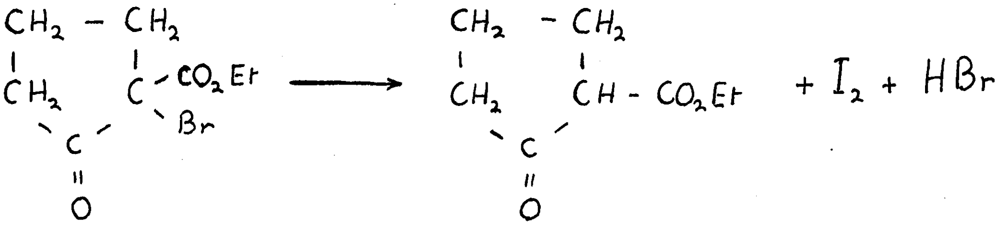
CHEMICAL ANALYSIS

As described in the preliminary kinetic experiments, estimation of the 2-carbethoxycyclopentanone as 2:4-dinitrophenylhydrazone was not sufficiently accurate, and it was decided to adapt the general method of enol-analysis described by Meyer (23), so that the total quantity of keto-enol system was measured.

5 ml. samples were withdrawn from the reaction mixture and run into stoppered bottles, which contained the exact quantity of cooled approximately 1N-hydrochloric acid solution to neutralise the alkali present, and thus terminate the reaction. Excess 0.5M. bromine in ethyl alcohol solution (15 mls.) was added, and allowed to stand overnight to allow the β-keto-esters to be converted completely to the bromo-compound



Excess bromine was removed by adding about 0.5 mls. β-naphthol/ethyl alcohol solution. After thorough mixing, 5 mls. of molar potassium iodide solution were added, and the samples left for 75 minutes to ensure complete liberation of iodine, which was found to be rather slow.



It is seen that one molecule of iodine is equivalent to one molecule of 2-carbethoxycyclopentanone, hence the quantity of 2-carbethoxycyclopentanone may be calculated.

The liberated iodine is estimated by titration with standard sodium thiosulphate solution, in the absence of starch.

The accuracy of the method was tested by analysing solutions of known 2-carbethoxycyclopentanone concentrations.

Concentration of 2-carbethoxycyclopentanone.	4.786 gms. per litre.
By analysis (a)	4.810 gms. per litre.
(b)	4.635 gms. per litre.
Concentration of 2-carbethoxycyclopentanone.	5.645 gms. per litre.
By analysis (a)	5.705 gms. per litre.
(b)	5.721 gms. per litre.

This shows that this analysis is dependable to within ± 2%.

Kinetic determinations were all carried out by means of chemical analysis, measurements being made on

diethyladipate
α-methyldiethyladipate
α-ethyldiethyladipate
α-i-propyldiethyladipate
β-methyldiethyladipate

in a reaction medium consisting of 2.85 ± 0.05 M. sodium ethoxide in anhydrous ethyl alcohol at 35°C, 40°C, 45°C and 50°C.

The reaction was also studied using:-

(a) dimethyladipate in 2.85 ± 0.05 M. sodium methoxide/methyl alcohol solution at 40, and 45°C.

(b) di-n-propyladipate in 2.3 M. sodium n-propoxide at 40°C. A saturated solution of sodium-n-propoxide in n-propyl alcohol contains only 2.3 - 2.4 gm. mols. per litre.

EXPERIMENTAL DETERMINATION.

The required quantity of ester was weighed from a weight pipette, into a dried graduated flask. This was placed in the thermostat to attain the correct temperature along with the solution of 2.8 M. sodium ethoxide in ethyl alcohol. After coming to thermal equilibrium the sodium ethoxide solution was added to the ester, the mixture well shaken up, and then replaced in the thermostat.

The added reactant must be evenly dispersed through the sodium ethoxide solution, and it was found that the ester was fairly difficult to dissolve. The reaction medium (sodium ethoxide in anhydrous ethyl alcohol) though viscous in the first place, became more so on addition of the ester.

5 ml. samples were withdrawn from the reaction mixture at the required time intervals and analysed as given on page 40 . The reaction medium was analysed by titration against standard hydrochloric acid solution, using screened methyl orange as indicator.

Specimens of the results obtained by this method are as follows.

I Diethyladipate

conc. of ester, = 0.1366 gm. mols. per litre.

conc. of sodium ethoxide, = 2.829 gm. mols. per litre.

Temperature = 35.05°C.

time. (mins.)	titre. (mls.)	log (te-t)	$K = \frac{2.303}{T} \log \frac{te}{(te-t)} (\text{mins})^{-1}$
0	0.30	-	-
30	0.98	1.0109	2.18×10^{-3}
60	1.61	0.9845	2.11×10^{-3}
90	2.27	0.9538	2.22×10^{-3}
120	2.80	0.9274	2.15×10^{-3}
150	3.31	0.9004	2.14×10^{-3}
180	3.82	0.8716	2.10×10^{-3}
	11.26	-	-

$K_1 = 0.49 \times 10^{-3}$ mins.$^{-1}$ $K_{-1} = 1.68 \times 10^{-3}$ mins.$^{-1}$

II β-methyl-diethyladipate

conc. of ester. = 0.1294 gm. mols per litre.

conc. of sodium ethoxide. = 2.853 gm. mols. per litre.

Temperature. = 45°C.

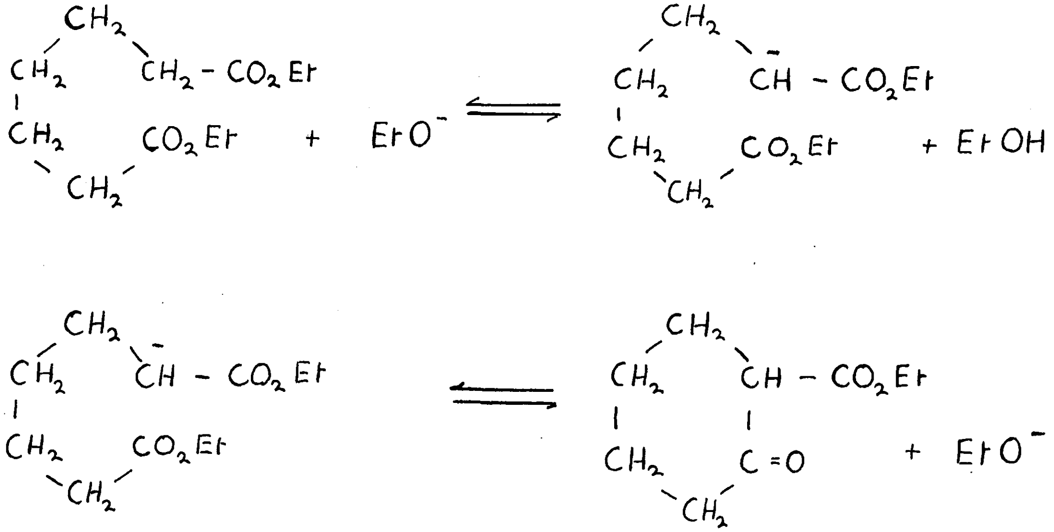
time (mins.)	titre (mls.)	log (te-t)	$K=\frac{2.303}{T}\log\frac{te}{(te-t)}$ (mins)$^{-1}$
0	0.50	-	-
15	3.56	0.8537	2.36×10^{-2}
25	4.98	0.7574	2.32×10^{-2}
35	6.07	0.6656	2.26×10^{-2}
45	6.87	0.5832	2.18×10^{-2}
60	7.71	0.4639	2.10×10^{-2}
75	8.49	0.3444	2.10×10^{-2}
240	10.42	-	-
540	10.70	-	-

$K_1 = 0.52 \times 10^{-2}$ mins.$^{-1}$ $K_{-1} = 1.68 \times 10^{-2}$ mins.$^{-1}$

Dieckmann Ring Closure of Diethylpimelate

It had been hoped that it would be possible to study the formation of six membered rings in an analogous manner to that used above for five membered ring formation.

Diethylpimelate ring closes as shown:-



The general method for enol-estimation could not be adapted for estimation of 2-carbethoxycyclohexanone.

It was found that a large amount of bromine was taken up in the first instance, since the enol-content of an alcoholic solution of 2-carbethoxycyclohexanone is much greater than of an alcoholic solution of 2-carbethoxycyclopentanone (24).

The iodine liberation, however, was very slow, only about 25% of the iodine having been liberated after standing for four hours. Allowing the iodine liberation to proceed for even longer intervals of time gave erratic results, so that the analytical method previously employed could not be adapted for measurements on six membered rings.

Analytical Methods

Further attempts to standardise those methods generally used for enol analysis (25) eg. copper salt formation and the colorimetric method proved fruitless, and the study of the formation of six membered ring compounds in a manner analogous to that employed for the study of the five membered ring compounds were discontinued.

Dilatometry

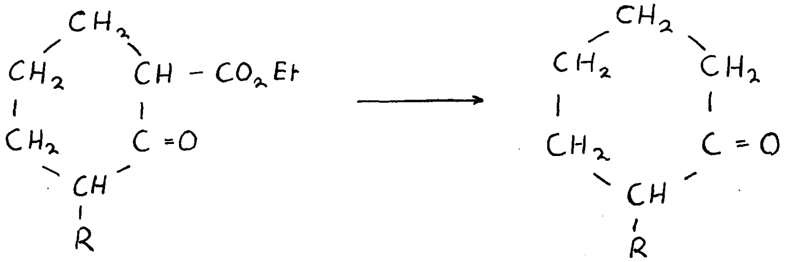
Dilatometry using such condensing agents as the lithium alkyls and sodium triphenyl methyl was attempted, but the technical difficulties encountered made any results which might have been obtained unreliable.

Competitive Method

The only condition governing the use of the competitive method of kinetic analysis of a reaction mechanism is that reactants and condensing agent should be in the same phase (26). Suitable condensing agents are the lithium alkyls and sodium triphenylmethyl.

To equivalent quantities of a solution of the two esters whose reaction rates are being compared is added a small quantity of condensing agent, sufficient to ring close not more than 10% of the total quantity of reactants. The comparative rate constants are obtained by analysis of the resultant reaction mixture. In the present work the product of such an experiment would be a mixture of two 2-alkyl-substituted 6-carbethoxycyclohexanones.

As shown above, direct analysis of 2-alkyl-6-carbethoxycyclohexanones was unsuccessful, but it was hoped that the products of a suitably controlled hydrolysis of the reaction mixture would be able to be estimated accurately.



R = alkyl

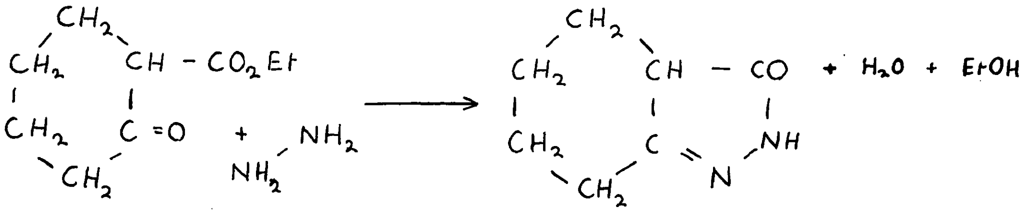
Of the hydrolytic methods available a 10% aqueous solution of potassium bicarbonate gave hydrolysis with the minimum of ring cleavage.

A weighed portion of 2-carbethoxycyclohexanone

(0.1 gms.) was measured into a flask, and 25 mls. 10% potassium bicarbonate solution was added. This was refluxed for 30 minutes, cooled and acidified with 5N HCl solution, until the specimen solution was acidic, (2N or slightly more). The cyclohexanone produced was estimated as the 2:4-dinitrophenylhydrazone according to the method of Iddles and his co-workers (27, 28). The overall results proved to be erratic and unreliable, all estimations being at least 10% below the theoretical value.

The 2:4-dinitrophenylhydrazone method of analysis had been chosen as these derivatives can be separated chromatographically on an alumina column using benzene as eluent according to the method of Strain (29).

The pyrazalone derivative which forms directly from the β-carbethoxyketone was also tested.

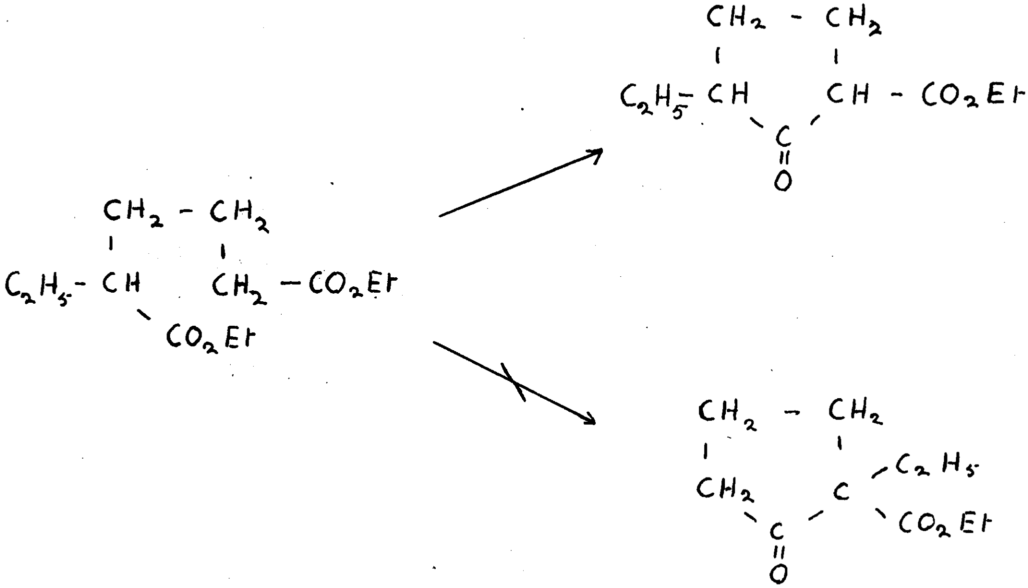


Using pure 2-carbethoxycyclohexanone under ideal conditions (30) a yield of only 80 - 85% was obtained.

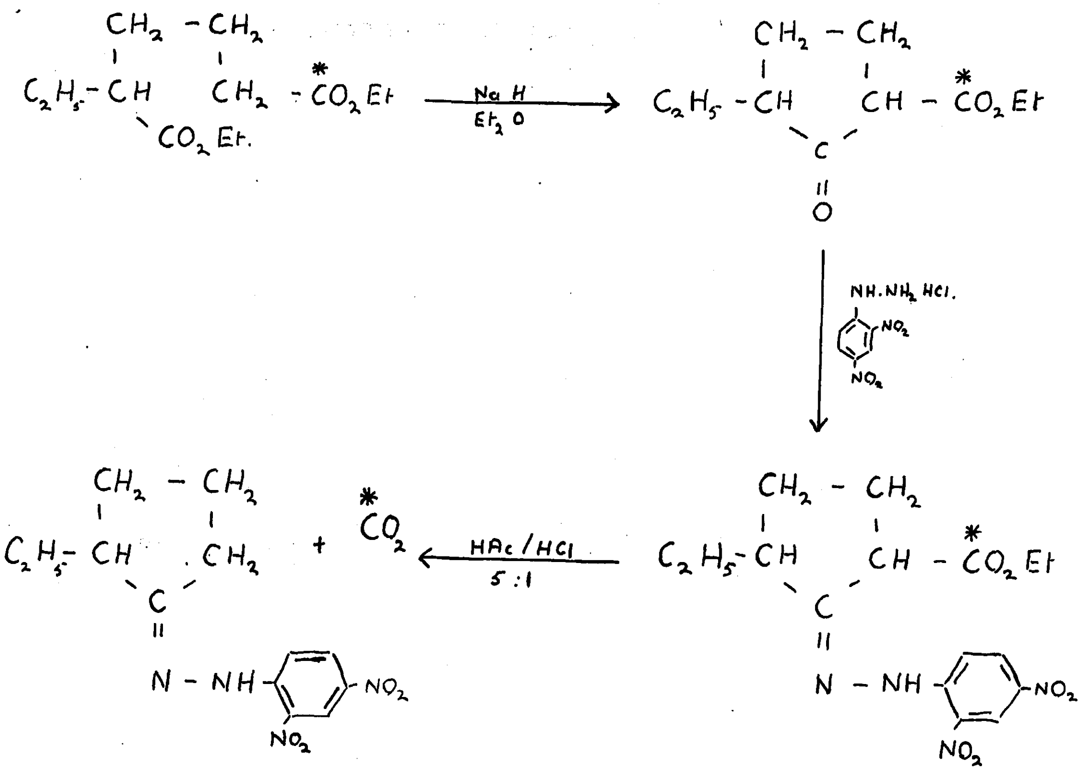
Since no dependable analytical method for estimating 2-alkyl-6-carbethoxycyclohexanones was devised, work on this topic was discontinued.

Formal Proof of Unique Ring Formation.

Theoretical interpretation of the results on the kinetic analysis of cyclisation in the cyclopentanone series assumed that ring closure took place to yield a single product. The evidence of previous workers is in agreement with this view (8, 19, 31, & 33.) eg. Dieckmann ring closure of diethyl-α-ethyladipate.



To establish a formal proof α-ethyladipic acid $COOH-\underset{Et}{C}H(CH_2)_3-\overset{*}{C}OOH$ and α-ethylpimelic acid $COOH-\underset{Et}{C}H(CH_2)_4\overset{*}{C}OOH$ were synthesised containing the labelled carbon atom, carbon-13, as shown. The esters were ring closed, and the 2:4-dinitrophenylhydrazones of the products hydrolysed, and decarboxylated according to the method of Bachmann, Wayne, Cole and Wilds (34).



The scheme above shows that for ring closure to take place exclusively in the direction assumed in the theoretical considerations of the results, all the isotopic carbon introduced into the molecule should appear again as isotopic carbon dioxide. This was measured using a Metropolitan-Vickers Ltd. Mass Spectrometer, Type M.S. 2, and showed that α-ethyldiethyladipate, when ring closed as shown above, liberated 99.3% of the isotopic carbon atom inserted into the molecule, while α-ethyl-diethylpimelate liberated 98.9% of the carbon-13 inserted. This proves that ring closure is unique.

[illegible]

The acids were esterified by the benzene-sulfonic acid method, and the esters ring closed using sodium hydride, according to the method of Pichat and [illegible] (28).

The products of ring closure were converted to their 2,4-dinitrophenylhydrazones by addition of the required quantity of a saturated solution of 2,4-dinitrophenylhydrazine in 2N hydrochloric acid. This was allowed to stand in the cold for 24 hours, and the precipitate was filtered off.

To remove any occluded reagent, the dinitrophenylhydrazones were dissolved in dry Analar benzene, passed through short columns of alumina, according to the method of Strain (29). 2:4-dinitrophenylhydrazone [illegible]

Experimental Procedure.

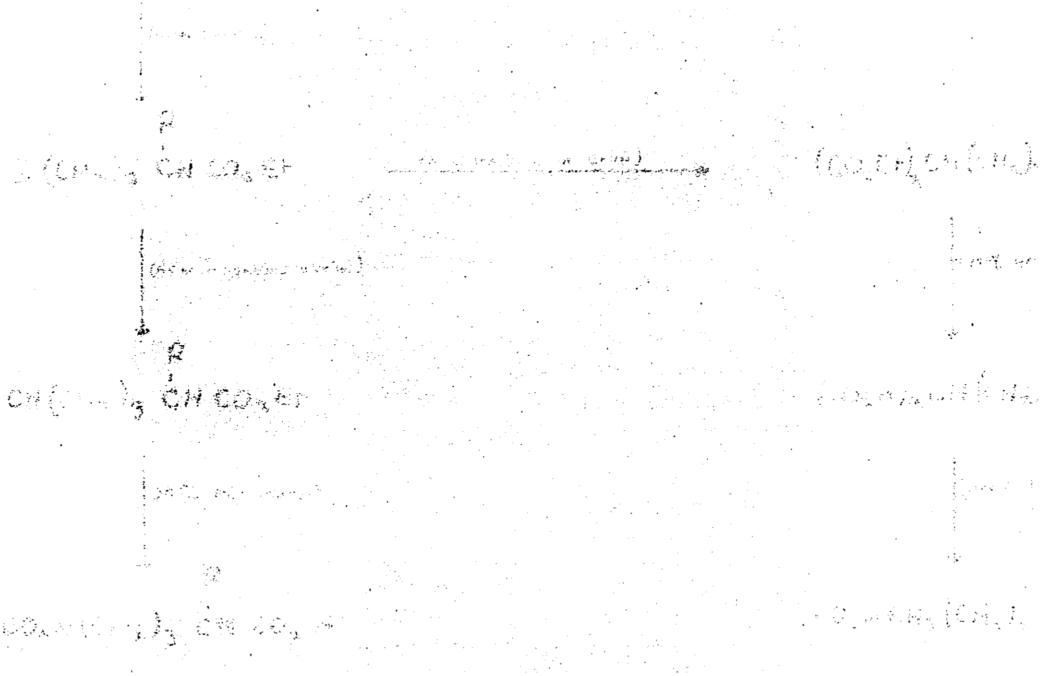
The synthesis of the acids followed table B page 56, stages 1to 5, α-ethylpimelic acid being synthesised from tetramethylenebromochloride in place of trimethylenebromochloride. The isotopic carbon atom, carbon-13, was introduced into the molecule at stage 3 where an isotopic sample of potassium cyanide was used.

The acids were esterified by the benzene, sulphuric acid method, and the esters ring closed using sodium hydride, according to the method of Pickard and Engles. (35).

The products of ring closure were converted to their 2:4-dinitrophenylhydrazones by addition of the required quantity of a saturated solution of 2:4-dinitrophenylhydrazine in 2N hydrochloric acid. This was allowed to stand in the cold for 24 hours, when the precipitate was filtered off.

To remove any occluded reagent, the 2:4-dinitrophenylhydrazones were dissolved in dry AnalaR benzene, and passed through short columns of alumina, according to the method of Strain (29). 2:4-dinitrophenylhydrazine is held firmly at the top of the column, and the product is eluted with dry benzene.

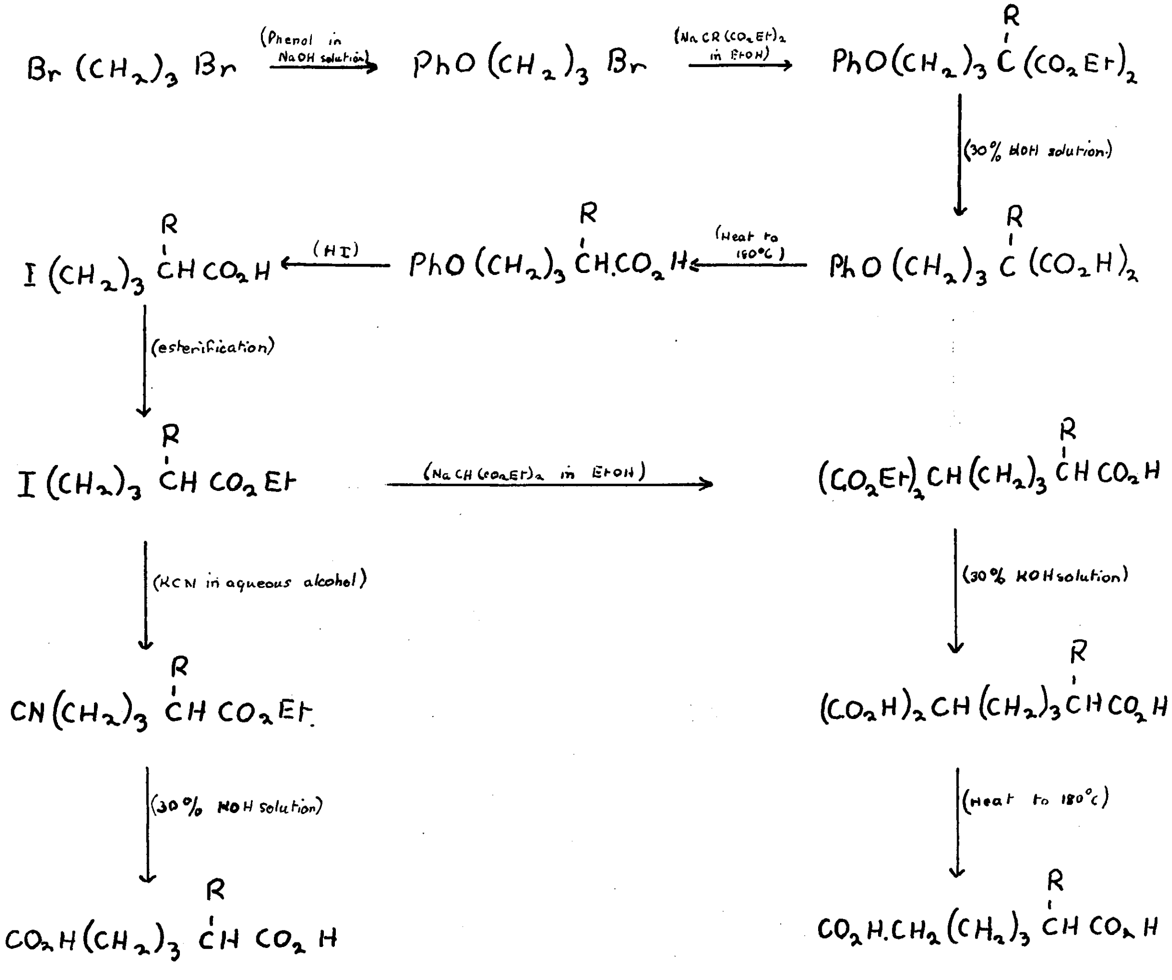
The eluents were evaporated to small bulk and portions transferred to break-seal tubes. The solvent was removed completely, and the product hydrolysed and decarboxylated, using a mixture of concentrated hydrochloric acid and glacial acetic acid in the proportions 1:5 as given by Bachmann, Wayne, Cole and Wilds (34).



PREPARATIVE WORK.

Synthesis of the α-substituted adipic and pimelic acids, $COOH.\underset{R}{CH}.(CH_2)_3COOH$ and $COOH.\underset{R}{CH}.(CH_2)_4COOH$ were carried out by two methods.

A. Synthesis of 2-alkyladipic and 2-alkylpimelic acids commencing with trimethylenedibromide.



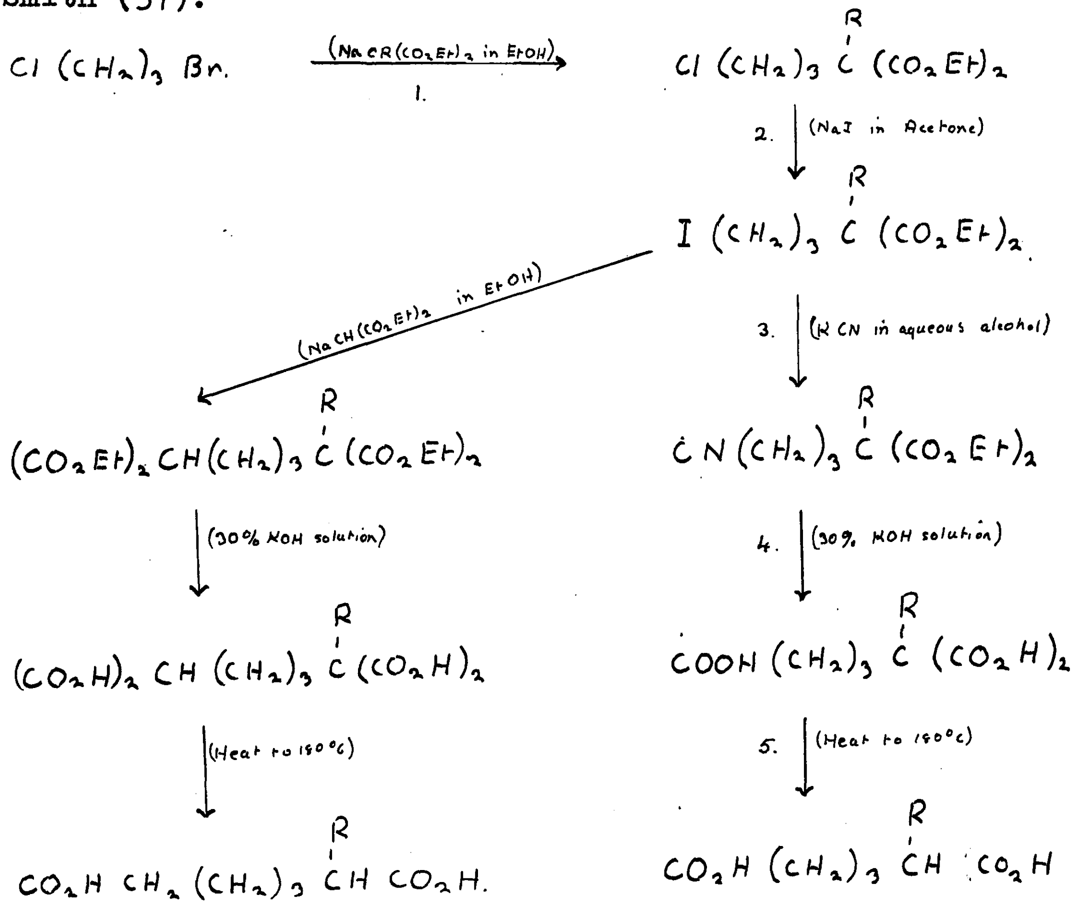
α-alkyladipic acid.

α-alkylpimelic acid.

The experimental procedure followed that given by Carter (36).

B. The second method starting from trimethylenebromochloride, was more convenient since there were fewer steps in the synthesis

Trimethylenebromochloride was synthesised according to the method of Cloke, Anderson, Lachmann, and Smith (37).



α-alkylpimelic acid.

α-alkyladipic acid.

β-methyladipic acid was prepared by the nitric acid oxidation of 3-methylcyclohexanone described by Markovnikoff (38).

It was found however that on salting out the acid it separated in white needle shaped crystals which were filtered off, melting point 94.5°C. This avoided both the extraction and the separation of β-methyladipic acid from α-methyladipic acid, which was found as a minor product by Markovnikoff (38).

Samples of each acid were recrystallised and characterised by their melting points as follows:-

Acid	Melting Point °C.	Reference
α-methyladipic acid	64	36
α-ethyladipic acid	49	40
α-n-propyladipic acid	59	41
α-i-propyladipic acid	66	42
β-methyladipic acid	94.5	38
α-methylpimelic acid	59	8
α-ethylpimelic acid	42	36
α-n-propylpimelic acid	56	-
α-i-propylpimelic acid	*	-

* This acid was obtained in the crude state as a yellow oil, and could not be crystallised. The sample so obtained was not purified further.

Part II

Kinetic Studies on the Thermal Decomposition of Sodium Adipate and Sodium β-methyl Adipate.

HISTORICAL SURVEY

Williamson (43) in 1852 described the preparation of n-butylmethyl ketone by dry distillation of potassium valerate and sodium acetate. He also predicted that an aldehyde would be produced when one of the salts used was a formate. This prediction was confirmed in 1886 by Limpricht and Ritter (44) who prepared acetaldehyde by the pyrolysis of a calcium acetate, calcium formate mixture, and by Piria (45) who obtained benzaldehyde and cinnamaldehyde by a similar method.

During the next forty years the method was generalised and adapted to improve yields, and in 1893 Wislicenus and Mager (46) prepared a cyclic ketone, cyclohexanone from calcium pimelate.

Preparation of ketones from the free acid by means of pyrolytic methods had been reported in 1853 by Gmelin (47), but the results were not satisfactory. In 1895,following upon this work Squibb (48) described the catalytic preparation of acetone by passing acetic acid vapour over a catalyst, barium or calcium carbonate, heated to about 400°C. This alternative method of ketone formation was extended to the preparation of unsymmetrical ketones principally by Sabatier and his co-workers (49), who tested many catalysts besides barium and calcium carbonates.

In 1906 Blanc (50) showed that the cyclic anhydrides of adipic and pimelic acids, when heated to 215 - 240 °C. at atmospheric pressure, gave the corresponding ketone with evolution of carbon dioxide.

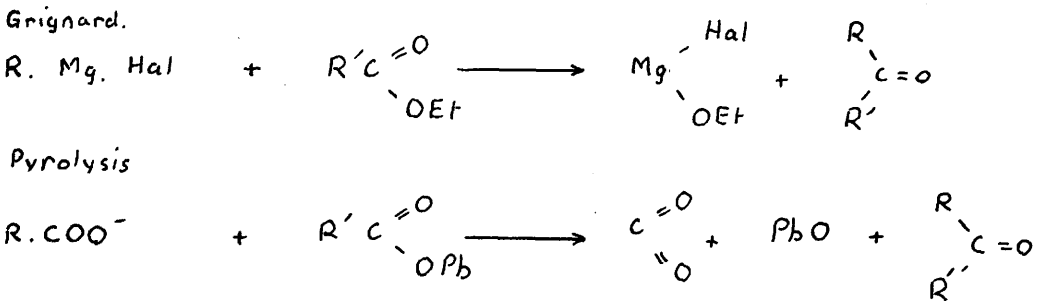
Following this Bamberger in 1910 (51) proposed the first theoretical explanation of the pyrolysis of the salts of acids. He stated that the reaction proceeded by alternate formation and decomposition of the anhydride of the acid employed.

This theory was supported by Dosios and Leucaditis (52), who postulated that mixed ketones resulted from the intermediate formation of the mixed anhydride.

Krönig (53) also used this theory to explain the decomposition of magnesium acetate giving acetone and magnesium oxide, instead of magnesium carbonate, which would have been expected at temperatures below that necessary for the decomposition of magnesium carbonate itself.

This theory fell into disuse as a result of the work of Hägglund and Hedman (54), who showed that the presence of water vapour during pyrolysis allows the reaction to be conducted at a lower temperature, thus increasing the yield of ketone. It has been proposed again as recently as 1948 by Bamdas and Shemyakin (55), but more recent work has not favoured this explanation.

Kenner and Morton (56) in 1939 studied the behaviour of lead salts on pyrolysis and showed that they often decomposed at lower temperatures than the corresponding calcium salts. During the reaction a solid intermediate was produced, which on treatment with formic acid liberated further quantities of ketone. To account for the behaviour of lead salts on pyrolysis a reaction mechanism analogous to the Grignard reaction was proposed.



Also in 1939 Neunhoeffer and Paschke (57) published a study of the pyrolysis of barium adipate. The salt was pyrolysed in the anhydrous state, and in presence of water vapour in an atmosphere of oxygen, when the reaction products were cyclopentanone, cyclopentene, and an appreciable quantity of carbon. The mechanism suggested was a type of Claisen condensation, in which the first step was the formation of the salt of the β-keto-acid, which decomposed to give the ketone.

e.g. pyrolysis of calcium acetate.

$$\begin{tikzcd} (CH_3COO)_2Ca \arrow[r] & CH_3COCH_2COOCaOH \arrow[d] \\ & CH_3COCH_3 + CaCO_3 \end{tikzcd}$$

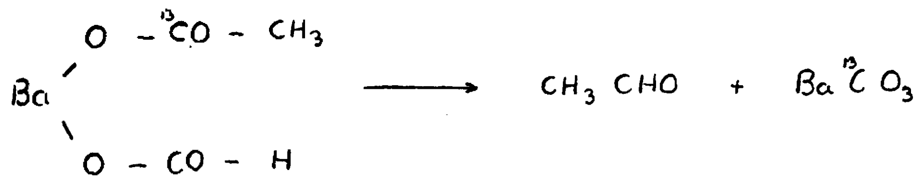
For this mechanism to operate the presence of an α-hydrogen atom is essential, and it was shown that calcium trimethylacetate gave no ketone on pyrolysis. This was further supported by the observations of Senderens (58), and of Farmer and Kracovski (59) who showed that no cyclic ketone was formed on pyrolysis of the cyclic acid anhydride of α-α-α'-α'-tetramethyl-adipic acid. This seemed to indicate that the presence of an α-hydrogen atom was necessary for primary enolisation and it was on this evidence that Neunhoeffer and Paschke based their theory.

Miller, Cook and Whitmore (60) however, have since shown that this is not the case. Studying the decarboxylation of trimethylacetic acid over a thoria catalyst at 490°C they found that a ketonic product was formed, namely ter-butyl-i-butyl ketone, along with a variety of other products resulting from the decomposition of this ketone. A reaction mechanism was proposed which postulated an aldol type of condensation as one of the steps leading finally to the ketone. The mechanism suggested, however, could not be a general one since salts of organic acids could not undergo such condensations. In addition, it cannot account for the formation of diaryl ketones from the pyrolysis of salts of aromatic acids.

Following the work of Rice (61, 62) on pyrolytic reactions, a free radical mechanism for the thermal decomposition of acid anhydrides and salts was suggested by Hurd, Christ and Thomas in 1933 (63).

Bell and Reed in 1950 (64) reported the possibility of a free radical mechanism for the pyrolysis of barium acetate and barium formate to give acetaldehyde. This mechanism was used by Brown (65) to explain the products of catalytic decomposition of isobutyric acid observed by Miller, Cook and Whitmore (60).

Bell and Reed in 1952 (66) gave an isotopic study of the formation of acetaldehyde by pyrolysis of barium acetate enriched with carbon-13 in the carbonyl group, and barium formate.



$$Ba\begin{matrix} / \; O-{}^{13}CO-CH_3 \\ \backslash \; O-CO-H \end{matrix} \longrightarrow CH_3CHO + Ba{}^{13}CO_3$$

The acetaldehyde produced had a normal carbon-13 content, and chain initiation was claimed to be the homolytic fission of the carbon-carbon bond to give free methyl radicals rather than free formyl radicals.

$$CH_3CO_2\ \tfrac{1}{2}Ba \longrightarrow CH_3^{\bullet} + {}^{\bullet}CO_2\ \tfrac{1}{2}Ba.$$

Acetaldehyde and acetone formation were then represented

$$CH_3^{\bullet} + HCO_2\ \tfrac{1}{2}Ba \longrightarrow CH_3\cdot CHO + {}^{\bullet}O\tfrac{1}{2}Ba$$

$$CH_3^{\bullet} + CH_3\ CO\tfrac{1}{2}Ba \longrightarrow CH_3\cdot CO\cdot CH_3 + {}^{\bullet}O\tfrac{1}{2}Ba$$

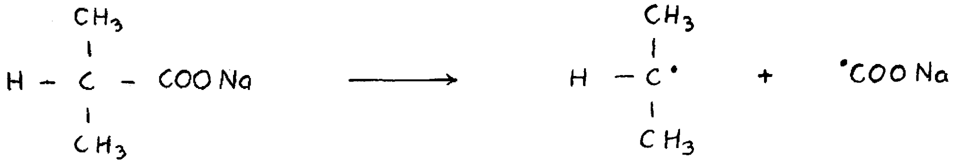
Chain continuation

$$CH_3\cdot CO_2\ \tfrac{1}{2}Ba + {}^{\bullet}O\tfrac{1}{2}Ba \longrightarrow CH_3^{\bullet} + BaCO_3$$

A number of alternative methods of chain termination were given, the relative importance of which could not be assessed by the experimental method employed.

Further support for this mechanism was claimed from the experiments of Miller, Cook and Whitmore (60) and also from the pyrolysis of sodium isobutyrate by O'Neill and Reed in 1953 (67). In addition to the expected product of reaction, di-i-propyl ketone, substantial quantities of both di-n-propyl ketone and i-propyl-n-propyl ketone were obtained.

It was assumed that rearrangement occurred within the alkyl radical produced



$$H-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-COONa \longrightarrow H-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^{\bullet}}} + {}^{\bullet}COONa$$

Lee and Spinks in 1953 (68, 69) studied the pyrolysis of calcium acetate, carbon-14 enriched in the carboxyl group, with equimolecular quantities of unlabelled calcium benzoate, p-toluate, phenylacetate, n-valerate, acetate, propionate, and formate. The results showed that the rate of loss of carbonyl group to form the ketone follows the order, acetate $>$ phenylacetate $>$ valerate $>$ formate $>$ benzoate.

They postulated that a free radical mechanism would predict the preferential formation of the benzyl radical to the methyl radical (70), while the results showed that in pyrolysis of a mixture of calcium acetate and calcium phenylacetate 2/3 of the benzyl methyl ketone results from the loss of the carboxyl group from the acetate.

Also, though the energy of the carbon-hydrogen bond is greater than that of the carbon-carbon bond (71) formates lose their carboxyl groups more readily than benzoates. This implies the formation of a hydrogen radical in preference to a phenyl radical.

Their third point of criticism was that established rearrangements in complex molecules proceeding by a free radical mechanism generally involve a rearrangement from the primary to the tertiary state

(72, 73). In pyrolysis of i-butyrates, however, a rearrangement from the secondary to the primary state is found.

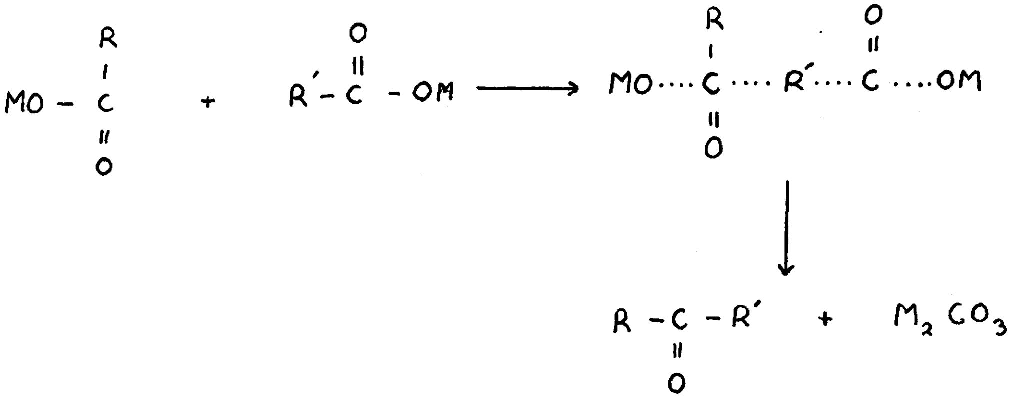
Finally it was suggested that the results of Miller, Cook and Whitmore (60) could be explained by a thermal decomposition of the reaction product which itself might have a free radical mechanism.

The alternative mechanism proposed by Lee and Spinks was an ionic mechanism in which the first step is the production of the acyl ion followed by an S_E2 decarboxylation, the acyl ion being the electrophilic component.

$$R.COOH \longrightarrow R-C^{+}=O + MO^{-}$$

$$R-C^{+}=O + R'COOH \longrightarrow RCOR' + M^{+} + CO_2$$

To avoid criticism of the ionic mechanism on the ground that carbonium ion formation is generally slow in comparison with other steps which follow, they also suggested the following mechanism, which could involve either heterolytic or homolytic cleavage of the bonds concerned.



$$MO-\underset{\overset{\|}{O}}{\overset{\overset{R}{|}}{C}} + R'-\overset{\overset{O}{\|}}{C}-OM \longrightarrow MO\cdots\underset{\overset{\|}{O}}{\overset{\overset{R}{|}}{C}}\cdots R'\cdots\overset{\overset{O}{\|}}{C}\cdots OM \longrightarrow R-\underset{\overset{\|}{O}}{C}-R' + M_2CO_3$$

Replying to the paper of Lee and Spinks, Reed (76) published some kinetic observations on the decomposition of sodium acetate. These measurements showed that, following the reaction by measurement of the rate of formation of sodium carbonate, the order is 3/2. This, and evidence from the decomposition of iso-butyric acid over a catalyst, was considered to indicate a free radical mechanism.

The work described in this thesis on the thermal decomposition of disodium adipate, and disodium β-methyladipate, was then started, and there have since been a number of relevant publications.

Reed in 1955 (74) extended the isotopic tracer technique used previously (66) to cover the catalytic formation of ketones. Mixtures of propionic acid enriched in carbon-13 in the carboxyl group, and unlabelled phenylacetic acid, benzoic acid, and formic acid were passed over various catalysts, and it was found that the results were essentially the same as those for salt pyrolysis. It was concluded that in this case, the reaction is in essence the breakdown of the salt formed initially by the acid with the catalyst. This work did not allow differentiation between the free radical and ionic mechanisms.

Also in 1955, Kuriacose and Jungers (75) studied kinetically the pyrogenetic formation of ketones from fatty acids using a thoria catalyst. The gas phase kinetics studied in a static system were greatly complicated by adsorption phenomena, and resort was made to a flow system. Results showed that catalytic decomposition of the acids was a bimolecular reaction on the surface of the catalyst. An attempt was made to correlate the pyrolysis of acetic acid vapour on a thoria catalyst, and thorium acetate. It was concluded that ketonisation of acids on a catalytic surface took place through the intermediate formation of the salt of the acid, which confirms the results of Reed (74). They also proved that acetic anhydride could not be an intermediate in the formation of acetone from acetic acid. No attempt was made to discuss a general mechanism for the reaction, or to interpret the results in the light of either the ionic mechanism of Lee and Spinks (69) or the free radical mechanism of Bell and Reed (64, 66).

The kinetic analysis of pyrolysis of salts of adipic and β-methyl adipic acids was undertaken to compare it with the Dieckmann ring closure discussed in part I of this thesis; and also to attempt to distinguish between the free radical and ionic mechanisms for such pyrolyses.

PRELIMINARY EXPERIMENTAL WORK.

Trial experiments proved that a suitable working temperature for the measurement of the course of the decomposition of sodium adipate to form cyclopentanone was 440°C. At this temperature, the reactions were complete within 2 to 3 hours. This was a necessary condition as the thermostat could not be run for much longer than 3 hours at the high temperatures required without breaking down.

The suitability of the sodium salt for a kinetic analysis of the course of the reaction was tested by an analytical run. Sodium adipate was pyrolysed in a silica boat at 440°C with a nitrogen flow of about 4 litres per hour (37). The reaction was allowed to go to completion, and the products were collected in a liquid air trap. It was noticed that the product remained clear till the end of the reaction, when the last few drops became yellow in colour.

The product was converted to 2:4-dinitrophenylhydrazone and estimated quantitatively according to the method of Iddles and his collaborators (27,28). The residual sodium carbonate was estimated by titration against standard hydrochloric acid solution, using screened methyl orange as indicator.

The results were as follows:-

	a (gms.)	b (gms.)
Wt. of salt pyrolysed.	0.2971	0.7407
Wt. of sodium carbonate, theoretically.	0.1657	0.4132
Wt. of sodium carbonate, formed.	0.1628	0.4112
Wt. of cyclopentanone, theoretically.	0.1314	0.3278
Wt. of cyclopentanone, formed.	0.1300	0.3231
% Yield of cylopentanone.	98.9	98.5

That the pyrolysis gave a single ketonic product was tested chromatographically using the method of Strain (29).

A portion of the 2:4-dinitrophenylhydrazone prepared in the estimation given above was dissolved in dry AnalaR benzene, and passed through a ten inch column of alumina. Only one band resulted, and it was assumed that by-products were formed to the extent of less than 1.5%.

Preparation of Sodium Salts.

Since the sodium salts of adipic acid and its substituted homologues are water soluble, and are not readily recrystallised, they were prepared by adding the stiocheiometric quantity of a standard solution of sodium hydroxide to a weighed sample of the acid, which had been recrystallised three times from distilled water. The aqueous solution of the sodium salt was evaporated to dryness on a water- bath, care being taken to exclude dust. The resulting solid was finely ground in a mortar and dried completely in an oven at 110°C. The salts were kept in screw capped bottles in a desiccator, so that they should not become contaminated with water.

By this method the salts of adipic acid and β-methyladipic acid were prepared, also mixtures of adipic acid and disodium adipate of known composition, since it is recorded in the literature that such mixtures pyrolyse at lower temperatures than the pure disodium salt, (15).

It was found however that these mixtures were unsatisfactory for kinetic analysis, as some of the free acid distilled off with the product during the reaction.

Analysis of Sodium Salts:

The salts were analysed by estimating their sodium content gravimetrically as sodium sulphate.

A sample of the sodium salt was weighed into a tared platinum crucible with platinum lid. This was heated to convert the salt to sodium carbonate. Heating was continued till all the carbon formed had been removed. Keeping the lid as tightly closed as possible, analar sulphuric acid (0.5ml.) was allowed to run down the side of the crucible. Excess sulphuric acid was removed by heating, and sodium bisulphate formed along with sodium sulphate decomposed by sprinkling the salt with a small quantity of solid ammonium carbonate and volatilising off the excess. The crucible containing the sodium sulphate was cooled and reweighed.

Analytical Results.

Salt.	% Sodium Theoretically.	% Sodium By analysis.
Disodium Adipate.	24.19	a. 24.16 b. 24.17
Disodium salt of β-methyladipic acid.	22.54	a. 22.55 b. 22.52
Monosodium salt of adipic acid.	13.68	a. 13.70 b. 13·67

This method proved generally suitable for analysis of metallic salts of organic acids.

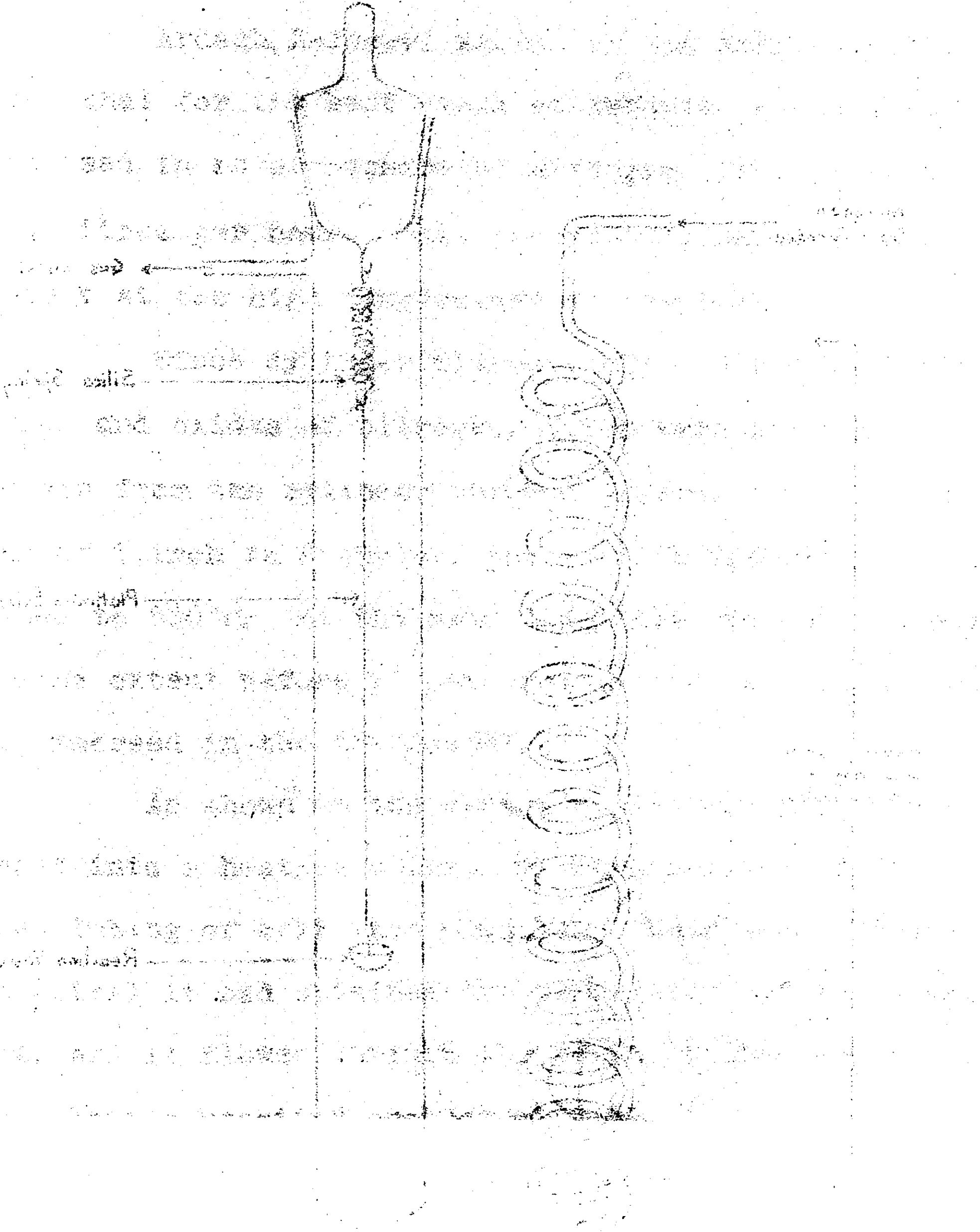
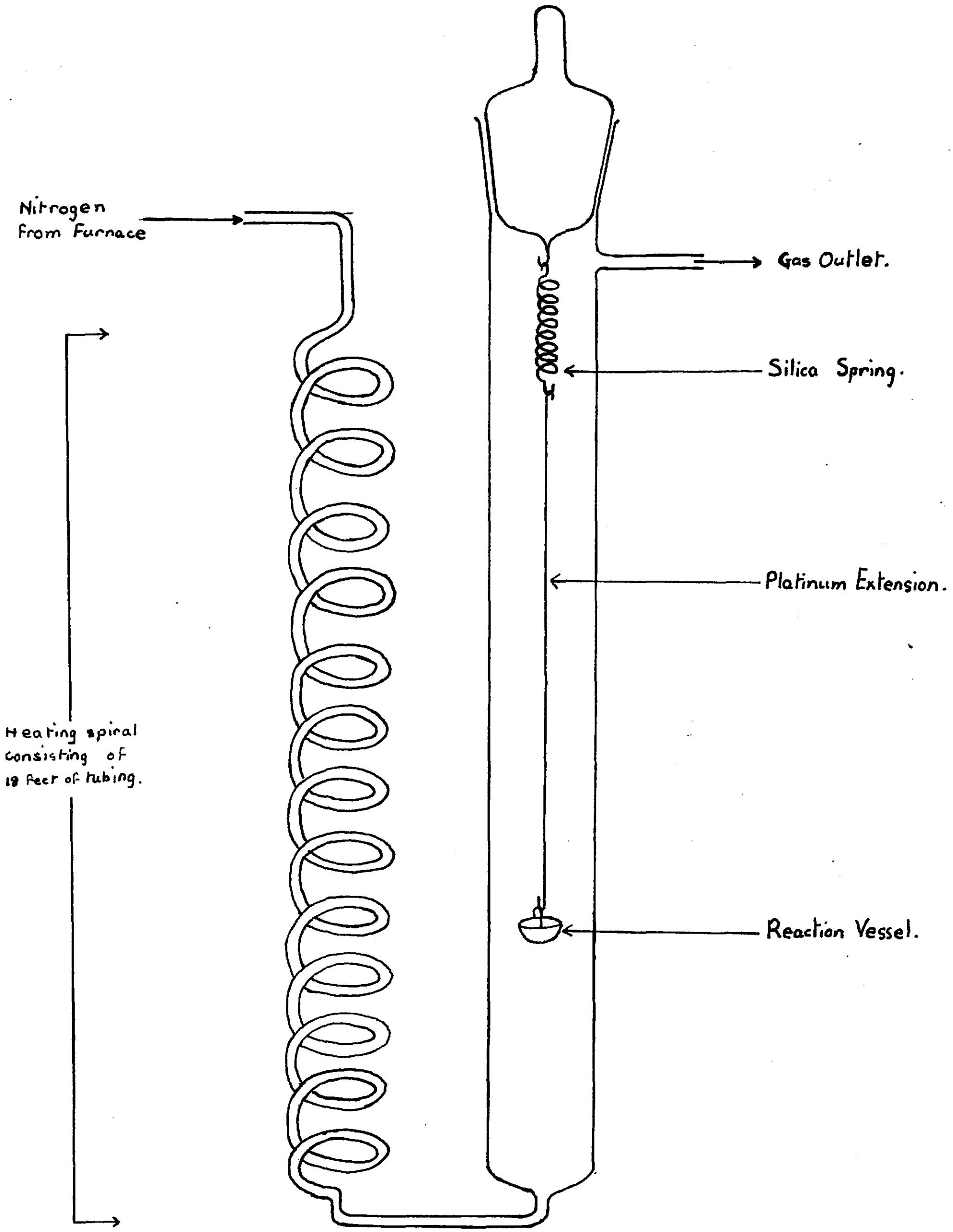

Gas
Silica Spring

Fig. 4.


Nitrogen from Furnace
Gas Outlet.
Silica Spring.
Platinum Extension.
Heating spiral consisting of 18 feet of tubing.
Reaction Vessel.

KINETIC OBSERVATIONS.

Unless otherwise stated, rate constants quoted in this work were obtained using an adaption of the sorption balance (77) shown in fig. 4.

Ardagh, Barbour, McClellan and McBride, (78) found that for the best yield of ketones, salts should be pyrolised in an atmosphere of nitrogen, flowing at the rate of 4 litres per hour. This prevents decomposition of the product at the high temperature of reaction.

Since cylinder nitrogen may contain a little oxygen and oxides of nitrogen, these were removed by passing the gas from the cylinder through a pyrex tube, 10 inches long by 1 inch in diameter, packed with reduced copper, heated to 600°C. At the same time this preheated the nitrogen to some extent before it passed into the apparatus, which was immersed in the thermostat.

As shown in the sketch opposite, the nitrogen passed into a heating spiral, which consisted of 18 feet of glass tubing of 3/16 inch diameter. When the nitrogen left the spiral it had attained the temperature of the thermostat, and it flowed through the reaction chamber, sweeping the volatile reaction product with it.

The rate of nitrogen flow was observed by the rate of escape of nitrogen from the apparatus through an Arnold's potash bulb.

Pyrolyses were conducted in small buckets of 1.5 ml. capacity made of platinum, silica or pyrex glass.

Experimental Method.

To ensure that the apparatus was in thermal equilibrium with the thermostat, it was set into position, and the nitrogen flow regulated fully half an hour before the reaction was commenced.

The weighed sample was attached to the silica spring and plunged into the apparatus at the temperature required for reaction. As there was generally a noticeable time lag before reaction started, the correct zero time used in calculation of the rate constants could be found by extrapolation.

The weight of the sample was measured at suitable intervals of time, by measuring the extension of the silica spring, using a travelling microscope which read to ± 0.001cm.

The helical silica springs employed were 1.5 cms. in diameter, and their extensions varied from 2.5 cms. per 1 gm. , to 1.0 cm. per 1 gm. They were not calibrated before use, as the measurements required for each run gave a measure of the sensitivity for each reaction. This was essential as the sensitivity of the springs varied with temperature.

When reaction was complete the bucket and its contents were reweighed, and the sensitivity of the spring calculated. The contents of the bucket were then dissolved in 100 mls. of water, and the residual sodium carbonate estimated by titration against standard hydrochloric acid, using screened methyl orange as indicator.

Specimen of Results.

(1) Pyrolysis of Disodium Adipate in a Silica Vessel.

Temperature. = 440°C.

Gm. mols. salt pyrolysed. = 7.532×10^{-4}.

Gm. mols. sodium carbonate produced (by analysis) = 7.498×10^{-4}.

Sensitivity of spring. = 1.197 cms/gm.

Rate of nitrogen flow. = 4 litres/sec.

Time lag. (by extrapolation) = 13.5 mins.

Height of travelling end of spring. (h_o) = 36.384 cms.

t (mins.)	h (cms.)	(ho-h) (cms.)	X x 10^{-4} (gm.mols.)	(a-x)x 10^{-4}	$\frac{1}{t}\log\frac{a}{a-x}$ x10^{-2}(min.$^{-1}$)
1	36.384				
5	36.382				
10	36.386				
12	36.385				
15	36.386	0.002	0.198	7.334	0.704
16	36.388	0.004	0.396	7.136	0.884
17	36.390	0.006	0.595	6.937	0.865
19	36.393	0.009	0.892	6.640	0.97
20	36.395	0.011	1.090	6.442	1.01
22	36.398	0.014	1.388	6.144	1.14
24	36.403	0.019	1.883	5.649	1.17
26	36.409	0.025	2.480	5.052	1.37
28	36.415	0.031	3.074	4.458	1.51
30	36.420	0.036	3.570	3.962	1.68
32	36.427	0.043	4.262	3.270	1.94
34	36.431	0.047	4.661	2.871	2.03
36	36.434	0.050	4.957	2.575	2.02
38	36.435	0.051	5.058	2.474	1.96
40	36.437	0.053	5.253	2.279	1.95
45	36.442	0.058	5.751	1.781	1.91
50	36.445	0.061	6.050	1.482	1.93
55	36.447	0.063	6.250	1.282	1.85
70	36.453	0.069	6.850	0.682	1.85

K uncatalysed. = 1.5 x 10^{-2} mins^{-1}.

K catalysed. = 3.84 x 10^{-2} mins^{-1}.

(2) Pyrolysis of Disodium β-methyladipate in a Platinum Vessel.

Temperature. = 427°C.

Gm. Mols. salt pyrolysed. = 6.399×10^{-4}.

Gm. Mols. sodium carbonate produced. (by analysis) = 6.397×10^{-4}.

Sensitivity of spring. = 2.25 cms. / gm.

Rate of nitrogen flow. = 4 litres / sec.

Time lag. (by extrapolation.) = 1 min.

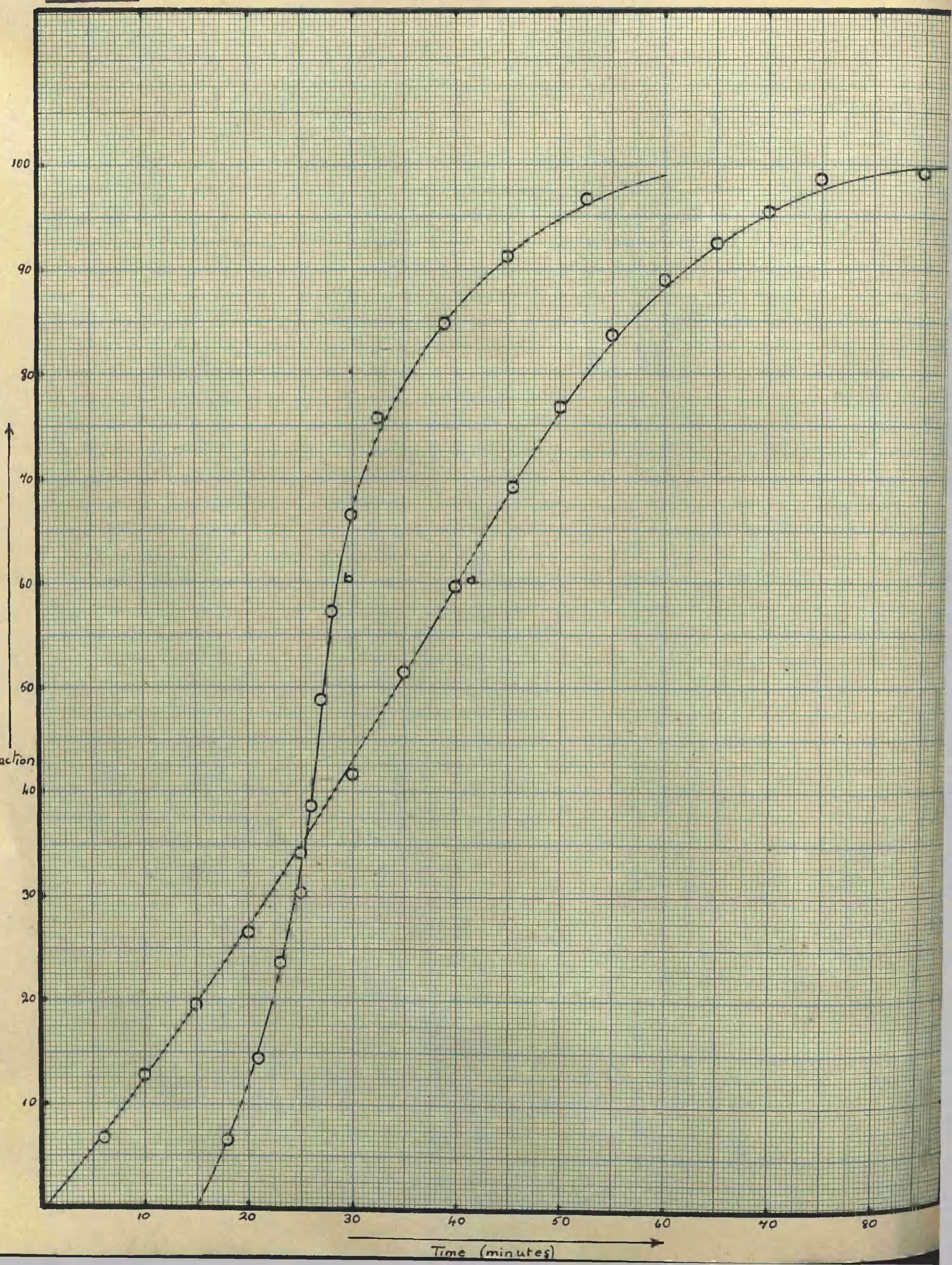
Initial height of travelling end of spring. (h_o) = 40.063 cms.

t (mins.)	h (cms.)	(ho-h) (cms.)	$X \times 10^{-4}$ (gm.mols.)	$(a-x) \times 10^{-4}$	$\frac{1}{t} \log \frac{a}{a-x}$ mins.$^{-1}$
1.5	40.083	0.020			
4	40.104	0.041	1.773	4.623	0.0354
10	40.141	0.078	3.522	2.864	0.0349
11	40.144	0.081	3.667	2.719	0.0347
12	40.153	0.090	4.075	2.321	0.0368
13	40.159	0.096	4.347	2.049	0.0380
14	40.162	0.099	4.481	1.915	0.0374
15	40.165	0.102	4.618	1.778	0.0371
16	40.168	0.105	4.754	1.642	0.0370
17	40.171	0.108	4.890	1.506	0.0370
18	40.172	0.109	4.935	1.461	0.0356
19	40.175	0.112	5.071	1.325	0.0360
20	40.177	0.114	5.162	1.234	0.0357
21	40.180	0.117	5.298	1.098	0.0364
22	40.182	0.119	5.388	1.008	0.0365
23	40.183	0.120	5.434	0.962	0.0358
25	40.186	0.123	5.569	0.827	0.0359
31.5	40.192	0.129	5.977	0.419	0.0376
∞	40.205				

$$K = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$= 2.303 \times 0.365 = 8.40 \times 10^{-2} \text{ mins.}^{-1}$$

Fig. 5.



100
90
80
70
60
50
40
30
20
10
% Reaction
b
a
10
20
30
40
50
60
70
80
Time (minutes)

EXPERIMENTAL RESULTS

Initial experiments on disodium adipate gave results which appeared to indicate that for 70% of its course the reaction was of zero order. Since the salt did not melt before reacting this was assumed to indicate heat transfer effects, the outer layer of salt insulating the inner portion.

Experiments on different weights of salt showed that heat transfer effects became appreciable when more than 0.25 gm. of salt was used. To avoid this the weight of salt pyrolysed in each analytical run was less than 0.15 gm.

This is illustrated graphically in Fig. 5, which shows the course of pyrolysis of disodium adipate in a platinum boat at 440°C., curve "a" using 0.3353 gm. salt, and curve "b" 0.0710 gm.

The sinusoidal curve "b" is typical of autocatalytic reactions, and a mathematical analysis to resolve the kinetics of these reactions was made by R.I. Reed. This assumed the reaction to consist of two first order reactions, the first of which is uncatalysed, and the second catalysed by a product or intermediate of reaction.

Mathematical Analysis

The reaction may be represented

$$A \longrightarrow \text{products}$$

Let the concentration of A at time $t = 0$ be a, and at time t be $a - x$.

For the uncatalysed reaction

$$\frac{dx}{dt} = k_1 \ (a - x)$$

The rate of the uncatalysed reaction was obtained by plotting the values of $\frac{2.303}{t} \log_{10} \frac{a}{a - x}$ against the percentage reaction and extrapolating this value to zero reaction.

For the autocatalytic case

$$\frac{dx}{dt} = kx \ (a - x) \qquad \ldots\ldots\ldots\ldots\ldots\ldots \ 1)$$

This is the general case, for if the catalyst produced is proportional to the product x, we can replace x by say $f\,x$ where f is a constant of proportionality and then incorporate it in k.

If $x \neq 0$

$$\frac{dx}{dt} = kx \ (a - x)$$

$$= \frac{2kx^2}{2x} \ (a - x) \qquad \ldots\ldots\ldots\ldots\ldots\ldots \ 2)$$

Consider the function

$$x + \frac{x^2}{a} + \frac{x^3}{a^2} + \frac{x^4}{a^3} + \ldots\ldots\ldots \frac{x^{n+1}}{a^n} + \ldots$$

$$- \left(\frac{x^2}{a} + \frac{x^3}{a^2} + \frac{x^4}{a^3} + \ldots\ldots\ldots \frac{x^{n+1}}{a^n} + \ldots\ldots\right)$$

If the series is convergent, i.e. $\frac{x^{n+2}}{a^{n+1}} \Big/ \frac{x^{n+1}}{a^{n}} < 1$ which it is if $\frac{x}{a} < 1$, provided $x < a$, the sum of the above function is x.

Now this series may be written

$$a\left(\frac{x}{a} + \frac{x^2}{a^2} + \frac{x^3}{a^3} + \ldots\ldots\frac{x^n}{a^n}\right) - x\left(\frac{x}{a} + \frac{x^2}{a^2} + \frac{x^3}{a^3} + \ldots\ldots\ldots\ldots\frac{x^n}{a^n}\right) = x$$

i.e. $$(a-x)\left(\frac{x}{a} + \frac{x^2}{a^2} + \frac{x^3}{a^3} + \ldots\ldots\ldots\frac{x^n}{a^n}\right) = x$$

i.e. $$(a-x)\log_e\left(1 - \frac{x}{a}\right) = x$$

Substituting in equation 2

$$\therefore \quad \frac{dx}{dt} = \frac{2kx^2}{x + x}(a-x)$$

$$= \frac{2kx^2(a-x)}{x + (a-x)\log_e\left(1 - \frac{x}{a}\right)}$$

In a kinetic run $x \not> a$ and only equals a when $t = \infty$ i.e. the condition that $a > x$ is satisfied throughout the reaction.

Since $\log \varphi = -\log \frac{1}{\varphi}$

$$\frac{dx}{dt} = \frac{2kx^2(a-x)}{x - (a-x)\log_e \frac{1}{1 - \frac{x}{a}}}$$

$$= \frac{2kx^2\ (a-x)}{x-\ (a-x)\ \log_e \frac{a}{a-x}}$$

Inverting and rearranging

$$2k.dt \;=\; \frac{x - (a - x)\ \log_e \frac{a}{a - x}}{x^2\ (a - x)}\ dx$$

Multiplying L.H.S. top and bottom by x

$$2kdt \;=\; \frac{x^2 - (ax - x^2)\ \log_e \frac{a}{a - x}}{x^2\ (ax - x^2)}\ dx$$

i.e. $$\int_0^t 2kdt \;=\; \int_0^x \left(\frac{1}{ax - x^2} - \frac{1}{x^2} \log_e \frac{a}{a - x} \right) dx$$

Integrating R.H.S. by parts we have

$$\int_0^t 2kdt \;=\; \frac{1}{x} \int_0^x d\ \log_e \frac{a}{a - x} + \int_0^x \frac{1}{x^2} \log_e \frac{a}{a - x}\ dx - \int_0^x \frac{1}{x^2} \log_e \frac{a}{a - x}\ dx$$

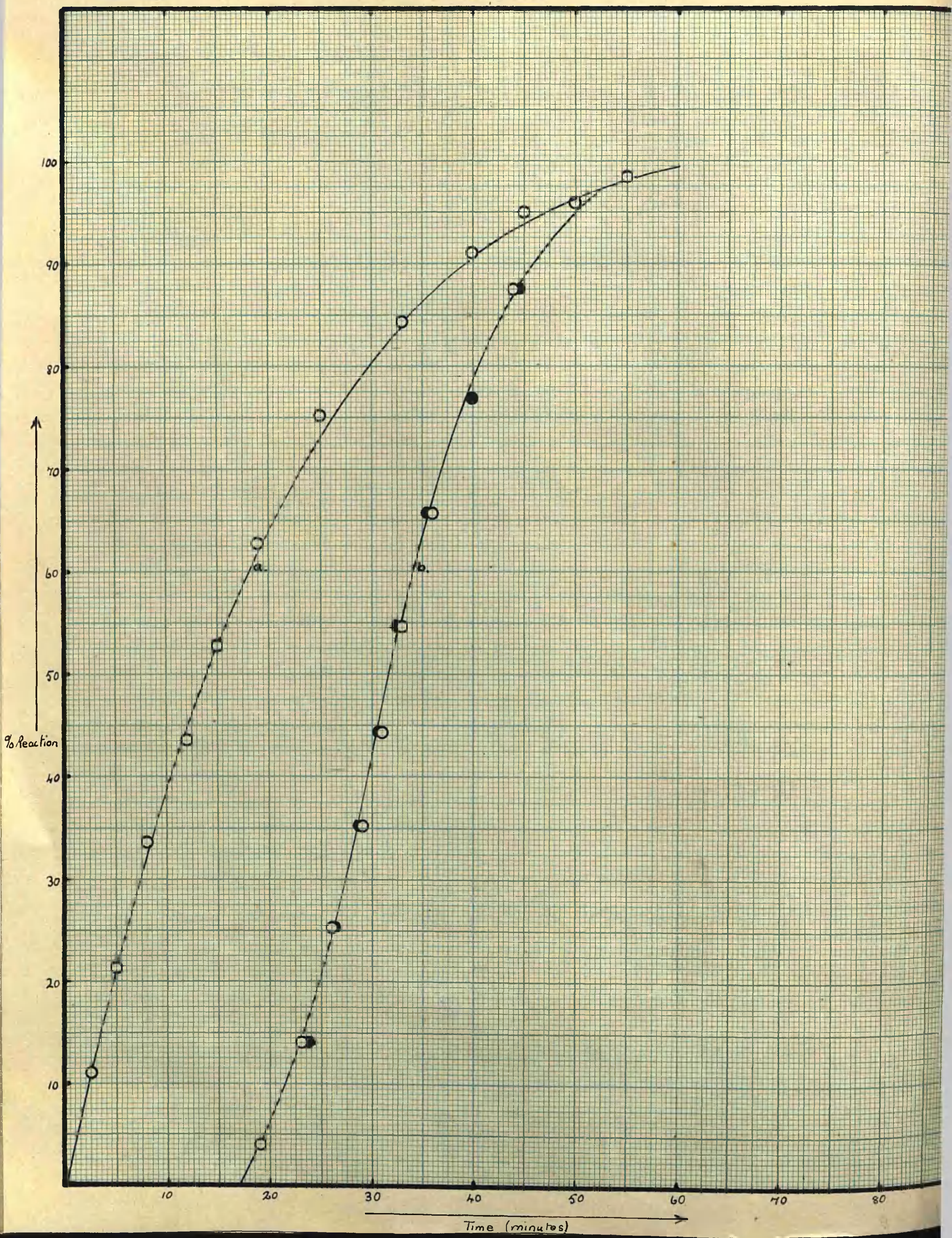
$$\therefore\quad 2kt \;=\; \frac{1}{x} \log_e \frac{a}{a - x} + c$$

Since c represents the amount of reaction before catalysis sets in, it may be equated to zero.

Thus $$\frac{1}{tx} \log_e \frac{a}{a - x} \;=\; 2k$$

and $$\frac{1}{tx} \log_{10} \frac{a}{a - x} \;=\; \frac{2k}{2.303}$$

Fig. 6.


100
90
80
70
60
50
40
30
20
10
% Reaction
a.
b.
10
20
30
40
50
60
70
80
Time (minutes)

Effect of the Nature of the Reaction Vessel

It was thought that the chemical nature of the reaction vessel might influence the course of the pyrolysis, metals such as platinum accelerating or altering the course of the reaction.

Pyrolyses of disodium adipate were therefore conducted in vessels of platinum, both clean and carbon coated, silica and pyrex glass.

The carbon deposit was made by pyrolysing a portion of disodium adipate in the platinum vessel. This was washed out carefully with ether, alcohol, and finally water, to remove reactants and products of reaction. A continuous coating of carbon was thus deposited firmly on the metal.

In the platinum, pyrex and silica vessels the reaction remained autocatalytic, but when the boat was carbon covered the reaction became simple first order.

These results may be compared graphically in Fig. 6, where "a" represents the course of the first order reaction conducted in the carbon coated vessel; "b" is that for pyrolysis in a silica boat. In each case a representative selection of experimental points are given " ○ ". The points " ● " on curve "b" were calculated from the theoretical equation governing the first order autocatalytic reaction given on p. 84.

The only observable difference in the course of the reaction on passing from platinum, to pyrex glass, to silica reaction vessels, was the length of time which elapsed before reaction began. As this time lag increases in the order platinum < pyrex glass < silica, this difference was assumed to be purely a thermal effect, since the platinum and pyrex glass vessels were made as light as possible weighing approximately 0.3 gm. and 0.5 gm. respectively. The silica bucket, however, weighed 1.2 gm. and had thicker walls than the others.

Table I gives the first order rate constants for the uncatalysed and catalysed reactions in the pyrolysis of disodium adipate at 440°C, in reaction vessels of different materials, and the last column gives the time which elapsed before reaction began.

Table I

Nature of Reaction Vessel	K uncatalysed $\times 10^2$ mins.$^{-1}$	K catalysed $\times 10^2$ mins.$^{-1}$	Time lag mins.
platinum	1.34	3.88	3.0
	1.34	4.38	2.7
silica	1.50	3.84	13.5
pyrex glass	1.39	3.43	10.0
carbon covered	-	3.08	3.7

Since the presence of the metal platinum had no apparent effect on the course of reaction, this vessel was used for all subsequent experiments unless otherwise stated; being the lightest and thus allowing the most sensitive silica spring to be employed.

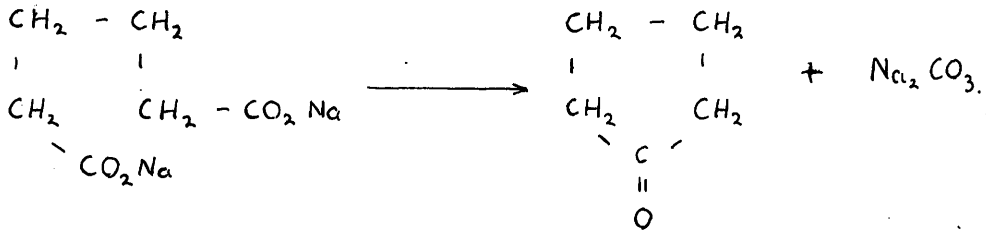
First order rate constants for the pyrolyses of disodium adipate at different temperatures are given in table II.

Table II

Temperature °C.	K uncatalysed $\times 10^2$ mins.$^{-1}$	K catalysed $\times 10^2$ mins.$^{-1}$
420	less than 0.4% reaction after 4 hours	
430	0.16	-
440	1.34	3.88
449	3.90	7.08
464	6.96	14.70

To Investigate the Effect of Reaction Products

During the pyrolysis of disodium adipate, one of the reaction products, cyclopentanone, distils away, but the other, sodium carbonate, remains in the reaction mixture.



It was noticed also that a small amount of carbon was formed during reaction. This was assumed to come from the breakdown of either the product cyclopentanone, or some reaction intermediate.

Samples of disodium adipate containing known amounts of sodium carbonate, and finely ground carbon were prepared. The first order rate constants for their pyrolyses are given in table III.

Table III

Temperature °C.	K uncatalysed $\times 10^2$ mins.$^{-1}$	K catalysed $\times 10^2$ mins.$^{-1}$
a. 444	2.64	5.94
b. 440	-	3.05
c. 440	-	3.08

a. Reaction mixture contained 9.94% added sodium carbonate.

b. Reaction mixture contained 10% added carbon.

c. Disodium adipate pyrolysed in a carbon covered vessel.

Reaction c, where the carbon is present as a lining on the boat is included, so that it may be compared with b. where the carbon is intimately mixed with the reactant.

Plotting the courses of reactions a. and b. a graph identical with Fig. 6 opposite p.86 is obtained, i.e. the autocatalytic character of the reaction is retained when sodium carbonate is present (curve b. Fig. 6), and carbon mixed with the reactant renders the reaction simple first order, (curve a. fig. 6.)

Comparing the values obtained for the rates of the uncatalysed and catalysed reaction it may be seen that catalysis is slight, the rate of the catalysed reaction being twice that of the uncatalysed reaction. It would also appear from table III that providing the quantity of salt pyrolysed is small, the catalyst is no more effective when the carbon is intimately mixed with the salt than when the disodium salt is pyrolysed in a carbon covered vessel.

Pyrolysis of Disodium-β-methyl-adipate

Preliminary experiments showed that though this salt pyrolysed more readily than disodium adipate, the conditions governing the pyrolysis of disodium β-methyl adipate were similar to those governing the decomposition of disodium adipate; namely that the nature of the reaction vessel did not affect the reaction velocity and the addition of carbon to the salt speeded up the reaction slightly.

In this case, however, the reaction was not autocatalytic, but followed a simple first order course.

Table IV gives the first order rate constants for pyrolysis of disodium-β-methyl adipate.

Table IV

Experiment number	Temperature °C.	$K = \frac{2 \cdot 303}{t} \log_{10}\frac{a}{(a-x)}$ $\times 10^2$ mins.$^{-1}$
1	427	8.40
2[a]	427	8.35
3[b]	427	8.24
4[c]	427	12.44
5[c]	427	13.01
6	410	2.89
7	395	1.06

a. Reaction mixture contained 10% of added sodium carbonate.

b. Reaction carried out in a silica vessel.

c. Reaction mixture contained 11% of carbon intimately mixed with the salt.

Other than for experiment 3^b all pyrolyses were conducted in a platinum reaction vessel.

[illegible]

[illegible]

It was noted that, whereas the pl[illegible] formation of both cyclopentanone and [illegible] pentanone was about 80% theoretical, [illegible] from sodium adipate was in the [illegible]

It was therefore to be expected that [illegible] would hold for the whole [illegible] osition, and it was found that at lo[illegible] atures, the pyrolysis obeyed a unimo[illegible] rate [illegible] for about 80% of the reaction.

The pyrolyses were conducted in a [illegible] platinum

Pyrolysis of Sodium Acetate.

As a control, some experiments were done on the pyrolysis of sodium acetate.

$$2CH_3COONa \longrightarrow CH_3.CO.CH_3 + Na_2CO_3$$

Preliminary work on this compound had been done by Reed (76), who found that the order of the reaction, as followed by the formation of sodium carbonate, was 1.5.

Using the method employed for disodium adipate and disodium β-methyladipate, i.e., following the reaction by the rate of formation of acetone, the course of the reaction was found to be more difficult to interpret than either of the dicarboxylates.

It was noted that, whereas the yield of ketone in the formation of both cyclopentanone and 3-methylcyclopentanone was about 98% theoretical, the yield of acetone from sodium acetate was in the region of 80%.

It was therefore to be expected that no simple reaction order would hold for the whole course of the decomposition, and it was found that at lower reaction temperatures, the pyrolysis obeyed a second order rate equat ion for about 50% of the reaction.

The pyrolyses were conducted in clean platinum reaction vessels. The second order constants are recorded in table V which follows.

Table V.

Temperature. (°C.)	K (litres. $mols^{-1}$. $mins^{-1}$.)
430	0.71×10^{-3}
440	1.12×10^{-3}
452	1.76×10^{-3}
453 *	2.74×10^{-3}

* Reaction mixture contained 9.85% added carbon.

Pyrolyses conducted at temperatures above 460°C. proceeded rather too rapidly for accurate kinetic analysis, and at still higher temperatures (480°C. and above) the yield fell, the residue being more carbonaceous. This may indicate that, at these higher temperatures, the reaction might proceed by a different mechanism.

The order of reaction was also determined with respect to acetate, by analysis of the reaction mixture at suitable intervals of time.

Experiments were performed on the salt sodium acetate as such, and mixed with carbon.

Experimental Method.

The reaction was conducted in sealed pyrex tubes.

Equal quantities of sodium acetate (about 0.1 gm.) were transferred to the tubes as a stock solution, containing 0.1 gm. sodium acetate per 1 ml. Finely ground carbon, amounting to 10% of the weight of acetate present, was also added to some of the tubes. These were then dried at 110°C. to evaporate the solvent.

The pyrolyses were conducted at 428°C., the tubes being withdrawn from the thermostat at suitable intervals of time, and the reaction quenched by dropping the tubes into water.

Each sample was made up to 100mls. in a graduated flask, and analysed for acetate using the spectrometric method of Hutchens and Kass (79). This method gave reliable results, only when each estimation was compared with known standards.

RESULTS. I. Pyrolysis of Sodium Acetate.

Gm. Mols. sodium acetate pyrolysed. = 1.173×10^{-4}.

Concentration of salt. (a) = 8.9 gm. mols. / litre

Time. (mins.)	a - x *	x *	K (litres mols.$^{-1}$ mins.$^{-1}$)
4	8.66	0.24	7.79×10^{-4}
6	8.58	0.32	6.99×10^{-4}
8	8.43	0.47	7.83×10^{-4}
10	8.34	0.56	7.54×10^{-4}
12	8.25	0.65	7.47×10^{-4}
14	8.16	0.74	7.28×10^{-4}
15.5	8.08	0.82	7.35×10^{-4}
18	7.99	0.91	7.11×10^{-4}

*Concentrations are expressed in gm. mols. per litre.

II. Pyrolysis of Sodium Acetate in Presence of Carbon.

Gm. mols. sodium acetate pyrolysed. = 1.173×10^{-4}.

Concentration of salt. (a) = 8.90 gm. mols./litre.

Time (mins.)	a - x *	x *	K (litres mols.$^{-1}$ mins.$^{-1}$)
4	8.56	0.34	1.11×10^{-3}
5	8.49	0.41	1.08×10^{-3}
6	8.41	0.49	1.09×10^{-3}
7	8.35	0.55	1.06×10^{-3}
8	8.25	0.65	1.11×10^{-3}
9	8.17	0.73	1.12×10^{-3}
10	8.11	0.79	1.09×10^{-3}
11	8.04	0.86	1.14×10^{-3}
12	7.96	0.94	1.10×10^{-3}
13	7.90	1.00	1.09×10^{-3}
14	7.84	1.06	1.08×10^{-3}
15	7.78	1.12	1.08×10^{-3}
16	7.71	1.19	1.08×10^{-3}
17	7.66	1.24	1.07×10^{-3}
18	7.59	1.31	1.08×10^{-3}

* Concentrations are expressed in gm. mols. per litre.

The calculated second order rate constants for the decomposition of sodium acetate, as followed by the rate of loss of acetate, are given in the last columns of the tables of results shown above. The values obtained are comparable with those of table V page 94, which were measured by the rate of formation of product.

conclusion as the rate of the catalysed [illegible] equal to the rate of decomposition of sodium [illegible] ate in the presence of carbon, within [illegible] rimental accuracy. Calculation of the [illegible] constants for such a composite reaction [illegible] es of values increasing rapidly to a [illegible], h is approximately equal to the first [illegible] that obtained for the pyrolysis of [illegible] on mixtures.

Calculation of the theoretical [illegible] [illegible] that graph shown in fig. 6, which [illegible] [illegible] a [illegible] agreement between the actual and [illegible] progress of reaction. The [illegible] [illegible] method of interpretation for [illegible]

DISCUSSION OF EXPERIMENTAL RESULTS

The results of the thermal decomposition of sodium adipate were interpreted by resolution of the observed reaction into two of the first order; one which probably takes place first, uncatalysed, and the other catalysed by carbon produced during the reaction. The results for disodium adipate shown in tables I, II and III, pages 87, 88 and 89, justify this conclusion as the rate of the catalysed reaction is equal to the rate of decomposition of sodium adipate in the presence of carbon, within the limits of experimental accuracy. Calculation of the first order rate constants for such a composite reaction yields a series of values increasing rapidly to a maximum, which is approximately equal to the first order constant obtained for the pyrolysis of disodium adipate carbon mixtures.

Calculation of the theoretical points on the product/ time graph shown in fig. 6, opposite page 86, demonstrates a good agreement between the actual and theoretical progress of reaction. The reasons for using this method of interpretation for disodium adipate pyrolyses are necessarily compelling, as in such studies carried out on the pure salt, the initial concentration of the reactant cannot be varied. Results provided by this analysis give a very satisfactory means of comparing the different experimental results, which together with the agreement detailed above, supports the validity of the interpretation.

Table IV, page 91, gives the first order rate constants for the decomposition of disodium β-methyladipate, which for fully 90% of the reaction obeys the first order rate equation. The presence of carbon accelerates the reaction slightly, but does not alter its course.

Sodium acetate which has been more extensively studied (76) was found to follow a more complicated course. No simple reaction order has been found which satisfies the whole reaction. However, in each case, at the temperatures quoted in table V, page 94 , it was found that for about 50% of the reaction a satisfactory second order rate constant was obtained - this is the value quoted in table V . Added carbon again catalyses the decomposition slightly, but it does not appear to alter the kinetic course of the reaction.

Disodium adipate, which does not seem to melt before decomposition, differs slightly in its mode of reaction from the other two systems studied. An attempt to determine the melting point of this salt showed that true melting appeared not to take place. The particles seemed to soften, and decomposition commenced, but they did not lose their crystalline form. This difference of phase may explain the slight variations in the progress of the pyrolysis of disodium adipate and disodium β-methyladipate.

Sodium acetate melts at 324°C (80); the melting point of disodium β-methyladipate was 390°C. These compounds react therefore in the liquid state, while disodium adipate apparently reacts in the more ordered solid state. The function of the carbon is difficult to determine, but it may be that it facilitates some step in the reaction by causing dislocations in the already weakened crystal lattice. If this were so, the magnitude of the catalytic effect would be expected to decrease with increasing temperature, as does occur.

For solid state reactions high activation energies are commonly obtained, e.g. in the decomposition of barium azide measured by Thomson and Tomkins (8) it is 145-166 K.cals. The activation energies calculated for the uncatalysed and catalysed decompositions of disodium adipate, compare well with these values.

E (uncatalysed reaction) = 150 ± 4 K.cals.

E (catalysed reaction) = 114 ± 4 K.cals.

These are substantially higher than those for the decomposition of sodium acetate and disodium β-methyladipate.

E (sodium acetate decomposition) = 44 K.cals

E (disodium β-methyladipate decomposition) = 62 K.cals.

A second function of carbon in the pyrolysis of disodium adipate, and the main one for the other two systems studied, may be the provision of suitable reaction sites.

As far as could be ascertained, fractional reaction orders were not encountered in the pyrolyses studied, hence it was concluded that the reaction proceeded by an ionic, rather than a free radical mechanism. Integral reaction orders were also observed by Kuriacose and Jungers (75) in the catalytic decomposition of acetic acid vapour on a catalyst.

A general theory for salt pyrolysis was proposed by Lee and Spinks (69). This ionic mechanism postulated the primary reversible formation of an acyl ion, followed by a rate determining S_E2 decarboxylation

$$R - COOM \longrightarrow R - \overset{+}{C} = O + OM^{-}$$

$$R - \overset{+}{C} = O + R' COOM \longrightarrow R - CO - R' + M^{+} + CO_2$$

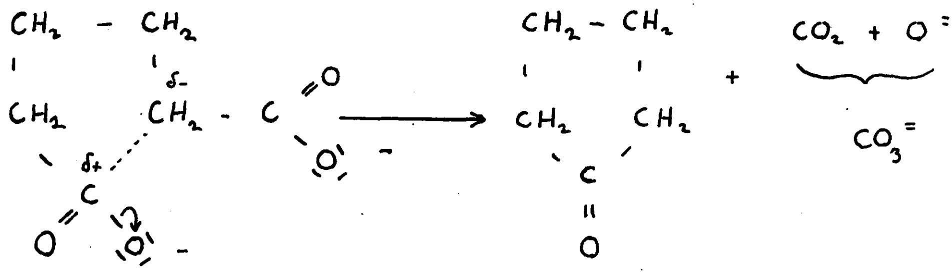
R and R' may be the same or different, hydrogen, aliphatic or aromatic groups, and M is a metal.

The kinetic results recorded do not exclude the theory of Lee and Spinks, nor do they give sufficient information to prove conclusively, a general mechanism for salt pyrolysis. The theory of the above authors needs to explain many anomalies by steric hindrance - e.g. the result from pyrolysis of acetate/ formate, benzoate/ formate, phenylacetate/ acetate and n-valerate/ acetate mixtures. The preferred cleavage of the carbon-carbon (carboxyl) bond in acetate to the carbon-carbon (carboxyl) bond in benzoates and toluates, was ascribed to the preferred attack of the $CH_3-\overset{+}{C} = O$ ion on the benzoate or toluate molecules to reaction of $C_6H_5 - \overset{+}{C} = O$ on the acetate.

They stated that the ease with which the carboxyl group was lost in forming the ketone decreases in the order -

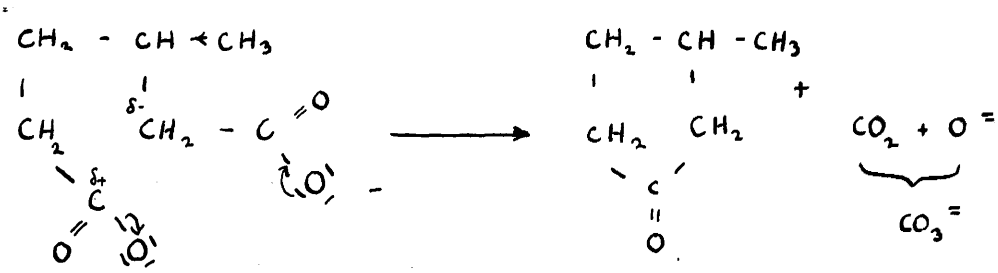
acetate > phenyl acetate > n-valerate ≫ formate > benzoate.

These authors assumed that the strengths of the carbon-carbon (carboxyl) bonds were similar in acetates and benzoates. Recent X-ray studies on benzoic acid by Sim, Robertson and Goodwin (82) showed that the length of the relevant bond is 1.48 Å, which is less than the length of the standard carbon-carbon bond - 1.54 Å. This suggests that the carbon-carbon (carboxyl) bond in benzoates has a certain amount of double bond character, and is therefore stronger than the normal carbon-carbon bond. Calculations in support of this have been made by Eadie (83). Reaction in disodium adipate is therefore represented as follows.



No separation of ions is postulated, as such a step must by its very nature surmount a high energy barrier. The activation energy for the uncatalysed reaction of disodium adipate is found to be greater than that for the decomposition of disodium β-methyladipate, but this may be accounted for by the difference in the condition of the reacting salt.

Pyrolysis of disodium β-methyladipate.



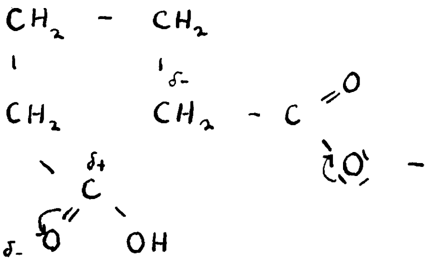
Disodium β-methyladipate reacts more quickly than does disodium adipate. One possible reason is because the methyl group in the β-position forces the reacting ends of the molecule closer together, making reaction more probable.

It should be noted that since a synchronous reaction process of ring-closure with concurrent loss of ($CO_2 + O^=$) has been proposed, the presence of the β-substituent further favours reaction in the direction shown, for the following reasons.

Firstly, the higher electron density around the potential anionic carbon atom, favours ring-closure to the incipiently positive carboxylate carbon.

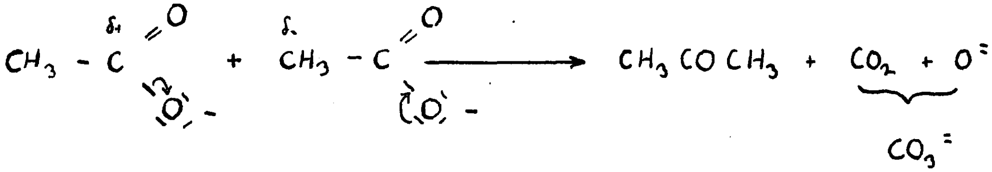
Secondly, any steric factor, such as may be expected to operate with a β-substituent, would tend to weaken the carbon-carbon (carboxyl) bond, and facilitate reaction.

This is in accordance with the observation, that adipic acid is readily converted to the ketone, when a small quantity of barium hydroxide is added. Under such conditions the acid salt must be present.



In this case, the distribution of charge favours ring closure to cyclopentanone.

A free radical mechanism is unlikely in the above two cases, and the explanation given applies equally to the decomposition of acetates.



$$\mathrm{CH_3-\overset{\delta+}{C}\genfrac{}{}{0pt}{}{O}{O^-} + CH_3-\overset{\delta-}{C}\genfrac{}{}{0pt}{}{O}{O^-} \longrightarrow CH_3COCH_3 + \underbrace{CO_2 + O^=}_{CO_3^=}}$$

The reaction order two is in agreement with this theory. At higher temperatures a free radical mechanism is not entirely excluded, and may be operative in the thermal decomposition of formates to yield oxalates (84).

It has been found that among the less electronegative metal salts, a residue of the oxide rather than the carbonate is often obtained. This was found by Krönig (53) who pyrolysed magnesium salts. These left a residue of magnesium oxide rather than magnesium carbonate at temperature much lower than that required to decompose magnesium carbonate. This is readily explicable using the above reaction mechanism.

When decomposition takes place in the liquid state, it has been suggested that the function of carbon is to provide suitable reaction sites. As carbon is always formed to a greater or lesser extent in pyrolyses of metal salts, its presence might account for the observations of O'Neill and Reed (67). They found that pyrolysis of i-butyrates yields, in addition to the expected product di-i-propyl ketone, substantial quantities of rearranged products - i-propyl-n-propyl ketone, and di-n-propyl ketone. Carbon is known to absorb strongly, and such rearrangements could occur by adsorption of the reactant on the surface of the carbon with subsequent migration of hydrogen atoms.

This explanation might equally apply to the observations of Cook, Miller and Whitmore (60), although it is likely that some of the by-products obtained were caused by the decomposition of the ketonic products of reaction, as was suggested by the authors.

The mechanism offered for the decomposition of adipates and acetates, explains the observations of Lee and Spinks, with less resort to steric effects. The preferred cleavage of the acetate molecule to benzoate, toluate, or formate molecules would now be expected. The observed results on pyrolysis of acetate/ n-valerate, acetate/ phenylacetate mixtures, are not incompatible with the proposed mechanism, since carbon has a definite effect upon the rate of decomposition, which is not necessarily the same for all salts. Thus the comparative values given by Lee and Spinks may not be kinetically significant, though it would be expected that the carbon-carbon (carboxyl) bonds in phenylacetate and n-valerate would break less readily than the relevant bond in acetate.

It may be concluded therefore, that salt pyrolysis may be interpreted by an ionic mechanism, though a free radical process is not excluded at higher temperatures, or for the decomposition of formates to yield oxalates.

No attempt has been made to compare the Dieckmann ring closure of diethyl adipate, (part I) and the thermal decomposition of disodium adipate, since the reactions are so vastly different in character.

The following sections refer to parts I and II.

APPARATUS AND REAGENTS.

Low Temperature Thermostat.

A precision thermostat was constructed for the dilatometric investigations, the regulator being of the helical variety. This enabled the temperature of the bath to be rigidly controlled, a necessary precaution in dilatometric studies. TO effect thorough stirring throughout the whole volume of liquid in the bath, the stirrer had a double set of blades, one at the foot of the bath, and the other about two inches below the surface of the liquid, and was driven by a high speed motor.

This thermostat operated satisfactorily between 20°C and 50°C.

High Temperature Thermostat.

The thermostat constructed for use between 300°C and 500°C was thermostatically controlled by a mechanical lever. This made and broke contact as an iron support expanded and contracted. Trial experiments showed that with vigorous stirring by a double set of blades as described in the construction of the low temperature thermostat above, provided the rate of heating nearly balanced the heat loss, the temperature of the bath was constant to within ±0.5C°. The thermostat fluid was an equimolecular sodium nitrate - potassium nitrate melt.

The temperature of the thermostat was recorded directly by a frequently calibrated 0-550°C borosilicate thermometer.

Ethyl Alcohol

Commercial absolute ethyl alcohol was dried by refluxing with magnesium ethoxide for six hours, followed by fractional distillation. To ensure utmost dryness this was repeated until the magnesium dissolved readily and without preliminary heating in the ethyl alcohol. This usually required about three operations. The fractional distillation was carried out in well dried apparatus, the fraction collected boiled at 78.5°C/ 760 mms.

Methyl Alcohol

Commercial methyl alcohol was dried and fractionally distilled in the same manner as given for ethyl alcohol. The fraction collected boiled at 64.1°C/ 760 mms.

n-Propyl Alcohol

Water was removed by refluxing over freshly roasted quicklime for six hours, followed by fractional distillation. Boiling point of the fraction collected was 97.4 °C/760 mms.

Bromine Solution

Liquid bromine was shaken up with two portions of concentrated sulphuric acid, separated and distilled. Pure bromine boils at 58.8°C/760 mms.

For the 2-carbethoxycyclopentanone estimation an approximately 0.5 molar solution of bromine in distilled ethyl alcohol was prepared.

β-Naphthol Solution

Commercial β-naphthol was purified by steam distillation, followed by recrystallisation from ethyl alcohol. Melting point of β-naphthol = 123°C.

The reagent used in the estimation of 2-carbethoxycyclopentanone, consisted of 1 gm. of β-naphthol dissolved in 20 mls. ethyl alcohol.

Oxide Free Sodium

Commercial stick-sodium was used; cutting away the outer coating of hydroxide under dry benzene.

Sodium Alkoxide Solution

To ensure that the sodium alkoxide solution was of approximately the correct strength, the required quantity of sodium was weighed out under dry benzene. The dried alcohol to be used was placed in a Quickfit and Quartz flask fitted with a condenser and calcium chloride tube, to prevent contamination by water, and the sodium added, excess benzene being blotted off with filter paper. After the first violent hydrogen evolution had ceased, the solution was gently refluxed till the last particles of sodium had disappeared. The flask was then stoppered and placed in the thermostat, so that the sodium alkoxide solution could reach the required temperature. This reagent was made up freshly for each kinetic determination as its age seemed to affect the progress of the reaction. This is probably due to water contamination and aerial oxidation, the solutions going very brown in colour and sediment forming on keeping.

Esters of Adipic Acid and its Substituted Derivatives

The esters were all prepared by refluxing the acids with excess of the appropriate alcohol, benzene and sulphuric acid. Pure samples were obtained by repeated distillation in Quickfit and Quartz apparatus.

2:4-Dinitrophenylhydrazine Solution

The reagent was prepared by dissolving the maximum amount of 2:4-dinitrophenylhydrazine in hot 2N hydrochloric acid solution; after cooling excess 2:4-dinitrophenylhydrazine was filtered off through a No. 3 sintered glass funnel.

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PUBLICATIONS.

The first, 'The Formation of Ketones. Part 11. The Formation of some Substituted Cyclopentanones by the Dieckmann Reaction.' appeared in the Journal of the Chemical Society, in 1953, page 2148. This refers to part 1 of the thesis.

'The Kinetic Course of Salt Pyrolysis,' published in Chemistry and Industry, in 1955, page 1217, is a note on the pyrolytic work described in part 2.

The third publication, 'The Spectrophotometric Determination of the Ionisation Constants of Aromatic Nitro-compounds,' from the Journal of the Chemical Society for 1952, page 1374, was work done before the period of research for this thesis. The measurements on the fluoro-substituted compounds were conducted by the author.