THE HYDROLYSIS OF ESTER-ANIONS BY A POLYMERIC QUATERNARY AMMONIUM HYDROXIDE AND RELATED STUDIES

A Thesis submitted to the University of London for the Degree of Doctor of Philosophy

by

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ABSTRACT

The hydrolysis, effected by both a simple and a polymeric alkali of the potassium ethyl monoesters of oxalic, malonic, succinic, glutaric and adipic acids, prepared in a high state of purity, have been studied. The polymeric alkali used was the (known) poly (vinyl-benzyltriethyl ammonium hydroxide), which was prepared as an aqueous solution from chloromethylated polystyrene by quaternisation and basification by ion exchange.

Second-order rate-plots, obtained for the oxalate conductimetrically and for the other esters by a titration technique, were found to be linear for the hydrolyses conducted in the presence of sodium hydroxide and convexly curved, in a manner indicating deceleration, for those conducted in the presence of the polymeric hydroxide.

For the temperature and concentration conditions used the instantaneous rate constants in the presence of the polymeric hydroxide were found to be higher by factors ranging between 1.78 and 7.86 than for those in sodium hydroxide.

The catalytic efficiency of the polymeric hydroxide has been discussed in terms of electrostatic association of
the charged monoesters near and within the polycation in which region there is also an enhanced concentration of hydroxyl counterions.

The fall-off of rate with time in the presence of the polymeric hydroxide, and the effect of temperature on the reaction rate, together with the effect of the increase in molecular length of the ester anion on the rate-increase factor, have also been considered.

Three condensation reactions involving compounds with active methylene groups in aqueous buffered solution alone and in the presence of three water-soluble polymers have been studied using a gravimetric technique.

Small increases in rates of condensation have been observed in the presence of the polymers. This latter investigation, commenced before the work described above, was discontinued since the accelerations observed were not large and the reaction situations are complex.
TO MY PARENTS

AND IN REMEMBRANCE OF MY BROTHER,

NIGEL.
ACKNOWLEDGMENTS

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PART I

THE HYDROLYSIS OF ESTER-ANIONS BY A POLYMERIC QUATERNARY AMMONIUM HYDROXIDE
INTRODUCTION
Incorporation of ionic constituents into the chain of a neutral polymer molecule superimposes the effects of electrostatic interactions on the properties of the unionized polymer. Thus there exists a counterpart in polymer chemistry to the division existing in classical chemistry between uncharged molecules and simple electrolytes. This presence of the ionized groups in a polyelectrolyte, however, gives rise to properties not present in either simple electrolyte alone or in neutral polymer solutions. It is found, for example, the osmotic pressure of the solution, the activity coefficient of the counterion, and the conductivity of the polyion are anomalously low compared to those in a simple electrolyte.

In the first part of the introduction, some of these unique properties will be considered from the point of view of physico-chemical measurements on polyelectrolytes, and in the next section, the influence of polyelectrolytes on rates of chemical reaction will be discussed.

Various theoretical models for polyelectrolytes in solution together with complex mathematical derivations are
to be found in the literature [1], but they will not be considered in this account.

**Types of polyelectrolytes**

Polyelectrolytes include a large number of diverse and complicated polymers. Many naturally occurring substances such as proteins, nucleic acids and polysaccharides are multiply charged compounds of high molecular weight. Thus the carboxy groups of glutamic and aspartic acids, the phenolic group of tyrosine and the amino groups of lysine within the tertiary structure of globular proteins, depending on their state of ionization, can allow the build up of a considerable net charge density. Discussion of these more complicated molecules, however, will not be further considered in this introduction which will be restricted to those polyelectrolytes derived from synthetic flexible linear polymers. Some examples of linear polyelectrolytes are shown in Table 1.
**TABLE 1.**

<table>
<thead>
<tr>
<th>Group A</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Poly(acrylic acid)</td>
<td>(-CH_2-CH-) _ n _ CO_2_H</td>
</tr>
<tr>
<td>(2) Poly(methacrylic acid)</td>
<td>(-CH_2-C-) _ n _ CO_2_H</td>
</tr>
<tr>
<td>(3) Poly(ethyleneimine)</td>
<td>(-CH_2-CH_2-N-) _ n _ H</td>
</tr>
<tr>
<td>(4) Poly((\frac{1}{2})-vinyl-pyridine)</td>
<td>(-CH_2-CH-) _ n _</td>
</tr>
<tr>
<td>(5) Poly(vinylsulphonic acid)</td>
<td>(-CH_2-CH-) _ n _ SO_3_H</td>
</tr>
<tr>
<td>(6) Poly(styrenesulphonic acid)</td>
<td>(-CH_2-CH-) _ n _</td>
</tr>
<tr>
<td>(7) Poly(vinylbenzyl-triethylammmonium hydroxide)</td>
<td>(-CH_2-CH-) _ n _</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group B</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5) Poly(vinylsulphonic acid)</td>
<td>(-CH_2-CH-) _ n _ SO_3_H</td>
</tr>
<tr>
<td>(6) Poly(styrenesulphonic acid)</td>
<td>(-CH_2-CH-) _ n _</td>
</tr>
<tr>
<td>(7) Poly(vinylbenzyl-triethylammmonium hydroxide)</td>
<td>(-CH_2-CH-) _ n _</td>
</tr>
</tbody>
</table>
TABLE 1*(Continued)

Group C. (8) Styrene - maleic acid \( (-\text{CH}_2 - \text{CH} - \text{CH} - \text{CH} -)_n \)
copolymer

\[
\begin{array}{c}
\text{CH}_2 \\
\text{CH} \\
\text{CO}_2 \\
\text{CO}_2\text{H}
\end{array}
\]

(9) Methacrylic acid - 4-vinyl-
pyridine copolymer. \( (-\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{C} -)_n \)

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CO}_2\text{H}
\end{array}
\]

Group A, represents materials in which the groups are weakly
ionized. The charge density along the molecular
chain for the weakly basic polymeric acids can be
varied by varying the degree of neutralisation.
Work done by Saunders\(^1\) and by Schaefgen\(^2\) has
shown that polyamides (weak Lewis bases), can
behave as strong polyelectrolytes when in strongly
acidic media (eg. formic acid).

Group B, represents basic or acidic strongly ionized polymers.
Included is poly(vinylbenzyltriethylammonium
hydroxide) used in this investigation.

Group C, (8) shows a polydibasic acid derived from the hydrolysis
of a copolymer of maleic anhydride with a comonomer
unit. The result is a macromolecule containing
closely spaced pairs of carboxyls separated by at least one comonomer unit. (9) shows an amphoteric polyelectrolyte obtained by copolymerization of suitable basic and acidic monomers.

**Qualitative representation of polyelectrolytes in solution**

In a solution of a polyelectrolyte, the charge centres are bound together by covalent bonds and are therefore constrained to remain near each other regardless of the stoichiometric concentration. Such a solution must necessarily behave as if it contained regions of concentrated solution with pure solvent in between.[4,5] The electrostatic potential will then be high in the region occupied by the polyion and fall off as the distance from the polyion increases. This will cause the small ions of sign opposite to the polyion (counterions), rendering the system electrically neutral, to be constrained by electrostatic attraction near to the polyion. Hence we can think of the counterions as being of two types, 'bound' and 'free'. The bound counterions may be visualized as forming a mobile layer adjacent to the polymer skeleton within a polyion domain.[6] That is, because of the large electrostatic field, the counterion is relatively free to move parallel to the polymer
skeleton but relatively restricted in any motion perpendicular to the polymer skeleton. There will hence be a highly peaked counterion distribution near to the polyion. This is in contrast to a simple electrolyte solution in which a more even distribution throughout the medium results to minimise mutual repulsive forces.

A further consequence of the charge centres on the polymer will show itself in differences in conformation from that of its uncharged analogue.

Uncharged flexible polymers adopt a randomly coiled configuration in solution, a net result of weak forces between polymer segments and solvent molecules, and nearest neighbour interactions. Dilution of the solution with solvent will cause the intermolecular interactions to decrease slightly as the molecules move apart. Polyions, on the other hand, will behave differently; here, increasing dilution will provide an increasing volume for the counterions to distribute themselves from the polyion. Hence the shielding of the fixed charges on the polyion will be reduced, their mutual repulsion will increase and the polyion will tend to expand. This expansion effect will greatly outweigh any contraction effect due to lessened intermolecular interactions.
Extension of the polyion in solution.

Evidence for this expansion of the polyion has been given by viscosity measurements.

Fuoss has measured the viscosity of the polyelectrolyte poly(N-butyl-4-vinyl-pyridinium bromide) in aqueous solution and in the presence of potassium bromide [7]. He found that in more concentrated salt free solutions (ca 1 g dl⁻¹), reduced viscosity $\frac{n^{sp}}{C}$ vs concentration C plots indicated that the polyions were in contact with each other and unexpanded to any marked degree. On dilution of the solution, a sharp increase in $\frac{n^{sp}}{C}$ was observed corresponding to the large expansion of the polyion postulated above. Extrapolation of the curve to zero concentration was not possible.

Measurements by Eisenberg and Pouyet [9] at low rates of shear showed that this sharp increase in $\frac{n^{sp}}{C}$ with dilution passed through a maximum indicating that the expansion of the polyion reached an upper limit and the effect on further dilution merely reflected the decreasing interference between the expanded polyions.

Addition of potassium bromide to the system [8] caused the values of the intercept on the C = 0 axis to decrease indicating contraction of the polyions. Explanation of this
is given in terms of an equivalent alternative approach which thinks of the polyion as surrounded by a membrane. Expansion of the polyion is considered to arise from the osmotic pressure forces from the retained counterions.\[10\] In the presence of excess electrolyte, as above, the difference between the counterion concentrations on the two sides of the membrane diminishes, with a result the tendency of the counterions to diffuse out of the polyion is suppressed. The overall effect is for the effective charge of the polyion to lessen and the polyion thus contracts.

Dilution of a salt free polyelectrolyte solution with a salt solution of a concentration such as to keep the ionic atmosphere surrounding the polyions unchanged during the dilution (i.e. isoionic dilution) would be expected to give a linear relationship of \( \frac{n_{SP}}{C} \) with polyelectrolyte concentration, indicating no change in expansion of the polyion. Such linear plots were obtained by Flory and Osterheld\[11\] for poly(sodium acrylate).

Viscosity studies have also been done on the polyelectrolyte sodium pectinate\[12\] in aqueous solution and on polyamides in acid solvent media (formic acid)\[3,13\]. Viscosity plots similar to those of Fuoss\[7\] were obtained.
Evidence for counterion binding has been given by osmotic techniques which provide a convenient method of counting the number of independent particles (regardless of size) in a given volume of a test solution.

Strauss and Fuoss[14] did measurements on the polyelectrolyte poly(4-vinyl-N-butyl-pyridinium bromide). They found that a plot of $\frac{\Pi}{C}$ for the parent unionized polymer, poly(4-vinyl-pyridene), increased linearly with C but for the polyelectrolyte, values of $\frac{\Pi}{C}$ were much higher and decreased as C increased. This was attributed to the fact that, from the point of view of the osmometer, the bromide counterions associated with the polycation could not be distinguished as independent kinetic units; hence, with decreasing concentration, due to escape of counterions from the polyion region, a greater proportion of osmotically active entities were observed.

Addition of moderately concentrated lithium bromide to either side of the osmometer membrane restored linearity to the osmotic pressure plot. In the presence of the added bromide ions, the counterions no longer tended to leave the regions occupied by the polyions and the solution could then
be described as molecular droplets of poly-salt distributed through a concentrated solution of 1:1 electrolyte.[15] Thus after automatic allowance for the addition of electrolyte, each polycation plus associated bromide ions counted as a single particle and behaved as a neutral polymer.

Theoretical treatments by Wall also lead to the conclusion that the counterion association near a polyion will decrease as the system is diluted.[16]

Similar osmotic pressure measurements on sodium polyacrylate[17] and poly(L-lysine hydrochloride)[18] indicate a large proportion of counterions (up to 80%) act as if they were bound to the polyion.

Counterion activity coefficients

From a practical point of view, the fact that the counterions act as if they were bound to the polyion is equivalent to saying that activity coefficients of the counterion are correspondingly low.[19] Experimentally, it has been found the activity coefficients of counterions are, in the presence of polyions, lower than when in simple electrolyte in which no polyions are present. A number of workers have studied the activity of counterions in poly-electrolyte solutions by immersing electrodes reversible to
these ions in the solution and measuring the potential of the half cell against a reference half cell. This potential was then assumed to be a measure of the 'single ion' activity coefficient. The polyelectrolytes studied by this method have been sodium polyacrylate and methacrylate, sodium polystyrene sulphonate, sodium poly(vinyl-alcohol sulphate), sodium carboxy-methyl cellulose, sodium cellulose sulphate, silver carboxy-methyl cellulose, potassium polystyrene sulphonate and poly(ethyleneimine hydrochloride).

Conclusions that can be drawn from the studies are summarised below.

(1) The activity coefficient of the counterions in a polyelectrolyte solution is small relative to that of the same ion in an equivalent solution of simple salt. For instance potassium ions in potassium polystyrene sulphonate have low activity coefficients of 0.25 over a concentration range 0.02 to 0.36M. Similar measurements by Kern showed much lower values for the sodium ion activity coefficient in sodium polyacrylate than in the monomeric analogue sodium butyrate.

(2) The activity coefficient of the byion (e.g. Cl in a sodium salt of a polyacid) does not show a corresponding
large decrease relative to the value in an equivalent simple salt solution.\textsuperscript{[22,27,28,29]}

(3) The activity coefficient of the counterion, in the absence of added salt tends to zero as the charge density of the polyion increases at a constant concentration of polyelectrolyte.\textsuperscript{[21]}

(4) The concentration dependence of the activity coefficient of the counterion show a species dependence indicating that non electrostatic forces must also be considered. Thus the counterion activity coefficient of silver ions in silver carboxy-methyl cellulose solutions increases as the concentration decreases.\textsuperscript{[23]} Unexpectedly however, since dilution would be thought to result in escape of counterions from the polyion region with consequent increase in activity coefficient, it is found that dilution of sodium polyacrylate solution results in a decrease in counterion activity coefficient.\textsuperscript{[21]}

This observation has been confirmed by conductance measurements.\textsuperscript{[30]}

* Counterions = gegenions are ions of opposite charge to polyion.

Byion = nebenion = coion are ions of same charge as polyion.
The activity coefficient has been found to be independent of the degree of polymerisation\[31\] for polymers of moderate molecular weight. A charged chain length of greater than five monomer units was found to be required for poly(ethyleneimine) before any considerable counterion binding was observed.\[25\] It has been found that, for large values of the spacing of the charge sites along the main chain, the mean activity coefficient is high and approaches that observed in simple electrolytes. When the spacing was less than a certain value, the mean activity coefficient was particularly low and almost independent of concentration.

6. Multivalent counterions have been found to be more extensively bound to polyions than univalent ions. Thus results from transference and diffusion studies \[32,33\], show that strontium counterions are more strongly bound to the polyacrylic ion than sodium counterions. Also chloride ions are displaced by sulphate anions from poly(ethyleneimine hydrochloride)\[25\]

7. The activity coefficients of ions in a system containing both polyelectrolytes and simple salts are the sums
of the activities of the ionic species in a salt free polyelectrolyte and a polyelectrolyte free salt solution. Experimentally this was verified by Mock and Marshall by pH measurements on polystyrene sulphonate acid and hydrogen chloride[34] and also by dialysis equilibrium studies.[22,35]

A similar additivity principle has been found to apply using osmotic pressure techniques[28] and conductance methods.[36]

Various workers have used electrolytic transference studies to demonstrate the association of counterions with polyions.

Thus Wall[32] reported measurements of the transference numbers of a polyacrylate by which it was shown that a significant fraction of the counterions moved with the polyion against an applied electric field. By the use of labelled sodium counterions, it was shown that the fraction of counterions associated with the polyion increased as the degree of neutralisation increased. Similar results were obtained from radiotracer diffusion studies[32] and refractivity measurements.[37] A steady state diffusion method applied to polyethylenimine hydrochloride showed the fraction of
associated chloride counterions was about one half.\[38\]

Two distinct rates of exchange of sodium counterions in polyacrylate solutions have been observed by Huizenga using radioactive tracer techniques,[39] a fast exchange between the sodium ions external to the polyion region and a slower one with those inside. In common with other polyelectrolyte properties, the mobility of polyions is independent of the molecular weight and of the overall viscosity of the solution.[40]

Measurement of ion binding by steady state electrolysis methods for sodium polyacrylate showed an increase in binding as the degree of neutralisation was increased.[41] Similar measurements on poly(\textit{vinylsulphonic acid}) which is fully ionized at all degrees of neutralization, showed ion binding to be independent of the degree of neutralisation.[42]

A polarographic technique has been used[43] to show that a large proportion of cadmium ions in cadmium polystyrene sulphonate solutions were retained close to the polyion.

Conductance studies on poly(\textit{vinyl-N-butyl-pyridinium bromide}) showed that increase in dielectric constant favoured escape of counterions from the electrostatic influence of the polycation.[44]
It has been found that apparent ion binding varies with the method of measurement. Some methods show as bound only ions that remain bound for a considerable time (minutes) whereas others count those ions bound for much shorter times. Thus equilibrium measurements gave higher values of apparent ion binding than transport measurements. For instance 80% of chloride ions were found to be bound to poly(L-lysine hydrochloride) by osmotic pressure measurements but only 43% by studies of sedimentation.

Further light on ion binding has been given by spectroscopic studies. Poly(ethylene sulphonlic acid) and poly(styrene sulphonlic acid) are known to be strong acids in aqueous solution as shown by conductometric titration curves\(^{[46]}\) yet poly(styrene sulphonlic acid) has a counterion activity coefficient of 0.38\(^{[32,34,47]}\) An NMR study of the latter however\(^{[48]}\) showed that all acidic protons were in an ionic state, the low activity coefficient being attributed to the strong electrostatic interactions within the polyions. This was further substantiated by Raman spectra studies on the polymeric acid and the monomeric analogue p-ethyl benzene sulphonlic acid\(^{[49]}\).
Previously it had been assumed that, because of the relatively small number of macroions compared with counterions, any changes in the thermodynamic properties of these macroions would have little effect on the properties of the solution. Recently, however, it has been shown that, while the "single ion activity coefficient" of the counterion in sodium polyacrylate, measured directly using a concentration cell, remained almost constant (0.29 to 0.28) over the concentration range 0.00435M to 0.227M, the "mean activity coefficient" was reduced from 0.32 to 0.15; that is the macroion activity coefficient decreased with an increase in concentration of the polyelectrolyte.[50]

The Nature of Ion Binding

Information about the nature of ion binding is not given by thermodynamic and electrochemical methods for measuring the activity coefficients of counterions. Evidence that sodium ions are mainly bound to carboxylic polymers by domain electrostatic field is shown by the fact that the fraction of sodium ions bound to a polyion containing ionized carboxyl groups depends only on the average distance between the groups and not on the distribution of the groups. [51]
This domain binding does not involve a dissociation equilibrium and would not be governed by mass action effects. Thus, the addition of salt having a common ion should not affect the binding. For sodium polyacrylate, this postulate has been found so \cite{23}.

On the other hand, site binding appears to predominate when the counterions or the sites on the polymer are multivalent. Thus magnesium and manganese salts of inorganic polyphosphates have been shown to be incompletely dissociated by NMR studies\cite{52}. Binding through complex formation occurs with copper ions and polyacrylates. Further, this binding was found to be governed by mass action effects\cite{53}. From the experimental evidence, we thus see that general electrostatic binding has been observed in some systems and site binding in others.

The observed properties of polyelectrolyte solutions described above lead to the view that flexible linear polyelectrolytes possess an extended, coiled, configuration in solution having a cylindrical, ionic atmosphere round the skeleton. Their anomalous activity coefficient effects and other properties are visualised in terms of the consequent ion association about the polyelectrolyte.
The effect of polyelectrolytes on reaction rates

It was first pointed out by Morawetz and Westhead in 1955\cite{54} that a study of the kinetics of reactions between simple ions, carried out in the presence of a charged macromolecule could give information on the distribution and magnitude of electrostatic interactions about the polyion. These authors also believed that insight into the related phenomena of ion exchange by resins and also enzyme catalysis could be obtained.

Over the last thirteen years, we find that a number of such reactions have been studied, and differences in rate between the reactions carried out alone and in the presence of polynomials have been detected. These effects may be the result of two different causes. Firstly if the polymer exerts forces on both the interacting species, it may modify their relative distribution in the system leading to an altered collision frequency. Secondly the polymer may associate with one of the reagents and the resulting complex may have a reactivity different from that of the unassociated complex. Any effect on the reaction rate due to the macroscopic viscosity is unlikely since it has been found\cite{55,56} that the mobility of small molecules is almost independent
of the viscosity, and in any case Flory\cite{57} has pointed out that even if such an effect did arise, no influence on the reaction rate necessarily follows.

In the following account some reactions in which polyions, present in solution, gave rise to catalytic activity will be considered, and the results will be interpreted in terms of the picture of the polyelectrolyte built up in the preceding sections.

Morawetz\cite{58} found that the hydrogen ion catalysed decomposition of ethyl diazoacetate proceeded at slower rates in poly(methacrylic acid) than in low molecular weight buffer solution at the same pH. To explain this result, it was suggested\cite{57,58} that ethyl diazoacetate was partially excluded from the regions around the polyanion so that with the counter hydrogen ions increased in this region and depleted in the intervening region, the substrate molecules were subjected to an effectively lower hydrogen ion concentration with a consequent diminution in rate.

In contrast to this the acid catalysed hydrolysis of various peptides, eg. glycyglycine, in the presence of the strong polymeric acid poly(vinyl sulphonic acid) at low concentration, was found to proceed faster by a factor of
between 3 and 5 than when in the presence of the simple acid, sulphuric acid, at the same hydrogen ion concentration. In this case both the protonated peptide cations RNH$_3^+$ and the hydrogen ions were electrostatically attracted to the region of the polyanion. By concentrating the two reagents in the same region, the polyanion acted as a catalyst and an increase in collision frequency and hence of reaction rate resulted. The polymeric enhancement in rate was found to be more pronounced for dilute solutions of the acid.

When the inversion of sucrose, a neutral substrate, was studied, it was found that with poly(vinylsulphonic acid) and sulphuric acid at the same strength, approximately equal rate constants were given while with hydrochloric acid, a slight increase in rate (ca 52%) was observed. In this case, the neutral sucrose molecules only weakly interact with the electrostatic field of the polyanions with little consequent modification of the rate.

It was also found that poly(vinylsulphonic acid) was a more effective catalyst than polystyrene sulphonic acid in the peptide hydrolyses. This was attributed to the higher density of anionic sulphonic acid groups in the polymer backbone. Catalytic effects were found to be independent
of the degree of polymerization.

The same authors also did work on protein hydrolyses in which similar catalytic effects were exhibited.\[59,61\]

Work done by Painter and Morgan\[62\] on the acid hydrolysis of polysaccharides carrying basic amino residues showed similar catalytic effects with polystyrene sulphonic acid compared with hydrochloric acid. When the amino group was replaced by a neutral acetamido group, the electrostatic attraction of the polyanion for the charged substrate disappeared and it was found that now the rates of hydrolysis with the polymeric and monomeric acids were equal.

The simple ester, ethyl acetate has been shown to be more rapidly hydrolysed by polystyrene sulphonic acid than by the monomeric analogue p toluene sulphonic acid. Again some associative mechanism with the polyion was postulated to be operating.\[63\]

In a reaction in which one of the reactants is cationic and the other anionic, the presence of a polyion would be expected to attract one and repel the other. The reaction rate would consequently be expected to be diminished because of the reduced collision frequency.
Work done by Morawetz and Schaefer\textsuperscript{[64]} has supported this view. They prepared a doubly charged cationic ester ethylene bis-[\(N,N\)-dimethyl-\(N\)-(phenoxy carbonyl-methyl)ammonium cation \(\text{PhO}_2\text{CCH}_2\text{N(CH}_3\text{)}_2\text{CH}_2\text{N(CH}_3\text{)}_2\text{CH}_2\text{CO}_2\text{Ph}\) and conducted its hydroxyl ion catalysed hydrolysis in the presence of polyanions. They found that polyanions with a high charge density lead to a more than twenty fold reduction in the reaction rate. For a single charged cationic ester, the reduction in rate was less whereas for the uncharged \(p\) nitrophenyl acetate, the rate was found to be equal to that in simple electrolyte solution, indicating an even distribution of the uncharged ester in the solution.

Recently, in this laboratory, the benzidine rearrangement was conducted in the presence of poly(styrenesulphonic acid) and benzenesulphonic acid of the same strength.\textsuperscript{[65]} The rate determining step involves the attack of a hydrogen ion on the monoprotonated species \(\text{NH}_2\text{PhNHPh}^+\), and thus the presence of the polyanion would be expected to act as a powerful catalyst. A 120 fold acceleration in rate of the rearrangement was observed.

The hydroxyl ion catalysed decomposition of \(N\) nitroso-triacetonamine by poly(vinylbenzyltriethylammonium hydroxide)\textsuperscript{[66]}
showed an increase of 59-77% compared to the reaction effected by sodium hydroxide or the monomeric analogue benzyl triethyl ammonium hydroxide. Here dipole-ion association with the polycation was postulated to account for the increase in rate.

The acceleration of the Cannizzaro reaction of glyoxal [67] by a similar reagent was 20 times greater than that in low molecular weight alkali. The electrostatic association of a negatively charged reaction intermediate with the polycation accounted for the considerable increase in rate. The above two reactions are considered in more detail at a later stage (p.159).

Recently the homogeneous hydrolysis of low molecular weight esters with a large number of polymeric sulphonic acids has been carried out in aqueous solution [68]. From their results Sakuruda et al. concluded that hydrogen ions are found only in the neighbourhood of the polymer molecules, and in dilute solution a region exists in which no hydrogen ions able to contribute to the hydrolysis exist; as a result, hydrolysis only takes place in the neighbourhood of polymer molecules.
It was found the rate of hydrolysis of butyl acetate was more than 10 times greater with a polymeric sulphonic acid than with hydrochloric acid - Association of the ester by hydrophobic interaction between a benzene ring and the alkyl group was postulated. When no increased concentration of the ester about the polymer occurred, no differences in rates between monomeric and polymer catalyst occurred.

An ester with amino groups was found to hydrolyse with a much higher rate with poly(styrene sulphonic acid) than with hydrochloric acid due to the electrostatic interaction between the ester and the polyanion.

Differences between electrostatic and hydrophobic interaction between the substrate and the polyelectrolyte were noted and summarised by Sakurada[68]:

(1) Addition of organic solvent to the reaction weakens hydrophobic interaction but in the case of electrostatic interaction, even in the presence of 50 vol.% aqueous acetone, considerable increase in reaction in the presence of polyanions was found.

(2) An addition of neutral salt to the reaction mixture depresses the catalyst activity when caused by electrostatic interaction.
(3) The catalytic activity increased as the degree of sulphonation increased for pure electrostatic interaction but the reverse was true for hydrophobic interaction.

A further series of experiments by Sakurada investigated the hydrolysis of partially acetylated polyvinyl alcohols with polymeric sulphonic acids.\[69]\] Generally the catalytic ratio was found to be greater than unity and was dependent on the degree of acetylation, distribution of acetyl groups and steric configuration of the ester and dependent on the degree of sulphonation of the acid catalyst but independent of degrees of polymerization. Again, increases in rate were attributed to hydrophobic binding of the polymer-catalyst and the polymer-ester.

The rates of solvolysis of anionic nitrophenyl esters in poly(4-vinyl pyridine)\[70]\] show a dependence on the degree of protonation of the polymer such that there is an optimum pH for the rate of each reaction. Letsinger proposed that the protonated pyridinium groups attract the anionic substrates to the polymer, where the catalytic quaternary nitrogen groups are able to effect the solvolysis readily. Similar results were obtained by Overberger et al.\[71]\]

Further catalytic effects have been reported using ion exchange resins where the polyion remains insoluble in the medium and heterogeneous catalysis is occurring. Such effects however, although related, will not be discussed here.
EXPERIMENTAL
PREPARATION OF CHLOROMETHYLATED POLYSTYRENE

The method was based on that developed by Morley[72].

Formulation

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mass (g)</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>18.0</td>
<td>0.173 monomoles</td>
</tr>
<tr>
<td>Chloromethyl methyl ether</td>
<td>236</td>
<td>2.93 moles</td>
</tr>
<tr>
<td>Zinc chloride (anhydrous)</td>
<td>70.5</td>
<td>0.517 moles</td>
</tr>
</tbody>
</table>

The above quantities are in the approximate molar ratio of 1:17:3. The polystyrene (batch DSS III), prepared by D.S. South in these laboratories was stored over calcium chloride in a vacuum desiccator; it was a white granular solid having a viscosity-average molecular weight $\bar{M}_v$ of 26,100 (see p.44).

Chloromethyl methyl ether was purified by fractional distillation through a 9" lagged column packed with 3-4mm Fenske helices, and a double surface condenser. A slow stream of dry nitrogen was passed into the boiling liquid during the distillation, the distillate being protected from atmospheric moisture by a calcium chloride guard tube. Two fractions were collected, the second, bp 57-59° $n_D^{25}$ 1.3930, was retained for the chloromethylation. All-
manipulations with this compound were carried out in the
fume cupboard because of its unpleasant vapour and the
fumes it produces in moist air.

Zinc chloride (BDH Laboratory reagent \( \geq 95\% \) as Zn) was fused in a porcelain basin and kept molten
for 20 minutes. The molten solid was allowed to solidify
by pouring dropwise into a mortar, where it was quickly
ground to an anhydrous white powder and stored in a
desiccator until use.

1,4-Dioxan (bp 100-101°) and methanol (bp 65-66°)
were distilled under nitrogen. Sodium-dried benzene was
distilled (bp 80-81°) before use.

**Procedure**

Polystyrene was added portionwise over one hour
to the chloromethyl methyl ether in a three necked 1 litre
round bottomed flask fitted with a mercury sealed stirrer
and a condenser with a calcium chloride guard tube, to give
a clear, pale yellow, slightly viscous solution. The
apparatus was cooled and maintained at 10° by appropriate
addition of ice to a surrounding ice-water bath both during
the addition and subsequently.
Zinc chloride, contained in a small flask connected to the apparatus by a short length of 1 cm diameter poly vinyl chloride tubing, was then added, via the tubing, over a period of one hour, to the stirred reaction mixture. The solution became cloudy and darkened to yellow-brown. The temperature rose to 13°. After stirring and cooling for 2½ hours, the reaction was stopped by the dropwise addition of aqueous 1,4-dioxan (240 ml 50% v/v) to the vigorously stirred solution. The bath temperature was lowered to 0°. The reaction mixture was not allowed to exceed a temperature of 15° by controlling the dropping rate of the dioxan mixture. During the addition, the liquid phase became clear and nearly colourless while finally a cream coloured, sticky resin separated. The resin was extracted twice with benzene (150 ml, 50 ml), then the pale yellow benzene solution was washed with water (16 x 200 ml). The washings were still found to be faintly acidic.

The dissolved polymer was isolated from the benzene solution by dropwise addition to vigorously stirred methanol (2 l) when, after filtration, washing with methanol and drying under reduced pressure (60 mm), the polymer was
obtained as a fine white powder (25.3g). The polymer was precipitated twice more with benzene (250ml) as solvent and methanol (21/4 l) as precipitant. It was dried over phosphorus pentoxide-paraffin wax at room temperature in a vacuum desiccator for 24 hours at 0.05 mm pressure. The batch (24.5g) was designated cpl.

Duplicate chlorine determinations (Found: Cl, 23.08, 23.17%) corresponded closely to that required for complete monochloromethylation (23.24%) of the phenyl groups of the polystyrene.
DETERMINATION OF THE VISCOSITY-AVERAGE MOLECULAR WEIGHT OF THE POLYSTYRENE USED

A sample of the polystyrene was dried to constant weight over phosphorus pentoxide-paraffin wax at room temperature and a solution (about 1g dl⁻¹) was accurately prepared in sodium-dry, distilled AR toluene (bp 110° nD 25 1.4923) and thermostatted at 25°.

An Ostwald U-tube viscometer, firmly held in a support (Townson and Mercer X294 Universal) so that the capillary portion was clamped vertically as checked by a plumb line, was immersed in a thermostat bath at 25.00±0.02°.

Dust-free solvent and solutions were added to the viscometer through a freshly burned off, 100 mesh Monel metal gauze filter dome and allowed to come to temperature equilibrium (30min).

Flow times t₀ and t were measured for the solvent and the polymer solutions with a consistent and accurate stop-watch as prechecked against an accurate electric clock. Five readings were recorded each consistent to within 0.2sec. The flow times were found not to have altered after a period of 6 hours.
The relative viscosity $n_r$, which, provided the flow times are in excess of 100 seconds and the solutions are sufficiently dilute, is given by $t/t_o$, was calculated. From this, the intrinsic viscosity $[n]$, was calculated using the Kraemer modification of Huggins equation [73] viz.

$$\ln \frac{n_r}{c} = [n] - (0.5 - k')[n]^2 c$$

where the Huggins constant $k' = 0.38$ [74] as obtained by Fox and Flory for a temperature of $30^\circ$.

The viscosity-average molecular weight was evaluated from the relation $[n] = X \bar{M}_v^\alpha$ using values of $K$ and $\alpha (1.16 \times 10^{-4}$ and 0.72) obtained by Green [75] for polystyrene samples of known weight-average molecular weights. Also the degree of polymerization $D_P$.

Viz: $$\frac{\text{Viscosity-average molecular weight}}{\text{Molecular weight of monomer}}$$

was calculated.

The results are shown below.

<table>
<thead>
<tr>
<th>Concentration g dl$^{-1}$x10^-1</th>
<th>$n/n_o$</th>
<th>[n] dl g$^{-1}$</th>
<th>$\bar{M}_v x 10^{-4}$</th>
<th>D.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.017</td>
<td>1.193</td>
<td>0.1750</td>
<td>2.61</td>
<td>251</td>
</tr>
</tbody>
</table>
DETERMINATION OF THE INTRINSIC VISCOSITY OF THE
CHLOROMETHYLATED POLYSTYRENE

Solutions of the dry polymer in toluene at 4 accurately
known concentrations (approximately 1.2, 0.8, 0.6, and 0.4 g dl\(^{-1}\)
respectively) were prepared and the relative viscosities were
determined in the same manner and under the same conditions as
those for polystyrene (p. 43). No variations in flow times
were observed after 6 hours.

Extrapolation of the logarithmic viscosity number
\[ \lim_{\text{c} \to 0} \ln \frac{\eta}{c} = 0.153. \]

Extrapolation of the logarithmic viscosity number
\[ \frac{\ln \eta}{c} \]
fig. 1 DETERMINATION OF THE INTRINSIC VISCOSITY OF CHLOROMETHYLATED POLYSTYRENE.
THE QUATERNISATION OF CHLOROMETHYLATED POLYSTYRENE WITH
TRIETHYLAMINE

Formulation

A  Chloromethylated polystyrene  20.74g (0.14 monomoles for 100% chloromethylation)
   1,4-dioxan  80ml
B  Triethylamine  28.33g (0.28 moles)
   1,4-dioxan  40ml

1,4-Dioxan was purified by boiling it under reflux for 8 hours in the presence of sodium wire with a slow stream of dry nitrogen bubbling through it. A resinous yellow-brown solid formed in the liquid together with beads of molten sodium. Fractional distillation of the mixture through a 12" lagged column containing 3-4mm Fenske helices while still passing dry nitrogen through it to prevent oxidation, gave two fractions, the second of which was retained as solvent for the quaternisation (bp 100-101°, n_D^25 1.4200). The distillate was protected from moisture by a calcium chloride guard tube.

The triethylamine, dried over sodium, was fractionally distilled through a 12" column (as above) and stored over sodium wire (bp 90°, n_D^25 1.3980). The distillate was again protected.
from moisture with a guard tube. Methanol was distilled under nitrogen, bp 64.5°; and diethyl ether was distilled, bp 36-38°.

**Procedure**

To the stirred, pale yellow solution A, contained in a 500ml r.b. flask fitted with a mercury sealed stirrer and water condenser and filled with dry nitrogen, was added solution B. Methanol (52ml) was then added when local precipitation and redissolution of chloromethylated polystyrene occurred.

The apparatus was thermostatted at 60° for 48 hours in a water bath with continual stirring, a dry nitrogen atmosphere being maintained in the flask during this time by passing a stream of gas through a T-piece on the top of the condenser.

After 20 minutes of reaction, further methanol (110ml) was added to dissolve a cloudy material slowly precipitating from solution. This was presumably the ionic quaternised material, formed by the reaction, rendered insoluble by the dioxan present. No further addition was found necessary.

After 48 hours had elapsed, the straw coloured, viscous solution was cooled and added dropwise to manually stirred diethyl ether (2 1/2 l) contained in a large beaker.
The polymeric quaternary ammonium chloride separated as a soft, white, sticky mass adhering to the stirrer. The soft polymer was cut from the stirrer with a stainless steel knife, after removing from the precipitant and draining off the excess liquid, and dried over calcium chloride-paraffin wax at room temperature and reduced pressure (15hrs, 2mm; 5hrs, 0.1mm).

The now brittle polymer was ground to a powder and further dried (2hrs, 0.05mm; yield 36g).

The product was then dissolved in distilled water (300ml) giving a clear, slightly alkaline solution and carefully evaporated to dryness on a rotary film evaporator at 45-50°. Frothing was severe. After drying at 5mm for 1 hour, the brittle, transparent yellow film was detached from the flask and ground to a fine, pale yellow hygroscopic powder. The product was dried to constant weight over phosphorus pentoxide (8x1 hour, 0.05mm, 33.0g). Aqueous solutions of the polymeric quaternary ammonium chloride were clear, colourless and neutral. The batch was designated qcl.
DETERMINATION OF THE CHLORIDE ION CONTENT OF THE POLYMERIC QUATERNARY AMMONIUM CHLORIDE, AND HENCE THE DEGREE OF QUATERNISATION

Chloride ion determinations were carried out by the Mohr method using potassium chromate (1.0ml 5% ex pipette) as indicator; the end point could be reasonably ascertained and consistency of triplicate determinations was good. Since the determinations were carried out at room temperature and in a neutral medium, it is unlikely that hydrolysis of any residual chloromethyl groups occurred. The silver nitrate solution used was standardised against AR sodium chloride which had been dried at 200° for 6 hours. Blank titrations were also carried out with AR calcium carbonate suspensions (0.5g in 60ml) and appropriate small indicator corrections were applied to the titre values. Results and the method of calculation are given below.

Normality of silver nitrate solution = 0.09304N (mN)

| Weight of polymeric chloride (Gg) dissolved in chloride-free distilled water (50ml) | 0.5153 | 0.5081 | 0.2842 |
| Silver nitrate titre (ex burette) | 20.90 | 20.58 | 11.60 |
| Correction (ml) | 0.10 | 0.10 | 0.10 |
| Corrected titre (v ml) | 20.80 | 20.48 | 11.50 |
| %Cl⁻ (Cl⁻=35.457) = \frac{35.457 \times \text{wt}}{10000} \times 100 | 13.31 | 13.29 | 13.36 |

Mean %Cl⁻ = 13.32
For completely monochloromethylated polystyrene of which the structural unit is \( \text{CH}_2\text{CHC}_6\text{H}_4\text{CH}_2\text{Cl} \), 1 mole = 152.628g also for one quaternised unit \( \text{CH}_2\text{CHC}_6\text{H}_4\text{CH}_2\text{N(C}_2\text{H}_5)_3\text{Cl} \), 1 Mole = 253.822g.

Let the %Cl\(^-\) estimated = \( p \)

Let the % chloromethyl groups converted into quaternary ammonium groups be \( x\% \).

Then, out of 100 original chloromethyl groups, \( x \) quaternised groups were produced and \((100-x)\) residual chloromethyl groups remained.

The %Cl\(^-\) estimated is now given by

\[
\frac{35.457x}{253.822x + 152.628(100-x)} = \frac{p}{100}
\]

When \( p = 13.32 \quad x = 92.50\% \)

Thus 92.5% of the chloromethyl groups were quaternised when batch qcl was prepared.
PREPARATION OF NITROGEN-SATURATED, OXYGEN AND CARBON DIOXIDE-FREE DISTILLED WATER

Water used in the preparation of volumetric solutions for analytical and kinetic work was prepared in the following manner except where otherwise stated.

Freshly distilled water in a conical flask (51) was slowly boiled for 30 minutes when all dissolved gases were expelled. The flask was then stoppered with a bung holding a T-piece and a length of glass tubing, having at the top an inverted U-bend, extending almost to the bottom of the flask. To the top of the tubing was connected a three feet length of clean poly vinyl chloride tubing with a glass tap at its extremity, and to one end of the T-piece was connected a gas bubbler containing distilled water. A stream of nitrogen gas as indicated by the bubbler was passed through the T-piece so that, on cooling of the flask and its contents, only nitrogen could dissolve in the water. When cold, water, as required, was siphoned off via the tap, the nitrogen flow being maintained at sufficient pressure to prevent air entering the system through the bubbler. When not in use a nitrogen atmosphere was maintained by sealing off the bubbler and nitrogen line. The boiling and nitrogen-saturation procedure was repeated each day as required.
CONVERSION OF THE POLYMERIC QUATERNARY AMMONIUM CHLORIDE
INTO THE HYDROXIDE IN AQUEOUS SOLUTION

The chloride was converted into its hydroxide in aqueous solution by means of an anion exchange resin.

The resin used, Amberlite IRA 401, was a lightly cross linked polymer, based on polystyrene, containing trimethyl ammonium groups supplied as chloride, with a capacity of three m-equivalents per g of wet resin.

Preparation of ion exchange column ready for use

A slurry of the small yellowish brown beads of resin (224g 0.672g equiv.) in water was poured into a vertical, water filled glass tube (50cmx3.5cm) with an outlet tube (0.5cm diameter) at its lower end.

Clean poly vinyl chloride tubing attached to the outlet was extended alongside the column. An inverted U-tube attached to its upper end was maintained level with the liquid in the column so preventing it from running dry. Finally a tap funnel (1), holding a self-indicating soda lime guard tube to exclude carbon dioxide, was inserted in the top of the column with a large rubber bung.
The resin was conditioned before use by passing sodium hydroxide solution (2N 400ml), water (1l) and hydrochloric acid (2N 400ml) down the column. After washing with water (2l), conversion of the resin to the hydroxide form was effected by passing a large volume of sodium hydroxide (2N 5l, 1N 6l) down the column. On testing the eluent for chloride ion with nitric acid and silver nitrate solutions, only a faint turbidity was produced; this did not diminish on the passage of a further volume of sodium hydroxide (1N 2l). The dark reddish brown resin was now washed with water (6l) till portions of the eluent (100ml) gave no pink colouration with phenolphthalein. The light reddish brown resin produced was used for the conversion of the quaternary chloride to the hydroxide.

**Preparation of the polymeric quaternary ammonium hydroxide solution**

A solution of the quaternary chloride, batch qcl (12.0g 0.047 equiv) in water (55ml) was passed down the column which was then eluted with more water (600ml). The slow passage of the viscous polyelectrolyte could be viewed by the dark reddish brown band slowly progressing down the column. When the eluent became alkaline it was collected under nitrogen in a clean
calibrated polythene bottle with a soda lime guard tube. When 500ml had been collected, the eluent was found to be still faintly alkaline but was not further collected. The solution, designated pH2, was a clear, pale yellow slightly viscous liquid.

Two further conversions were carried out at different times in a similar manner; in one the quaternary chloride qcl (13.4g 0.053 equiv) and resin (247g 0.741 equiv) were used; the other was on a smaller scale, with qcl (5.57g 0.022 equiv) and resin (44g 0.132 equiv). These gave the hydroxides ph4 and phl respectively. The alkaline solutions were stored under nitrogen in polythene bottles.

Analysis of the polymeric quaternary ammonium hydroxide solutions

(1) Hydroxyl ion

The hydroxyl ion concentrations of the solutions were determined by adding aliquots to excess of standard potassium hydrogen phthalate solution, and back titration with standard sodium hydroxide solution (0.02N).

Precautions to exclude carbon dioxide were taken where applicable. Full details of the solutions used for the kinetic work are given later (p. 68).
(2) **Chloride ion**

Attempted chloride ion determination, both gravimetrically and by the Mohr method (p. 50) showed no detectable concentration of chloride ion in ph1, ph2 or ph4.
THE PREPARATION OF POTASSIUM ETHYL ESTERS OF ALIPHATIC
DICARBOXYLIC ACIDS

The diethyl esters were fractionally distilled at reduced
pressure and absolute alcohol was distilled (bp 78°) under
nitrogen before use. Clear, colourless, alcoholic potassium
hydroxide solutions were prepared by filtering a concentrated
solution of the AR solid (BDH\textsuperscript{1} 85% KOH \textsuperscript{2} 2% CO\textsubscript{3}) through a
small glass sinter (porosity 4), under a blanket of nitrogen, to
remove traces of insoluble material (carbonate, etc.).

In all the preparations following, the reactants were
protected from carbon dioxide by self-indicating, soda lime
guard tubes. The analytical method for determining the purity
of the half esters is given later (p.73).

Potassium ethyl oxalate

The compound was prepared by Nielsons method\textsuperscript{76}. 

Procedure

Potassium hydroxide (8.0g 0.143 mole) in alcohol (100ml)
was added dropwise to a stirred solution of excess diethyl
oxalate (bp 92° 25mm \(n^D_{25}\) 1.4070 23.0g 0.158 mole) in alcohol
(115ml) at room temperature over a period of 30 minutes. The
white, crystalline product precipitated from solution as it
formed and, after stirring for a further 1½ hours, it was filtered off, washed, recrystallised from alcohol and dried over calcium chloride under reduced pressure (24hrs. 1mm). The product, white translucent platelets, was found to have a purity factor of 99.55%. It was stored over calcium chloride at 1mm.

**Potassium ethyl malonate**

**Procedure**

Potassium hydroxide (11.2g 0.2 mole) in alcohol (133ml) was added dropwise to a stirred solution of excess diethyl malonate (bp 103° 31mm nD 1.4109 34.7g 0.217 mole) in alcohol (174ml) in a three-necked flask with a water condenser over a period of 40 minutes. A white crystalline solid precipitated from the clear solution during the addition. After stirring for a further 10 minutes the mixture was heated to 65° and the slightly cloudy solution filtered hot through a 3" glass sinter.

White crystals of potassium ethyl malonate separated on cooling, and were filtered off, recrystallised from alcohol, and dried under reduced pressure over calcium chloride. Determination of the equivalent gave a purity factor of 98.5%.

Further batches prepared by this method, and simple variations on it, gave products of 98.5% purity. Batches
of higher purity, up to 99%, were obtained by fractional precipitation with dry ether from absolute alcohol solution but yields were low. For the kinetic work envisaged, a product of higher purity was desirable so further purification was carried out.

**Hydrogen ethyl malonate preparation**

To a stirred solution of the crude potassium ethyl malonate (36.8g) in water (25ml) maintained at 5° in an ice bath was added concentrated hydrochloric acid (20ml) dropwise over 20 minutes. The precipitated potassium chloride was filtered off on a sinter and washed with ether (50ml). The aqueous layer was separated, washed with ether (3x35ml) and the ether extracts combined, washed with water (2x5ml) and dried over magnesium sulphate (24hrs.). After filtering and washing, the ethereal solution was distilled at atmospheric pressure leaving a clear, colourless, sweet-smelling liquid. Determination of the equivalent of the liquid was done by direct titration of portions of the liquid with aqueous sodium hydroxide (0.35N) using phenolphthalein as indicator. Equivalents of 133.9 and 134.1 were obtained. Mean 134.0. The equivalent of
hydrogen ethyl malonate is 132.1, indicating traces of ether were still present.

Procedure

Portions of the hydrogen ethyl ester (0.7g accurately weighed) in preneutralised aqueous alcohol (20ml 50% v/v) were titrated with carbonate-free alcoholic potash (14g in 500ml approximately 0.5N) solution. The calculated volume of the alcoholic potash solution (244.3ml) was then added dropwise from a burette with a CO₂-guard tube to the hydrogen ethyl malonate (13.37g 0.1 mole) in alcohol (100ml) under nitrogen in a 1 flask. The flask was swirled continually during the addition to prevent a local excess of alkali being formed.

After the addition of 140ml of alkali, solid potassium ethyl malonate suddenly came out of solution as fine white crystals. These were dissolved by the addition of water (10ml) and titrating was completed. Three ml of the solution were withdrawn at this stage and were found, with phenolphthalein, to be just faintly alkaline. The solution was rotary-evaporated to dryness giving a white powder which was dried and stored over calcium chloride at 1mm.

Analysis showed it to be potassium ethyl malonate of purity factor 100.0%.
Potassium ethyl succinate

Preliminary work showed the potassium ethyl ester to be extremely soluble in water and in alcohol so, for the preparation, dried alcohol was prepared[77].

Absolute alcohol, i.e. 99% ethanol (75ml), dried over fresh sodium sulphate was refluxed with magnesium (5g) and iodine (0.5g) in a 2l r.b. flask for 20 minutes till the brown iodine colour disappeared to give white magnesium salts. Further alcohol (950ml) was added and the mixture refluxed for 30 minutes, the dried alcohol was then distilled off (bp 75.5°C) into a clean dry Winchester. The distillate was protected during distillation by a calcium chloride guard tube.

Procedure

Carbonate-free potassium hydroxide (11.2g 0.2 mole) in dried alcohol (112ml) was added dropwise with stirring to diethyl succinate (bp 107°C 21mm nD 1.4169 34.8g 0.2 mole) in dried alcohol (135ml) over a period of 1½ hours. Towards the end of the addition, the solution became very cloudy and warm and on further stirring for 10 minutes, a dense white precipitate came out of solution. The mixture was refluxed for 5 minutes, cooled to 10°C and filtered.
Analysis of the white cake of residue showed it to be mainly dipotassium succinate. The filtrate was rotary-evaporated to small bulk (8ml) and sodium-dried ether was added. The sticky flocculent precipitate formed was filtered off portionwise with difficulty on a glass sinter and washed with dry ether to remove excess diethyl ester. The deliquescent white solid after drying over calcium chloride-paraffin wax at 0.1mm was redissolved in dried alcohol (10ml) and reprecipitated with dry ether. Final filtration, washing, and drying, as above, gave a white, finely crystalline cake of potassium ethyl succinate. It had a purity factor of 100.0%.

Potassium ethyl glutarate

The method for preparing the crude material is due to Clark[78].

Potassium hydroxide (8.4g 0.15 mole) in dried alcohol (100ml) was added to a stirred solution of diethyl glutarate (bp 118° 17mm nD 1.4221 28.2g 0.15 mole) in dried alcohol (100ml). After vigorous stirring (6min.) refluxing (5min.) and allowing to cool, a white insoluble material was filtered off. The filtrate was rotary-evaporated to small bulk (10ml) and dry ether added when potassium ethyl glutarate precipitated.
The solution was cooled to 5° and filtered on a sinter giving a white deliquescent solid. Solution and precipitation were repeated. Two batches, after drying at 0.1mm over calcium chloride, had purity factors of 97 and 98%.

**Preparation of hydrogen ethyl glutarate**

The procedure was similar to that adopted for the hydrogen ethyl malonate preparation.

The crude half ester (17.7g) in water (25ml) was treated with concentrated hydrochloric acid (7.5ml) at 5°. Ether extraction (20,10,5ml) washing with water (2x5ml), drying over magnesium sulphate, filtration and removal of ether were carried out as before leaving a clear, colourless liquid. Direct titration with aqueous standard sodium hydroxide (0.035N) solution gave equivalents for the liquid of 160.3, 160.9; Mean 160.6. Equivalent for hydrogen ethyl glutarate is 160.2.

**Procedure**

Alcoholic potassium hydroxide (0.4313N) was standardised against portions of potassium hydrogen phthalate in water (10ml). The calculated volume of potassium hydroxide (163.9ml) was then added dropwise to hydrogen ethyl glutarate (11.352g) in alcohol (100ml). The resulting clear, colourless, alcoholic solution
was rotary-evaporated to dryness and the white solid dried over calcium chloride at 0.1mm. The potassium ethyl glutarate so prepared had a purity factor of 99.3%.

**Potassium ethyl adipate**

Attempts at preparing the compound by half saponification of the diethyl ester gave products contaminated by up to 50% of the dipotassium salt. Extraction, fractional precipitation and recrystallisation procedures gave improved products but not in sufficient yield or quality for kinetic work.

**Preparation of hydrogen ethyl adipate**

The method[79] was adapted to requirements.

**Formulation**

\[
\begin{align*}
A & \\
& \text{(Adipic acid) 109.5g (0.75 mole)} \\
& \text{(Diethyl adipate) 87.9g (0.435 mole)} \\
& \text{(Di-n-butyl ether) 37.5ml} \\
& \text{(Hydrochloric acid 36L19 19ml} \\
B & \text{Ethanol 96% 70ml}
\end{align*}
\]

Adipic acid was recrystallised from water (mp 151.5°). Diethyl adipate was distilled (bp 120-121° 9mm). Di-n-butyl ether was tested for peroxides by the addition of sodium iodide/acetic anhydride when a brown colour developed.
Peroxides were removed by shaking it (75ml) with alkaline ferrous hydroxide (3g ferrous sulphate hydrate in excess sodium hydroxide), washing with water (4x10ml), sulphuric acid to remove the brown colouration (3N 2x10ml), water (4x10ml) and drying over potassium carbonate. No peroxides were now present and pure di-n-butyl ether was distilled (bp140-141°). Ethanol was distilled (bp78°) under nitrogen.

Procedure

The mixture A was heated in a 1l rb flask to 150° in a heating mantle under reflux till the mixture became homogeneous (1hr.). As hydrogen chloride was evolved, a hydrogen chloride absorption apparatus was attached to the top of the condenser. The mantle was then lowered to 110° and ethanol (B, 55ml) was added and refluxing continued.

Further ethanol (15ml) was then added after 2 hours and refluxing continued for a further 4½ hours. After allowing to cool the mixture was then fractionally distilled from the top of the condenser under water pump pressure (mantle at 90°) to remove ethanol, water, and di-n-butyl ether (bp50-60° 60-70mm) which formed 2 layers in the receiver. The mixture was then allowed to cool and the water condenser replaced by a 9", silver
vacuum jacketed, column filled with 3-4mm Fenske helices to which was attached a vacuum distillation, variable ratio, take-off head.

Very efficient fractionation at oil pump pressure was attained using this apparatus.

The fractions collected were:

1. 110-111° 4mm liquid large fraction
2. 130-152° 4mm liquid small fraction
3. 152±1° 4mm liquid major fraction
4. 152-175 4mm white solid/liquid small fraction
5. 175-180° 4mm white solid

During the distillation of fraction (3) the drops were collected at the rate of 1 drop per 10 seconds, the drop distillation ratio being 5:1.

Fraction (1) and a sample of distilled diethyl adipate used in the preparation were compared by gas liquid chromatography using a carbowax column at 172° and shown to be identical. Melting point determinations of fraction (5)(mp130-145°) showed it most likely to be decomposition products of adipic acid. They were not further investigated. Fraction (3), a clear, colourless, viscous liquid ($n_D^{25} 1.4354$), on standing, crystallised to a white waxy solid (mp28-30°). Direct titration with
aqueous standard sodium hydroxide solution (0.04N) gave equivalents of 174.3 and 174.1 Mean 174.2. Equivalent of hydrogen ethyl adipate: 174.2.

Conversion to potassium ethyl adipate

The same procedure as that used for the hydrogen ethyl malonate conversion was used.

The calculated quantity of alcoholic potassium hydroxide (14g/500ml 237ml) was added to hydrogen ethyl adipate (18.13g) in ethanol (100ml). After rotary-evaporation to dryness, the white, deliquescent solid was dried over calcium chloride-paraffin wax at 1mm. Analysis showed it to be potassium ethyl adipate of purity-factor 100.0%.
PREPARATION OF REAGENTS AND SOLUTIONS FOR KINETIC WORK

General - Analytical balances were checked periodically against certificated weights to guard against faults in the balance.

Aqueous, non-alkaline solutions were prepared in works certificated, grade A, volumetric glassware using nitrogen saturated water (p. 52).

All burettes and pipettes were similarly works certificated. A drainage time of 15 seconds was allowed in dispensing non-polymeric aqueous solutions from pipettes. For polymeric solutions, the drainage time was increased by a factor \( n \) where \( n = \frac{\text{Discharge time of polymer solution}}{\text{Discharge time of aqueous solution ex same pipette}} \).

Potassium hydrogen phthalate A.R. (KHP)

One, new bottle of analytical grade (B.D.H. reagent) was used throughout. Before use this reagent was dried at 120° for 2 hours and allowed to cool over calcium chloride. It was used as a primary standard in all alkalimetric titrations and its aqueous solution was used in the kinetic work.

Benzoic acid A.R.

The white solid mp 21° was dried for 48 hours over calcium chloride and used as a secondary standard in determining the
normality of two sodium hydroxide solutions (0.05N, 0.02N) pre-standardised with potassium hydrogen phthalate. Good agreement was obtained.

**Phenolphthalein indicator solution**

To phenolphthalein (0.5g) in ethanol (96% 50ml) was added water (50ml) with stirring. Three drops were used for all titrations. Its capacity as an indicator was checked periodically by verifying that a solution (3 drops) in water (10ml) was pinked by a trace of alkali.

**Sodium hydroxide solutions**

Precautions were taken to exclude carbon dioxide by using soda lime guard tubes where applicable.

A concentrated solution (~25N) of analytical grade sodium hydroxide (11g) in water (10ml) under nitrogen was prepared in a stoppered 50ml pyrex conical flask. Appropriate accurate dilution[81] of this concentrated solution, freshly prepared each time, gave the three, dilute sodium hydroxide solutions listed below.

(1) 0.05N stored in a 1.1 polythene bottle under nitrogen (dilution of concentrated solution: 2ml l⁻¹). On careful dilution to the required strength (p. 76) it was used
as the low-m.w. alkali in the kinetic runs. The solution was
standardised, in duplicate, daily as required, by direct
titration from a 50ml burette against potassium hydrogen
phthalate (0.14g) in water (10ml).

After each opening of the bottle, air was displaced
by nitrogen. The solution was not kept for more than 1 week.

(2) 0.035N. Used for the determination of percentage
purities of esters. Prepared, standardised and stored as
above. (Dilution of concentrated solution: 1.4ml l⁻¹.)

(3) 0.02N. (Dilution of concentrated solution:
0.8ml l⁻¹.) This solution was used for back titrations in
all the kinetic measurements. For this purpose it was stored
in a 2½l polythene bottle bearing a rubber bung with a T-piece
and a length of glass tube extending nearly to the bottom of
the bottle. The other end of the tubing was connected via
poly vinyl chloride and clean glass tubing to the three-way
tap of a 10ml semi-micro grade A burette graduated in 0.02ml
(read to 0.01ml). One end of the T-piece was connected to
the top of the burette via a bung and poly vinyl chloride
tubing, the other, to a soda lime guard tube. The bottle was
clamped above the top of the burette. The burette was filled
by applying a reduced pressure to the top of the burette with the tap open to the reservoir. During use, the burette was always topped to the zero mark after each titration. After standing unused for 24 hours, the burette and connecting tubes were emptied, refilled with fresh alkali from the reservoir, again emptied then refilled. The solution was standardised in triplicate each day against potassium hydrogen phthalate (0.04g) in water (10ml). The contents of the reservoir were renewed every 2-3 days.

**Poly(vinylbenzyltriethylammonium hydroxide) (PVAH) solutions**

Preliminary standardisation of the batches was done by back titration with sodium hydroxide (0.02N) of potassium hydrogen phthalate solution (10ml 0.026N) to which PVAH (2ml) had been added.

Batches PH2 and PH4 were then diluted to give solutions approximately 0.045N, and restandardised in triplicate by titrating sodium hydroxide (0.02N) against a solution of KHP (0.125g) in water (10ml) to which PVAH (10ml) had been added. The resulting standard solutions were designated PH3 and PH5 respectively and were used in the main sequence of runs.
Care was taken to exclude carbon dioxide and a nitrogen atmosphere was always maintained above the solutions. Repeat standardisations carried out before each set of PVAH runs showed the normality to vary by <1% over a period of two months.

Final normalities of solutions are given below in Table 2.

<table>
<thead>
<tr>
<th>Batch collected</th>
<th>Normality</th>
<th>Diluted to</th>
<th>Designated</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH1 used for preliminary work only</td>
<td>0.109</td>
<td>0.03735</td>
<td>PH1a</td>
</tr>
<tr>
<td>PH2</td>
<td>0.0617</td>
<td>0.04560</td>
<td>PH3</td>
</tr>
<tr>
<td>PH4</td>
<td>0.0575</td>
<td>0.04568</td>
<td>PH5</td>
</tr>
</tbody>
</table>
DETERMINATION OF THE PERCENTAGE PURITY OF THE POTASSIUM ETHYL ESTERS

The procedure adopted was the same for each ester prepared. Duplicate determinations were carried out before and after the set of six kinetic runs for each ester. Furthermore, for the succinate monoester, the equivalent was determined after the set of temperature runs. The principle of the method is the same as that used in the kinetic runs.

Procedure

Portions of the ester (0.12g) were weighed into a conical flask (150ml) previously flushed with nitrogen. Sodium hydroxide (20ml 0.035N) was added from a burette and the flask loosely stoppered. The flask was heated at 60-70° on an asbestos mat on a hot plate for 2 hours, when, as shown by control experiments, complete hydrolysis was known to have occurred. On cooling, KHP (0.12g) was weighed in and, after dissolution, the solution was back titrated with sodium hydroxide (0.035N) using phenolphthalein as indicator. Calculation gave the equivalent of the potassium ethyl ester.
An example is given

Normality alkali = 0.3457N
Back titre = 14.70ml
Wt KHP weighed in = 0.1270g
Wt potassium ethyl adipate = 0.1226g

Then

\[
\text{equiv. ester} = \frac{0.3457 \times (20 + 14.70) - 0.1270}{1000} \times \frac{204.23}{212.4} \text{ equivalent sodium hydroxide from which 1 equiv. sodium hydroxide} = 212.4g = \text{ equivalent weight of potassium ethyl adipate.}
\]

Table 3. shows the results obtained.

<table>
<thead>
<tr>
<th>Ester</th>
<th>Mol. wt.</th>
<th>Equivalent determined</th>
<th>Mean</th>
<th>Purity factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalate</td>
<td>156.2</td>
<td>156.8, 157.0, 156.8, 156.9</td>
<td>156.9</td>
<td>99.55</td>
</tr>
<tr>
<td>Malonate</td>
<td>170.2</td>
<td>170.2, 170.1, 170.1, 170.8</td>
<td>170.3</td>
<td>100.0</td>
</tr>
<tr>
<td>Succinate</td>
<td>184.2</td>
<td>184.1, 184.2, 184.2, 184.2, 184.0, 184.3</td>
<td>184.3</td>
<td>100.0</td>
</tr>
<tr>
<td>Glutarate</td>
<td>198.3</td>
<td>199.8, 199.7, 199.8, 199.6</td>
<td>199.7</td>
<td>99.3</td>
</tr>
<tr>
<td>Adipate</td>
<td>212.3</td>
<td>212.4, 212.3, 212.6, 212.3</td>
<td>212.4</td>
<td>100.0</td>
</tr>
</tbody>
</table>
THE REACTION KINETICS OF THE HYDROLYSES OF A HOMOLOGOUS
SERIES OF ALIPHATIC ESTER ANIONS BY A MONOMERIC AND
POLYMERIC HYDROXIDE

Five ester anions of the general formula
\[ C_{2}H_{5}O_{2}C(CH_{2})_{n}CO_{2}K \] were studied. For the comparatively fast
oxalate anion hydrolysis \((n=0)\), it was found necessary to use
a special electrodeless conductivity technique to follow the
reaction. A separate section is devoted to the work (p.102).
For the others \((n=1-4)\) a semi-automatic apparatus was
devised to study the reaction by a titrimetric method. Runs
were done at concentration 0.01 in ester and 0.02N in alkali
for the malonate and succinate ester \((n=1 \text{ and } 2)\) and 0.01N
in alkali for the glutarate and adipate ester \((n=3 \text{ and } 4)\)
at a temperature of 25°. Further temperature runs were done
at 20°, 15° and 10° for the succinate monoester. For all
conditions runs were done in triplicate.

Preparation of reactant solutions

(1) Potassium ethyl malonate and succinate

The solutions prepared were arranged to give, on
mixing in the reaction vessel, a final solution of the
concentrations stated above.

The sodium hydroxide solutions were prepared in a 100ml standard flask by diluting sodium hydroxide solution (0.05N), delivered from a burette into the nitrogen filled flask, to 100ml and then further diluting the volume with water from a grade A 10ml burette to render the normality 0.0220N. PVAH alkali solution was prepared by diluting aliquots (50ml) from a pipette to 100ml, and rendering the solution accurately 0.0220N as before. The total volume of alkali solutions was 103-104ml to enable 100ml aliquots to be withdrawn. The flask was thermostatted before use for a minimum of 1 hour at the temperature at which the run was to be conducted (2 hours for the 10° runs).

Quench solution - Potassium hydrogen phthalate solution was prepared by dissolving the solid (5m moles) in water in a 250ml standard flask.

(2) Potassium ethyl glutarate and succinate

The alkali solutions were rendered 0.0110N by dilution of half the volumes of concentrated alkali used before to 103-104ml as described.
Quench solution - Prepared as before using KHP (3.75m moles) in water (250ml).

Ester solutions were prepared in both cases by dissolving the ester (2.2m moles) in water in a standard flask (20ml) and thermostating as for the alkali solutions.

Back titrant - For both cases pre-standardised sodium hydroxide (0.02N) contained in the self-filling burette as already described (p. 70) was used.
DESCRIPTION OF THE SEMI-AUTOMATIC KINETIC APPARATUS

A diagram of the apparatus, constructed of pyrex glass, Quickfit joints, and good quality vacuum stopcocks, is given. It consisted of two sections, the lower section consisting of an exdented flask $F$ of 100ml capacity which contained the alkali solution and a B19 side arm $S$ with its attached, rubber serum capped, B14-19, expansion adaptor. The upper section consisted of a bulb $B$ of known capacity (approx. 8ml) which, when connected to the lower half, could be filled with liquid through a capillary tube $C$ (internal diam. 2mm) by an external nitrogen pressure applied through tap $T_1$. The capillary tube $C$ was arranged to extend into the exdent in the flask $F$. The liquid rose to the bulb via a tap $T_2$ and a 3-way tap $T_3$. The third exit of tap $T_3$ was tapered 0 to allow liquid to drain out and be collected. To enable liquid to drain back into the flask, a bypass tap $T_4$ was included. Below the bulb was a graduation mark $G$ and above the bulb was a tapered capillary tube surrounded by a glass envelope with an exit $E$.

The lower half with its B34 cone was attached to the B34 socket on the upper half with two springs over hooks $H$. 
The B19 adaptor and the taps were lightly greased with vaseline. The total height of the apparatus when assembled was 37 cms.

Calibration of bulb B

Calibration of the bulb B was performed by thermostating water (100ml) in the apparatus at 25.00 ± 0.02°C and weighing aliquots delivered by the manipulative procedure to be described. Conversion to volume gave –

Volume delivered ex 0 = 7.978ml (mean of 12 determinations)

The volume delivered was redetermined at the end of the runs and differed from the above by <0.1%. For the runs done at 100, the temperature of the effluent (12-13°C) was measured, but, since the total time the reaction mixture was out of the thermostat bath did not exceed 30 seconds, no corrections for gain in temperature were applied.

Calibration of syringe

The syringe (Chances all glass Luer tip 10ml) with the stainless steel cannula (20G x 6") was calibrated by the weight of water delivered in a similar manner.

Volume delivered = 9.86ml (mean of ten determinations)
Thermostat bath calibration

The thermostat bath was standardised at the temperatures at which the runs were conducted by use of N.P.L. standard thermometers.

The thermostat itself was stable to 0.02°.

Temperature of runs:

10.00 ± 0.05°
14.98 ± 0.05°
20.02 ± 0.05°
25.02 ± 0.05°

(These are the true temperatures at the exact 10, 15, 20, 25° marks on the standard thermometer.)

Time measurements

The accurate stop-watch as used for the viscosity measurements (p.43) was used.

Procedure

Dry nitrogen was supplied to the apparatus by a line to which was attached a bunsen valve immersed in mercury so that, at pressures in excess of a few cm of mercury, nitrogen was allowed to escape via the valve. The line led to a T-piece, one end of which was connected to T1, the other to a
length of rubber tubing with a pinch clip. This could then be connected to E, as required, to eject the residual reaction mixture.

The apparatus was thermostatted in the bath up to the lower hook and flushed with nitrogen by opening T1, T3(1-3) and alternately T2 and T4. The alkali (100ml) was added to the flask through S from a pipette with the nitrogen flow increased and T2 closed and T4 open. The adaptor A was then replaced. After half an hour further thermostating with T1, T2 and T4 closed, T4 and T1 were again opened and the bulb filled with nitrogen. The ester solution (10ml) was then swiftly injected, via the serum cap R, into the alkali solution and the flask gently agitated. The stop-watch was started at the time of half addition of the ester solution.

T3 (1-2) and T2 were opened. When the reactant mixture had filled the outlet 0 to overflowing T3(1-3) was opened to fill the bulb to overflowing. The filling process took 10 seconds. T3 (3-2) was now opened and the aliquot allowed to drain (20-23 secs.) into the quench solution (10ml) in a conical flask (150ml.). The time reading was taken when the first drop of reactant solution touched the quench solution.
During the discharge, T4 was opened to allow the liquid filling the capillary to drop back into the flask. After discharge, the tube 0 was drained, and, by opening T3 (1-2, 1-3 and 1-2-3), traces of old solution were blown out, with the assistance of the rubber tubing attached to E as indicated above. To take the next reading, the procedure was repeated.

In filling the bulb, care was taken to ensure no air bubbles formed. The quenched solutions were back titrated with sodium hydroxide at intervals during the run.

A maximum of 12 readings could be obtained at 1 minute intervals from an initial charge of 110ml.
General Method of Calculation of Results

(1) Malonate and Succinate Monoesters.

Weights in g, volumes in ml

Let
Wt ester dissolved in 20ml = \( e \)
Equivalent weight of ester = \( E \)
Purity factor of ester = \( r \)
Volume ester solution ex syringe = 9.86
Volume delivered by apparatus = 7.978
Alkali concentration \( \text{[a]} \) = 0.0200
Total volume reaction mixture = 109.86
Wt KHP in 250ml (quench) = \( g \)
Equivalent weight KHP = 204.23
Normality of back titre = \( N \)
Volume back titre = \( p \)
Volume quench = 10

The concentration of reactants are \((\text{mole}\,\text{l}^{-1})\).

\[
a = 0.0200
\]

\[
b = \frac{er \times 9.86 \times 1000}{100E \times 20 \times 109.86}
\]

Equivalents \(\text{OH}^-\) remaining in 7.978ml

\[
= \frac{g}{204.23} \times \frac{10 - pN}{250 \times 1000}
\]
Hence the instantaneous a-x = \frac{1000}{7.978} \cdot \frac{5105.75}{1000} \cdot \frac{\text{DN}}{7.978}

and instantaneous b-x = b-a+(a-x)

concn. of ester at time t

call z = \frac{\text{DN}}{7.978}

decrease in concn. OH in time t

% reaction is given by \frac{x}{b} \times 100

By substitution of the values of (a-x) and (b-x) in the integrated form of the second order rate equation

\[ k_t = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} \]  

values of k_t were obtained.

For the sodium hydroxide runs, a plot of k_t against t gave a straight line graph, the slope of which gave the rate constant k.

For the PVAH runs a similar plot gave a smooth convex curve (p. 95). In order to obtain rate constants (these are instantaneous rate constants, which are also termed specific rates), it was necessary to graphically
differentiate the curve. For values of \( x = 0.1b, 0.2b, 0.3b, \) etc. (i.e. 10, 20, 30% reaction) the value of \( k_t \) was calculated. Then, using a 90° glass block as a reflecting and transmitting surface, normals were mechanically drawn to the curve for successive 10% increments in reaction. The normal angle was measured to \( \pm 1/4^\circ \) and from this, the tangent and hence instantaneous values of \( k \) were obtained. For greatest accuracy, the curve was plotted so that the initial slope of the curve gave \( \theta = 45^\circ \).

The initial rate constant \( k_0 \) was obtained by extrapolation using a flexicurve of the plot % reaction vs. \( k \) instantaneous.

A manually worked example of the calculation of the rate function for a sodium hydroxide and a PVAH run are given (p. 87, 93) together with the appropriate graphical plots. Also a computer programme for the evaluation of the rate function, \( k_t \), is given (p. 100) together with computer print-out sheets (p. 89, 94) for the sodium hydroxide and PVAH run for comparison with the manually worked example.
Typical Kinetic Run with Sodium Hydroxide-Potassium

Ethyl Succinate (Rate plot p-90)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature</th>
<th>2SNaOH1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>14.98</td>
</tr>
<tr>
<td>Wt ester in 20ml. e</td>
<td>0.4058g.</td>
<td></td>
</tr>
<tr>
<td>Equivalent of ester E</td>
<td>184.24</td>
<td></td>
</tr>
<tr>
<td>Purity factor r</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>Wt KHP in 250ml</td>
<td>1.0242g.</td>
<td></td>
</tr>
<tr>
<td>Back titrant normality</td>
<td>0.02152</td>
<td></td>
</tr>
</tbody>
</table>

[a] = 0.02000 mole 1⁻¹
[b] = 0.0098840 mole 1⁻¹
[a]-[b] = 0.010116 mole 1⁻¹
Z = 0.025143
Q = 0.00269741
b-a+Z = 0.015027
R = ln₁₀(b/a) = 1.69390
S = \frac{2.30259}{a-b} = 227.62
<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Titre (ml.)</th>
<th>( pQ \times 10^3 )</th>
<th>( (a-x) \times 10^2 )</th>
<th>( (b-x) \times 10^3 )</th>
<th>( \ln_{10} (a-x) )</th>
<th>( \ln_{10} (b-x) )</th>
<th>( \ln_{10} \frac{b(a-x) \times 10^2}{T-U+R} )</th>
<th>( k\ell ) 1 mole(^{-1}) min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.01</td>
<td>5.4217</td>
<td>1.9721</td>
<td>9.605</td>
<td>( \frac{2.29493}{3.98250} )</td>
<td>( \frac{6.33}{1.44} )</td>
<td>5.18</td>
<td>1.44</td>
</tr>
<tr>
<td>4.5</td>
<td>2.26</td>
<td>6.0961</td>
<td>1.9047</td>
<td>8.931</td>
<td>( \frac{2.27983}{3.95090} )</td>
<td>2.283</td>
<td>5.20</td>
<td>5.20</td>
</tr>
<tr>
<td>8.0</td>
<td>2.45</td>
<td>6.6086</td>
<td>1.8534</td>
<td>8.418</td>
<td>( \frac{2.26797}{3.92521} )</td>
<td>3.666</td>
<td>8.34</td>
<td></td>
</tr>
<tr>
<td>11.5</td>
<td>2.66</td>
<td>7.1751</td>
<td>1.7968</td>
<td>7.852</td>
<td>( \frac{2.25450}{3.89498} )</td>
<td>5.342</td>
<td>12.16</td>
<td></td>
</tr>
<tr>
<td>15.0</td>
<td>2.83</td>
<td>7.6336</td>
<td>1.7509</td>
<td>7.393</td>
<td>( \frac{2.24326}{3.86882} )</td>
<td>6.834</td>
<td>15.56</td>
<td></td>
</tr>
<tr>
<td>18.5</td>
<td>2.97</td>
<td>8.0113</td>
<td>1.7132</td>
<td>7.016</td>
<td>( \frac{2.23381}{3.84609} )</td>
<td>8.162</td>
<td>18.58</td>
<td></td>
</tr>
<tr>
<td>22.0</td>
<td>3.12</td>
<td>8.4159</td>
<td>1.6727</td>
<td>6.611</td>
<td>( \frac{2.22342}{3.82027} )</td>
<td>9.705</td>
<td>22.09</td>
<td></td>
</tr>
<tr>
<td>25.5</td>
<td>3.27</td>
<td>8.8205</td>
<td>1.6322</td>
<td>6.206</td>
<td>( \frac{2.21276}{3.79281} )</td>
<td>11.385</td>
<td>25.91</td>
<td></td>
</tr>
<tr>
<td>29.0</td>
<td>3.38</td>
<td>9.1172</td>
<td>1.6026</td>
<td>5.910</td>
<td>( \frac{2.20482}{3.77159} )</td>
<td>12.713</td>
<td>28.94</td>
<td></td>
</tr>
<tr>
<td>32.5</td>
<td>3.50</td>
<td>9.4409</td>
<td>1.5702</td>
<td>5.586</td>
<td>( \frac{2.19595}{3.74710} )</td>
<td>14.275</td>
<td>32.49</td>
<td></td>
</tr>
<tr>
<td>36.0</td>
<td>3.60</td>
<td>9.7106</td>
<td>1.5432</td>
<td>5.316</td>
<td>( \frac{2.18843}{3.72558} )</td>
<td>15.675</td>
<td>35.68</td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>3.69</td>
<td>9.9534</td>
<td>1.5190</td>
<td>5.074</td>
<td>( \frac{2.18156}{3.70535} )</td>
<td>17.011</td>
<td>38.72</td>
<td></td>
</tr>
</tbody>
</table>

From the gradient of the slope of the plot \( k\ell \) v. \( t \)

\( k = 0.975 \) 1 mole\(^{-1}\) min\(^{-1}\)
**FIG 3**

**RUN 2 SNAOH 15 DEGREES NOV 2**

**D.F.C. LINNECAR**

**COMPUTATION OF SECOND ORDER RATE FUNCTION**

**CONCENTRATIONS OF REACTANTS ARE**

**ALKALI (A) =** 0.02000000, 0.00988406

**ESTER (B) =** 0.000278 0.008932 0.007853 0.006207 0.005911 0.005587 0.005317 0.005074

<table>
<thead>
<tr>
<th>X</th>
<th>B-X</th>
<th>A-X</th>
<th>P/C PURITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000278</td>
<td>0.000953</td>
<td>0.001465</td>
<td>0.002031</td>
</tr>
<tr>
<td>0.00606</td>
<td>0.008932</td>
<td>0.008419</td>
<td>0.007953</td>
</tr>
<tr>
<td>0.019722</td>
<td>0.019048</td>
<td>0.018535</td>
<td>0.017969</td>
</tr>
</tbody>
</table>

**SECOND ORDER RATE FUNCTION**

<table>
<thead>
<tr>
<th>KT</th>
<th>TIME</th>
<th>P/C REACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>2.813</td>
<td>P/C REACTION</td>
</tr>
<tr>
<td>4.500</td>
<td>9.635</td>
<td>VALUE OF INTEGRAL</td>
</tr>
<tr>
<td>8.000</td>
<td>14.820</td>
<td>5.19247</td>
</tr>
<tr>
<td>11.500</td>
<td>20.551</td>
<td>8.33776</td>
</tr>
<tr>
<td>15.000</td>
<td>25.191</td>
<td>12.15491</td>
</tr>
<tr>
<td>20.000</td>
<td>29.011</td>
<td>15.54738</td>
</tr>
<tr>
<td>25.000</td>
<td>37.190</td>
<td>18.57428</td>
</tr>
<tr>
<td>30.000</td>
<td>43.476</td>
<td>22.08399</td>
</tr>
<tr>
<td>35.000</td>
<td>48.661</td>
<td>25.90493</td>
</tr>
<tr>
<td>40.000</td>
<td>46.205</td>
<td>28.93346</td>
</tr>
<tr>
<td>45.000</td>
<td>43.476</td>
<td>32.48401</td>
</tr>
<tr>
<td>50.000</td>
<td>40.201</td>
<td>35.66298</td>
</tr>
<tr>
<td>55.000</td>
<td>37.190</td>
<td>38.71530</td>
</tr>
<tr>
<td>60.000</td>
<td>34.23359</td>
<td>40.000</td>
</tr>
<tr>
<td>65.000</td>
<td>31.36401</td>
<td>42.070</td>
</tr>
<tr>
<td>70.000</td>
<td>28.49501</td>
<td>44.135</td>
</tr>
<tr>
<td>75.000</td>
<td>25.53601</td>
<td>46.205</td>
</tr>
<tr>
<td>80.000</td>
<td>22.57701</td>
<td>48.276</td>
</tr>
<tr>
<td>85.000</td>
<td>19.61801</td>
<td>50.347</td>
</tr>
<tr>
<td>90.000</td>
<td>16.65901</td>
<td>52.418</td>
</tr>
<tr>
<td>95.000</td>
<td>13.70001</td>
<td>54.489</td>
</tr>
</tbody>
</table>
Fig. 4 RATE PLOT. RUN 2S NaOH 1,2 15°
Typical Kinetic Run with PVAH - Potassium Ethyl Succinate

(rate plot p.95)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>6SPVAH 1,2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>10.00</td>
</tr>
<tr>
<td>Wt ester in 20ml. e</td>
<td>0.4061g.</td>
</tr>
<tr>
<td>Equivalent of ester E</td>
<td>184.24</td>
</tr>
<tr>
<td>Purity factor r</td>
<td>100.00</td>
</tr>
<tr>
<td>Wt KHP in 250ml.</td>
<td>1.0223g.</td>
</tr>
<tr>
<td>Back titrant normality</td>
<td>0.02141</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
[a] &= 0.02000 \text{ mole l}^{-1} \\
[b] &= 0.0098913 \text{ mole l}^{-1} \\
[a] - [b] &= 0.010109 \text{ mole l}^{-1} \\
Z &= 0.025097 \\
Q &= 0.00268362 \\
b - a + Z &= 0.014988 \\
R &= \ln_{10}(b/a) = 1.69422 \\
S &= \frac{2.30259}{a-b} = 227.78
\end{align*}
\]
<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Titre (ml.)</th>
<th>$pQ \times 10^3$</th>
<th>$(a-x) \times 10^2$</th>
<th>$(b-x) \times 10^3$</th>
<th>$\ln_{10} (a-x)$</th>
<th>$\ln_{10} (b-x)$</th>
<th>$\ln_{10} \frac{h(a-x) \times 10^2}{a(b-x)}$</th>
<th>$k \cdot t \cdot \text{mole}^{-1}$</th>
<th>$S(T-U+R)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.37</td>
<td>6.3602</td>
<td>1.8737</td>
<td>8.628</td>
<td>2.2720</td>
<td>3.93591</td>
<td>3.101</td>
<td>7.06</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>2.59</td>
<td>6.9506</td>
<td>1.8146</td>
<td>8.037</td>
<td>2.25878</td>
<td>3.90509</td>
<td>4.791</td>
<td>10.91</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>2.97</td>
<td>7.9704</td>
<td>1.7127</td>
<td>7.018</td>
<td>2.23368</td>
<td>3.84621</td>
<td>8.169</td>
<td>18.61</td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>3.30</td>
<td>8.8559</td>
<td>1.6241</td>
<td>6.132</td>
<td>2.21062</td>
<td>3.78760</td>
<td>11.724</td>
<td>26.71</td>
<td></td>
</tr>
<tr>
<td>8.5</td>
<td>3.51</td>
<td>9.4195</td>
<td>1.5677</td>
<td>5.568</td>
<td>2.19527</td>
<td>3.74570</td>
<td>14.379</td>
<td>32.75</td>
<td></td>
</tr>
<tr>
<td>9.75</td>
<td>3.59</td>
<td>9.6342</td>
<td>1.5463</td>
<td>5.354</td>
<td>2.18929</td>
<td>3.72868</td>
<td>15.483</td>
<td>35.27</td>
<td></td>
</tr>
<tr>
<td>10.75</td>
<td>3.68</td>
<td>9.8757</td>
<td>1.5221</td>
<td>5.112</td>
<td>2.18244</td>
<td>3.70859</td>
<td>16.807</td>
<td>38.28</td>
<td></td>
</tr>
<tr>
<td>11.75</td>
<td>3.73</td>
<td>10.0099</td>
<td>1.5087</td>
<td>4.978</td>
<td>2.17860</td>
<td>3.69705</td>
<td>17.577</td>
<td>40.04</td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>3.80</td>
<td>10.1978</td>
<td>1.4899</td>
<td>4.790</td>
<td>2.17315</td>
<td>3.68034</td>
<td>18.703</td>
<td>42.60</td>
<td></td>
</tr>
<tr>
<td>14.0</td>
<td>3.89</td>
<td>10.4393</td>
<td>1.4658</td>
<td>4.549</td>
<td>2.16608</td>
<td>3.65792</td>
<td>20.238</td>
<td>46.10</td>
<td></td>
</tr>
</tbody>
</table>

By graphical analysis of the $kt$ v. time rate plot as described (p. 86),

the following table was obtained
\[ k \text{ (1 mole}^{-1}\text{min}^{-1}) = \tan \theta \times \text{factor 5} \]

<table>
<thead>
<tr>
<th>% reaction</th>
<th>( \theta )</th>
<th>( \tan \theta )</th>
<th>( k \text{ (1 mole}^{-1}\text{min}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>57( \frac{1}{4} )</td>
<td>1.5547</td>
<td>3.89</td>
</tr>
<tr>
<td>20</td>
<td>56( \frac{1}{2} )</td>
<td>1.5253</td>
<td>3.81</td>
</tr>
<tr>
<td>30</td>
<td>55</td>
<td>1.4281</td>
<td>3.57</td>
</tr>
<tr>
<td>40</td>
<td>49( \frac{1}{4} )</td>
<td>1.1606</td>
<td>2.90</td>
</tr>
<tr>
<td>50</td>
<td>40( \frac{1}{2} )</td>
<td>0.8541</td>
<td>2.14</td>
</tr>
</tbody>
</table>

From the final plot of \( \% \text{ reaction v. } k(p.96) \), extrapolation to 0\% reaction gave

\[ k_0 = 3.93 \text{ 1 mole}^{-1}\text{min}^{-1} \]
RUN 6SPVH 10 DEGREES OCT 28 DFCL

D.F.C. LINNECAR COMPUTATION OF SECOND ORDER RATE FUNCTION
CONCENTRATIONS OF REACTANTS ARE
ALKALI (A) =
ESTER (B) = 0.00989137

<table>
<thead>
<tr>
<th>TIME</th>
<th>X</th>
<th>B-X</th>
<th>A-X</th>
<th>KT</th>
<th>P/C REACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.001263</td>
<td>0.008628</td>
<td>0.018737</td>
<td>7.06998</td>
<td>12.769</td>
</tr>
<tr>
<td>2.000</td>
<td>0.001853</td>
<td>0.008038</td>
<td>0.018147</td>
<td>10.90543</td>
<td>18.738</td>
</tr>
<tr>
<td>3.000</td>
<td>0.002417</td>
<td>0.007474</td>
<td>0.017583</td>
<td>14.97555</td>
<td>24.433</td>
</tr>
<tr>
<td>4.000</td>
<td>0.002873</td>
<td>0.007018</td>
<td>0.017127</td>
<td>18.60520</td>
<td>29.048</td>
</tr>
<tr>
<td>6.500</td>
<td>0.003759</td>
<td>0.006133</td>
<td>0.016241</td>
<td>26.69692</td>
<td>38.001</td>
</tr>
<tr>
<td>8.500</td>
<td>0.004323</td>
<td>0.005569</td>
<td>0.015678</td>
<td>32.73932</td>
<td>43.698</td>
</tr>
<tr>
<td>9.750</td>
<td>0.004537</td>
<td>0.005354</td>
<td>0.015463</td>
<td>35.26438</td>
<td>45.869</td>
</tr>
<tr>
<td>10.750</td>
<td>0.004779</td>
<td>0.005113</td>
<td>0.015231</td>
<td>38.27319</td>
<td>48.311</td>
</tr>
<tr>
<td>11.750</td>
<td>0.004913</td>
<td>0.004979</td>
<td>0.015087</td>
<td>40.02817</td>
<td>49.667</td>
</tr>
<tr>
<td>13.000</td>
<td>0.005101</td>
<td>0.004791</td>
<td>0.014899</td>
<td>42.59363</td>
<td>51.566</td>
</tr>
<tr>
<td>14.000</td>
<td>0.005342</td>
<td>0.004549</td>
<td>0.014658</td>
<td>46.09431</td>
<td>54.008</td>
</tr>
</tbody>
</table>

P/C REACTION VALUE OF INTEGRAL
5.00  3.59718
10.00  5.49515
15.00  8.45196
20.00 11.77105
25.00 15.40281
30.00 19.39641
35.00 23.81258
40.00 28.72733
45.00 34.23742
50.00 40.46034
55.00 47.59666
60.00 55.81966
65.00 65.48821
70.00 77.06593
75.00 91.28709
80.00 109.39444
85.00 133.72058
90.00 169.51817
95.00 233.57827
fig. 6 RATE PLOT, RUN 6S PVAM 1,2 10°
Fig. 7. Extrapolation of the instantaneous rate k to O reaction.
(2) **Glutarate and Adipate Monoesters**

The glutarate and adipate runs were done using approximately equimolar concentrations of alkali and ester (*i.e. a = b = 0.01)*.

For these conditions, the integrated form of the second order rate equation is

\[ k_t = \frac{x}{a(a-x)} \]  \hspace{1cm} (2)

It was found, however, that the differences between \([a]\) and \([b]\) were sufficiently large to allow computation of \(k_t\) by the non-equimolar form of the rate equation (eqn. 1). A computer programme was compiled which allowed values of \(\frac{x}{a(a-x)}\) and \(\frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)}\) to be directly compared. In all cases \(k_t\) from equation (1) was between, and close to, the values given from equation (2). The results were treated graphically in an identical manner to the malonate and succinate runs.
Computer Programme for the Evaluation of the Rate Function

The autocode programme for the I.C.T. Sirius computer for the evaluation and enumeration of values of $kt$ and the per cent reaction is given (p.100). The data fed into the computer on 5 hole punched tape are:

- $n_1 = \text{Number of time and titre values to be computed}$
- $V_1 = \text{Concentration of alkali } \left[ a \right] \text{ mole}^{-1}$
- $V_2 = \text{Weight ester (g.) in 20ml.}$
- $V_3 = \text{Equivalent of ester used (theoretical).}$
- $V_4 = \text{Back titrant sodiumhydroxide normality/1000}$
- $V_5 = \text{Volume delivered by kinetic apparatus (ml.)}$
- $V_6 = \text{Weight KHP(g.) dissolved in 250ml.}$
- $V_7 = \text{Purity factor of ester}$
- $V_8 = \text{Values of times (minutes)}$
- $V_{27} = \text{Values of titres for corresponding times (ml.)}$

The programme was used for all the runs. In the programme, values of $kt$ are built up stepwise for each successive titre value in the same way as in the numerical calculation. Values of $x_{b-x}$ $a-x$ $kt$ time and per cent reaction were printed out in columns. Then, for use in the graphical analysis in the PVAH plots, values of the integral
were computed for successive 5% steps in the reaction.

For the glutarate and adipate runs further sets of columns of
\[ x^{1/(a-x)} \frac{x}{a(a-x)} \text{ time } 1/(b-x) \frac{x}{b(b-x)} \% \text{ reaction} \]
were printed out for comparison of the two integral expressions.
D.F.C.\textsc{ullinear} computation of second order rate function

Concentrations of reactants are

\begin{align*}
\text{alkali (a)} &= \quad \text{ester (b)} = \quad \text{p/c purity} = \\
\end{align*}

\begin{verbatim}
PRINTV1, 3088
PRINTV40, 4148
PRINTV7, 4243
n=8
n=27
\end{verbatim}

\begin{verbatim}
X D-X A-X KT TIME P/C REACTION
\end{verbatim}

\begin{align*}
\no & = 0 \\
\ni \) v_{300} &= v_{n3} v_{v4} \\
v_{301} &= 10000 v_{v5} \\
v_{302} &= v_{41} \\
v_{303} &= v_{302} - v_{300} \\
v_{304} &= v_{301} v_{v303} \\
v_{305} &= v_{1} - v_{304} \\
v_{306} &= v_{40} - v_{305} \\
v_{310} &= v_{305} v_{40} \\
v_{310} &= v_{310} v_{100} \\
v_{315} &= v_{305} v_{v1} \\
v_{317} &= 100 v_{304} \\
v_{318} &= v_{31} 6 v_{317} \\
v_{319} &= v_{305} v_{40} \\
v_{320} &= 100 v_{306} \\
v_{321} &= v_{320} v_{319} \\
\rightarrow, \no = n1 \\
\i ) v_{306} &= v_{40} - v_{305} \\
v_{307} &= v_{1} - v_{305} \\
v_{308} &= v_{1} - v_{40} \\
v_{308} &= 100 v_{308}
\end{align*}
\[ v_{109} = v_{307}/v_{306} \]
\[ v_{209} = v_{209}/v_{109} \]
\[ v_{309} = \log v_{209} \]
\[ v_{309} = v_{308} \times v_{309} \]

-3, 3o = \text{null}

PRINT v_{305}, 3046
PRINT v_{306}, 4046
PRINT v_{307}, 4046
PRINT v_{309}, 4106
PRINT v_{310}, 4063
PRINT v_{310}, 4083
n_0 = n_0 + 1
n_2 = n_2 + 1
n_3 = n_3 + 1
- i, n_0 = n_1
- 6, 0, 7 > v_{43}

- 7

\[ n_2 = 27 \]

TEXT

\[ x \times \frac{1}{\lambda-x} \times A/(A-x) \times \text{TIME} \]
\[ x/B - x \times B/(B-x) \times \text{PC REACTION} \]

- 3

\[ \text{PRINT} v_{305}, 3046 \]
\[ \text{PRINT} v_{317}, 4084 \]
\[ \text{PRINT} v_{318}, 4084 \]
\[ \text{PRINT} v_{320}, 4043 \]
\[ \text{PRINT} v_{321}, 4084 \]
\[ \text{PRINT} v_{310}, 4043 \]
\[ n_7 = n_7 + 1 \]
\[ n_2 = n_2 + 1 \]
\[ n_3 = n_3 + 1 \]
- i, n_7 = n_1

- 6

TEXT

\[ \text{P/C REACTION} \]
\[ \text{VALUE OF INTEGRAL} \]

- 2

\[ v_{311} = 1 \]
\[ v_{312} = n_8 \]
\[ v_{313} = v_{31} + v_{313} \]
\[ v_{314} = v_{313}/20 \]
\[ v_{315} = v_{31} \times v_{314} \]
\[ v_{305} = v_{40} \times v_{314} \]
- 3

\[ \text{PRINT} v_{315}, 3083 \]
\[ \text{PRINT} v_{309}, 4205 \]
\[ n_8 = n_8 + 1 \]
- 4, n_8 = 19

STOP

\( (\rightarrow \omega) \)

**********
THE REACTION KINETICS OF THE HYDROLYSES OF POTASSIUM ETHYL OXALATE

Preliminary measurements by a conductivity method using bright platinum electrodes and also by a sample withdrawing procedure gave the half life for the reaction between sodium hydroxide (0.01N) and the ester (0.005N) to be in the range 7-8 minutes at 0°C. In order to follow the reaction conveniently, a chart recording high frequency oscillator was used.

The high frequency oscillator

Introduction

If a solution is placed in an alternating, electric or magnetic field of high frequency (in the range 10-50 Mc/s), it is possible to produce ionic or dipolar motion without the introduction of electrodes into the system. Energy is required to produce this motion and a solution introduced into the circuit of such an oscillator causes a change in its characteristics.

The apparatus [84], as developed by Lee and Saadi [85] from an original apparatus by Flom and Elving [86], was used by them to study the hydrolyses of some cyclic carbonates.
Circuits and block diagrams are given (p.105,106).

An outer jacket rigidly mounted on a wooden block was held in place by a tight-fitting copper band. The band also acted as an earthed shield to minimise changes in oscillator current caused by a change in the level of the liquid in the cell. Solution cells of varying width could be fitted into the jacket by means of a B40 cone. Distilled water could be circulated round the solution cell from an external water bath with a circotherm pump giving a temperature control of ± 0.07°C in the cell. A trapped pocket of air above the outlet tube was expelled by means of a fine polythene tube secured below the B40 joint extending into the outlet tube. The solution cell was closed with a rubber bung containing orifices for the inlet and outlet of nitrogen and for a spiral mini stirrer.

The voltage developed by the oscillator anode current across a resistor R2 was measured on a Honeywell Brown Electronik recording potentiometer (No. 153 x 16- (VBH)-11-111-118). It had a full scale deflection time of 1/4 second and a range of 0-10mV. The chart drive speed (2 inches per minute) was checked with an accurate stop-watch. A Solartron (model SRS151A) constant voltage power supply provided the
300 volts high tension voltage for the oscillator, while a heavy duty 6V accumulator provided the continuous, steady, 1.3 amps required for the valve filaments.

This battery was recharged after every 12 hours use.

The frequency of the oscillator could be varied from 15 to 20 Mc/s. The optimum resonant frequency for which the anode current was a minimum was obtained at about 18.5 Mc/s. The oscillator current at this frequency was about 20 ma rising to 45 ma when oscillations were completely damped out.

To reduce strong capacitance effects, the apparatus was housed in an earthed cage, on earthed copper sheets, protected from mechanical vibrations and draughts in a thermostatted room at 25°C.

Operating Procedure

The oscillator and recorder were switched on at least three hours before use. The capacitance dials C1, C2 and C3 were adjusted in turn until minimum oscillator anode current was obtained (m2 = 20 ma). The resistances R9 and R10 of the balancing circuit (which produced a current in opposition to the oscillator current so that the ammeter M1 always recorded the difference between them) were adjusted to give zero at M1.
fig. 9 OSCILLATOR CIRCUIT DIAGRAM

R1 40k
C3 100 pf
T1 301
Clq
C1
C10
C11
C5
C6 = 0.01 pf
L2
L1 4-5 turns thick Cu wire.
C2
100 pf
C4
C5
6C5
R8 180A
R9 1.5k
R3 5k
R10 5k
C8
C9
R7 50k
R6 0-1k
R5 200Ω
S2
S3
S4
S5
S6
R4 1k
S1
-300V
M2 μA
Recorder
+ -
fig. 10 BLOCK DIAGRAM OF HIGH FREQUENCY APPARATUS

Balancing circuit

Ayrton shunt

Recorder

Power supply

Oscillator

Constant temperature bath
fig. 11 SOLUTION CELL.

Nitrogen

B₄O
cone+ socket

solution cell.

mini-stirrer.

from thermostat bath.
Calibration of Syringes

A 2ml. and 5ml. syringe were calibrated as before (p. 80)

Volume delivered ex 2ml. syringe = 2.01ml. (mean of 10 determinations)

Volume delivered ex 5ml. syringe = 5.00ml. (mean of 10 determinations)

Linear response of the instrument

It was shown by Saadi that the oscillator anode current rose to a maximum and then decreased with further increase in electrolyte concentration. He showed that the oscillator responds to the conductance of the electrolyte in a manner related to its equivalent conductance by

\[ \delta = M/100C \]

where \( C \) = a cell constant
\( \delta \) = the conductance
\( M \) = molarity

The response of the instrument was tested by injecting successive 2ml samples from a calibrated syringe to stirred conductivity water contained in the cell under nitrogen and noting the successive rises in recorder reading. The response of the chart recorder was found to be linear over the range 0.003 to 0.01N sodium hydroxide. The calibration curve (p. 109) is given. One cell of medium internal diameter (1 inch) having optimum dimensions
Fig. 2: Oscillator Calibration Curve.
for the reactant concentrations used, was chosen and used throughout the kinetic work. The response to change in dielectric constant of the medium was tested by injecting successive 10ml. samples of dioxan into conductivity water (100ml.). Negligible change in the anode current was observed and hence the oscillator was insensitive to changes in dielectric constant over a wide range. The mixing-time for the spiral stirrer used was tested by injecting permanganate solution (2ml.) into water (100ml.) in the cell. Very rapid mixing was seen to occur.

**Kinetics of hydrolysis**

**Preparation of solutions**

Aqueous solution were prepared from conductivity water (conductivity $<10^{-6}$ mhos) obtained by passing distilled water down a mixed bed ion exchange column (containing Permutit Biodeminrolit) and boiling out as before (p. 52). Preliminary experiments showed that reactant concentrations 0.006N in base and 0.003N in ester at 25°C gave half lives which could be conveniently followed by this technique. To this requirement, the ester (3.06m.mole) was dissolved in water (20ml.) and thermostatted at 25°C. Alkali reactants
were prepared as before, by appropriate dilution of the prestandardised concentrated solution to 0.00612N. 100ml aliquots were required per run. Carbon dioxide was carefully excluded in the preparation of all the basic solutions.

Procedure for run

The base (100ml.) was pipetted into the cell under nitrogen, the stirrer started, and the solution allowed to come to temperature equilibrium. The span and zero controls were adjusted so that the total conductance change for complete reaction could occupy maximum chart width. The chart drive was switched on and, when the instrument had stabilised, i.e. a vertical line was produced by the recorder, the ester solution (2.01ml.) was injected into the cell from a calibrated syringe. A displacement of the recorder line was produced as the conducting half ester solution was added after which the recorder traced out the change of conductance of the reactants with time. The line stabilised about 50 seconds after injection. For an infinity reading, ten times the half life was allowed ( \( > 99.9\% \) reaction). It was found that, for the sodium hydroxide runs (half life approx. 200secs.), to attain the infinity reading, the apparatus
had to be left running for 35 minutes. This was unsatisfactory since the oscillator current drift, as reproduced by the recorder, was appreciable after about twenty minutes. To eliminate this error, a better technique was devised whereby excess KHP solution (5ml. 0.184N) was injected after about 6 minutes, so stopping the reaction. Aliquots (25ml.) of the solution were then withdrawn and back titrated against standard sodium hydroxide (0.026N).

From these measurements the per cent reaction at the point of injection of quench solution was found; from this, the change in recorder reading corresponding to 100% reaction was determined.

Method of calculation

As the oxalate anion reacts with hydroxide ion thus:

\[
C_2H_5O_2CCO_2^- + OH^- \rightarrow 5_2CCO_2^- + C_2H_5OH
\]

and the hydroxide ion is always in excess, the total change in recorder reading at time \( t \) is proportional to the decrease in concentration of hydroxyl ions in time \( t \) for the linear range of response considered. Also the total drop for 100% reaction is proportional to the initial ester concentration \( b \). Denoting the total drop as \( 1_0 - 1_\infty \) and
the drop in time $t$ as $l_o - l_t$

then $x = \frac{b(l_o - l_t)}{(l_o - l_\infty)}$

The value of $l_o$ was obtained from the charts by linearly extrapolating back from about 50 seconds when the recorder had stabilised, to the time of injection of the ester solution.

A computer programme (p. 123) was used to calculate values of $x$ (as in the numerical calculation) and then by substitution in the normal second order rate equation, values of $kt$ were computed. The graphical data obtained by plotting $kt$ vs time were analysed as for the other ester runs. Again the monomeric alkali gave straight line plots of second order kinetics and the PVAH plots were curved. A worked example of an arrested NaOH plot is given, and of a non arrested PVAH plot.
Sodium Hydroxide Run (Arrested) (Rate plot p.117)

Run No. 13 OX8NAOH7KHP3

Wt ester in 20ml. 0.4808g.
Vol ester delivered 2.01ml.
Purity factor 99.55
Equivalent 156.2

Wt KHP in 50ml. 1.6746g.
Vol delivered (quench) 5.00ml.
Back titre normality 0.02501
Volume back titre 3.20ml.

\[ [a] = 0.005999 \text{ mole l}^{-1} \]
\[ [b] = \frac{0.4808 \times 2.01 \times 1000 \times 99.55}{100 \times 156.2 \times 20 \times 102.01} = 0.003019 \text{ mole l}^{-1} \]

P/C reaction = 65.82 at point of injection

Drop on chart = 11.0 units, i.e. 100% drop = 16.7 units
\[ = i_0 - i_\infty \]
<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Drop ( l_0 - l_t )</th>
<th>( x \times 10^4 )</th>
<th>(-x \times 10^3 )</th>
<th>(-x \times 10^3 )</th>
<th>( k t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.9</td>
<td>3.435</td>
<td>5.656</td>
<td>2.676</td>
<td>20.74</td>
</tr>
<tr>
<td>60</td>
<td>2.1</td>
<td>3.797</td>
<td>5.620</td>
<td>2.640</td>
<td>23.16</td>
</tr>
<tr>
<td>70</td>
<td>2.7</td>
<td>4.882</td>
<td>5.511</td>
<td>2.531</td>
<td>30.70</td>
</tr>
<tr>
<td>80</td>
<td>2.9</td>
<td>5.243</td>
<td>5.475</td>
<td>2.495</td>
<td>33.32</td>
</tr>
<tr>
<td>90</td>
<td>3.8</td>
<td>6.870</td>
<td>5.312</td>
<td>2.332</td>
<td>45.82</td>
</tr>
<tr>
<td>100</td>
<td>4.0</td>
<td>7.232</td>
<td>5.276</td>
<td>2.296</td>
<td>48.78</td>
</tr>
<tr>
<td>110</td>
<td>4.8</td>
<td>8.678</td>
<td>5.132</td>
<td>2.151</td>
<td>61.28</td>
</tr>
<tr>
<td>120</td>
<td>5.2</td>
<td>9.401</td>
<td>5.059</td>
<td>2.079</td>
<td>67.99</td>
</tr>
<tr>
<td>130</td>
<td>5.7</td>
<td>10.305</td>
<td>4.969</td>
<td>1.989</td>
<td>76.86</td>
</tr>
<tr>
<td>140</td>
<td>6.2</td>
<td>11.209</td>
<td>4.878</td>
<td>1.898</td>
<td>86.31</td>
</tr>
<tr>
<td>150</td>
<td>6.5</td>
<td>11.752</td>
<td>4.824</td>
<td>1.844</td>
<td>92.28</td>
</tr>
<tr>
<td>160</td>
<td>6.9</td>
<td>12.475</td>
<td>4.752</td>
<td>1.772</td>
<td>100.64</td>
</tr>
<tr>
<td>170</td>
<td>7.0</td>
<td>12.656</td>
<td>4.734</td>
<td>1.754</td>
<td>102.80</td>
</tr>
<tr>
<td>180</td>
<td>7.5</td>
<td>13.960</td>
<td>4.643</td>
<td>1.663</td>
<td>114.09</td>
</tr>
<tr>
<td>190</td>
<td>8.0</td>
<td>14.464</td>
<td>4.553</td>
<td>1.573</td>
<td>126.24</td>
</tr>
<tr>
<td>200</td>
<td>8.4</td>
<td>15.187</td>
<td>4.481</td>
<td>1.501</td>
<td>136.66</td>
</tr>
<tr>
<td>210</td>
<td>8.5</td>
<td>15.368</td>
<td>4.463</td>
<td>1.482</td>
<td>139.38</td>
</tr>
</tbody>
</table>

From the gradient of the slope of the plot \( ktvt \) (p. 117)

\[
k = 46.5 \text{ mole}^{-1} \text{ in}^{-1}
\]
Oscillator Chart

RUN 130X8NAOH7KHP3
Fig. 14 RATE PLOT. RUN 130X8NAOH7KHP3
PVAH RUN NON ARRESTED

Run No. 2
Wt ester in 20ml. 0.4805g.
Vol ester delivered 2.01ml.
Purity factor 99.55
Equivalent 156.2

Drop on chart after 10 half lives is 75.0-44.5

\[ \Delta t = 0.5 = 1.0 - 1.0 \]

\[ \mathbf{a} = 0.005944 \]
\[ \mathbf{b} = 0.003017 \]

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Drop (I_o - I_t)</th>
<th>(x \times 10^4)</th>
<th>(a - x \times 10^3)</th>
<th>(b - x \times 10^3)</th>
<th>(\Delta t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>5.5</td>
<td>5.441</td>
<td>5.399</td>
<td>2.473</td>
<td>35.14</td>
</tr>
<tr>
<td>40</td>
<td>6.0</td>
<td>5.936</td>
<td>5.350</td>
<td>2.424</td>
<td>38.90</td>
</tr>
<tr>
<td>45</td>
<td>7.0</td>
<td>6.925</td>
<td>5.251</td>
<td>2.325</td>
<td>46.77</td>
</tr>
<tr>
<td>55</td>
<td>8.5</td>
<td>8.409</td>
<td>5.103</td>
<td>2.176</td>
<td>59.51</td>
</tr>
<tr>
<td>65</td>
<td>10.0</td>
<td>9.893</td>
<td>4.954</td>
<td>2.028</td>
<td>73.56</td>
</tr>
<tr>
<td>75</td>
<td>11.3</td>
<td>11.179</td>
<td>4.826</td>
<td>1.899</td>
<td>86.96</td>
</tr>
<tr>
<td>85</td>
<td>12.5</td>
<td>12.366</td>
<td>4.707</td>
<td>1.781</td>
<td>100.50</td>
</tr>
<tr>
<td>95</td>
<td>13.5</td>
<td>13.356</td>
<td>4.608</td>
<td>1.682</td>
<td>112.78</td>
</tr>
<tr>
<td>105</td>
<td>14.0</td>
<td>13.850</td>
<td>4.559</td>
<td>1.632</td>
<td>119.29</td>
</tr>
<tr>
<td>115</td>
<td>15.0</td>
<td>14.840</td>
<td>4.460</td>
<td>1.533</td>
<td>133.16</td>
</tr>
<tr>
<td>145</td>
<td>16.8</td>
<td>16.620</td>
<td>4.281</td>
<td>1.355</td>
<td>161.42</td>
</tr>
<tr>
<td>175</td>
<td>18.8</td>
<td>18.599</td>
<td>4.084</td>
<td>1.157</td>
<td>199.18</td>
</tr>
</tbody>
</table>
As described (p. 86) graphical analysis of the kt vs. time rate plot gave the following table:

<table>
<thead>
<tr>
<th>% reaction</th>
<th>$\theta^0$</th>
<th>$\tan \theta$</th>
<th>$k \text{ mole}^{-1}\text{min}^{-1} = \frac{\text{Tan } 0 \times 2 \times 60}{\text{Tan } 0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>37$\frac{1}{2}$</td>
<td>0.7673</td>
<td>92.07</td>
</tr>
<tr>
<td>25</td>
<td>36</td>
<td>0.7265</td>
<td>87.18</td>
</tr>
<tr>
<td>35</td>
<td>34$\frac{1}{2}$</td>
<td>0.6873</td>
<td>82.48</td>
</tr>
<tr>
<td>45</td>
<td>31$\frac{3}{4}$</td>
<td>0.6188</td>
<td>74.26</td>
</tr>
</tbody>
</table>

Extrapolation of the % reaction vs. k plot (p. 122) to 0% reaction gave

$$k_0 = 98.7 \text{ mole}^{-1}\text{min}^{-1}.$$
Oscillator Chart

Run 20X4PVAH1
Figure 7: Extrapolation of the instantaneous rate $k$ to O$_2$ reaction
Computer programme for the evaluation of the rate function (oxalate hydrolysis).

Data fed in on 5 hole punched tape as follows:-

n1 Number of points on graph.
v1 Weight of oxalate in 20ml.
v2 Volume ester solution delivered ex syringe.
v3 Normality of alkali (100ml)
v4 Total drop $i_0 - i_\infty$.
v5 Purity factor of ester.
v7 Values of $i_0 - i_t$.
v27 Values of times from chart corresponding to values of v7.

```
Jv1
n1=TAPE
v1=TAPE5
v7=TAPE*
v27=TAPE*
v50=v2+100.0
v51=v50x2
v52=v1/156.18
v53=v52xv5
v54=v52xv2
v55=v52/v51
v5=v3x100.0
v5=v3/v50
v54=v52/v4
v55=v3-v52
v55=1.0/v55
TEXT
D.F.C.LINNECAR
OXALATE ANION HYDROLYSIS
OXALATE(B) P/C PURITY ALKALI(A)
PRINTv52,3088
PRINTv5,4108
PRINTv3,4208
n2=7
n3=27
TEXT
X A-X B-X P/C REACTION TIME KT
```
no=0
1) v60=v54xv1n2
3) v61=v3-v60
v62=v52-v60
v63=v61/v62
v63=v63xv52
v63=v63/v3
v63=LOGv63
v63=v55xv63
+4, no=n1
v64=v60/v52
v64=v64x100.0
PRINTv60, 3048
PRINTv61, 4048
PRINTv62, 4043
PRINTv64, 4042
PRINTv63, 4063
PRINTv63, 4105
no=no+1
n2=n2+1
n3=n3+1
+1, no=n1
TEXT

P/C REACTION INTEGRAL

n2=0
2)v100=1
v101=n2
v102=v100+v101
v103=v102/20
v104=v103x100.0
v60=v52xv103
+3
4)PRINTv104, 3082
PRINTv63, 4205
n2=n2+1
+2, n2=19
STOP
(→0)
KINETIC RESULTS

KEY :

M: Potassium ethyl malonate
S: Potassium ethyl succinate
G: Potassium ethyl glutarate
A: Potassium ethyl adipate
NaOH: Sodium hydroxide
PVAH: Poly(vinylbenzyltriethylammonium hydroxide)
1,2: Ester concentration 0.0100N; alkali concentration 0.0200N
1,1: Ester concentration 0.0100N; alkali concentration 0.0100N
k: NaOH runs - second order rate-constant
   PVAH runs - instantaneous rate-constant or specific rate.
μ: Rate-constant in presence of PVAH
   Rate-constant in presence of NaOH under same reaction conditions
OX: Potassium ethyl oxalate; 0.00300N in ester; 0.00600N in alkali
KHP: Arrested reaction by injection of potassium hydrogen phthalate solution.

For actual values of temperatures, refer to p. 81.

Actual concentrations did not differ by more than 1% and 0.7% respectively from the concentrations of ester stated above.
### TABLE 4.

Values of $k$ in Aqueous Solution for NaOH Runs at 25°

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$k$ (1 mole$^{-1}$min$^{-1}$)</th>
<th>Mean $k$ (1 mole$^{-1}$min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1MNaOH 1,2</td>
<td>1.229</td>
<td>1.214 ± 0.62%</td>
</tr>
<tr>
<td>2MNaOH 1,2</td>
<td>1.206</td>
<td></td>
</tr>
<tr>
<td>3MNaOH 1,2</td>
<td>1.207</td>
<td></td>
</tr>
<tr>
<td>1SNaOH 1,2</td>
<td>2.025</td>
<td>1.998 ± 1.15%</td>
</tr>
<tr>
<td>2SNaOH 1,2</td>
<td>1.952</td>
<td></td>
</tr>
<tr>
<td>3SNaOH 1,2</td>
<td>2.017</td>
<td></td>
</tr>
<tr>
<td>1GNaOH 1,1</td>
<td>2.571</td>
<td>2.580 ± 0.30%</td>
</tr>
<tr>
<td>2GNaOH 1,1</td>
<td>2.573</td>
<td></td>
</tr>
<tr>
<td>3GNaOH 1,1</td>
<td>2.595</td>
<td></td>
</tr>
<tr>
<td>1ANaOH 1,1</td>
<td>2.450</td>
<td>2.443 ± 0.81%</td>
</tr>
<tr>
<td>2ANaOH 1,1</td>
<td>2.474</td>
<td></td>
</tr>
<tr>
<td>3ANaOH 1,1</td>
<td>2.406</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 5

Values of $k$ in Aqueous Solution for NaOH Runs at Different Temperatures for Potassium Ethyl Succinate

<table>
<thead>
<tr>
<th>Temp. Run No.</th>
<th>$k$ 1 mole$^{-1}$ min$^{-1}$</th>
<th>Mean $k$ 1 mole$^{-1}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 1SNaOH 1,2</td>
<td>1.399</td>
<td></td>
</tr>
<tr>
<td>2SNaOH 1,2</td>
<td>1.391</td>
<td></td>
</tr>
<tr>
<td>3SNaOH 1,2</td>
<td>1.375</td>
<td>1.388±0.51%</td>
</tr>
<tr>
<td>15 1SNaOH 1,2</td>
<td>0.948</td>
<td>0.968±1.06%</td>
</tr>
<tr>
<td>2SNaOH 1,2</td>
<td>0.975</td>
<td></td>
</tr>
<tr>
<td>3SNaOH 1,2</td>
<td>0.981</td>
<td></td>
</tr>
<tr>
<td>10 1SNaOH 1,2</td>
<td>0.676</td>
<td>0.671±0.40%</td>
</tr>
<tr>
<td>2SNaOH 1,2</td>
<td>0.668</td>
<td></td>
</tr>
<tr>
<td>3SNaOH 1,2</td>
<td>0.668</td>
<td></td>
</tr>
<tr>
<td>% Reaction</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>------------</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>4MPVVAH 1,2</td>
<td>3.81</td>
<td>3.73</td>
</tr>
<tr>
<td>5MPVVAH 1,2</td>
<td>4.40</td>
<td>4.37</td>
</tr>
<tr>
<td>6MPVVAH 1,2</td>
<td>4.01</td>
<td>4.00</td>
</tr>
<tr>
<td>Mean</td>
<td>4.07</td>
<td>4.03</td>
</tr>
<tr>
<td>4SPVVAH 1,2</td>
<td>10.38</td>
<td>10.18</td>
</tr>
<tr>
<td>5SPVVAH 1,2</td>
<td>9.40</td>
<td>9.33</td>
</tr>
<tr>
<td>6SPVVAH 1,2</td>
<td>12.74</td>
<td>12.13</td>
</tr>
<tr>
<td>Mean</td>
<td>10.84</td>
<td>10.55</td>
</tr>
<tr>
<td>4APVVAH 1,1</td>
<td>11.85</td>
<td>9.66</td>
</tr>
<tr>
<td>5APVVAH 1,1</td>
<td>15.50</td>
<td>12.13</td>
</tr>
<tr>
<td>6APVVAH 1,1</td>
<td>13.70</td>
<td>11.40</td>
</tr>
<tr>
<td>Mean</td>
<td>13.68</td>
<td>11.06</td>
</tr>
<tr>
<td>4APVVAH 1,1</td>
<td>11.60</td>
<td>9.66</td>
</tr>
<tr>
<td>5APVVAH 1,1</td>
<td>12.50</td>
<td>9.66</td>
</tr>
<tr>
<td>6APVVAH 1,1</td>
<td>13.00</td>
<td>12.27</td>
</tr>
<tr>
<td>Mean</td>
<td>12.37</td>
<td>9.86</td>
</tr>
</tbody>
</table>
TABLE 7

Values of $k$ ($\text{mole}^{-1} \text{min}^{-1}$) in Aqueous Solution for PVAH Runs at Different Temperatures for Potassium Ethyl Succinate at Increasing Values of Per Cent Reaction

<table>
<thead>
<tr>
<th>Temp $^\circ$C</th>
<th>% Reaction</th>
<th>Run No.</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4SPVAH 1,2</td>
<td></td>
<td>9.06</td>
<td>8.77</td>
<td>8.17</td>
<td>7.95</td>
<td>7.97</td>
<td>6.31</td>
<td>4.66</td>
</tr>
<tr>
<td></td>
<td>5SPVAH 1,2</td>
<td></td>
<td>8.36</td>
<td>8.24</td>
<td>8.03</td>
<td>7.54</td>
<td>6.68</td>
<td>6.07</td>
<td>4.88</td>
</tr>
<tr>
<td></td>
<td>6SPVAH 1,2</td>
<td></td>
<td>10.38</td>
<td>9.91</td>
<td>8.77</td>
<td>8.10</td>
<td>6.68</td>
<td>5.37</td>
<td>5.37</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td></td>
<td>9.27</td>
<td>8.97</td>
<td>8.32</td>
<td>7.86</td>
<td>6.81</td>
<td>5.92</td>
<td>4.97</td>
</tr>
<tr>
<td>15</td>
<td>4SPVAH 1,2</td>
<td></td>
<td>7.83</td>
<td>7.08</td>
<td>6.17</td>
<td>5.09</td>
<td>4.46</td>
<td>3.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5SPVAH 1,2</td>
<td></td>
<td>7.62</td>
<td>7.14</td>
<td>6.46</td>
<td>5.50</td>
<td>3.98</td>
<td>3.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6SPVAH 1,2</td>
<td></td>
<td>7.37</td>
<td>6.88</td>
<td>6.52</td>
<td>5.41</td>
<td>4.20</td>
<td>4.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td></td>
<td>7.61</td>
<td>7.03</td>
<td>6.38</td>
<td>5.33</td>
<td>4.21</td>
<td>3.91</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4SPVAH 1,2</td>
<td></td>
<td>4.38</td>
<td>4.16</td>
<td>3.85</td>
<td>3.41</td>
<td>3.15</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5SPVAH 1,2</td>
<td></td>
<td>3.92</td>
<td>3.85</td>
<td>3.71</td>
<td>3.60</td>
<td>3.29</td>
<td>2.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6SPVAH 1,2</td>
<td></td>
<td>3.93</td>
<td>3.89</td>
<td>3.81</td>
<td>3.57</td>
<td>2.90</td>
<td>2.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td></td>
<td>4.08</td>
<td>3.97</td>
<td>3.79</td>
<td>3.53</td>
<td>3.11</td>
<td>2.37</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 7

Values of $k$ (1 mole$^{-1}$ min$^{-1}$) in aqueous solution for PVAH runs at different temperatures for potassium ethyl succinate at increasing values of per cent reaction.

<table>
<thead>
<tr>
<th>Temp $^\circ$C</th>
<th>% Reaction Run No.</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4SPVAH 1,2</td>
<td>9.06</td>
<td>8.77</td>
<td>8.17</td>
<td>7.95</td>
<td>7.07</td>
<td>6.31</td>
<td>4.66</td>
</tr>
<tr>
<td></td>
<td>5SPVAH 1,2</td>
<td>8.36</td>
<td>8.24</td>
<td>8.03</td>
<td>7.54</td>
<td>6.68</td>
<td>6.07</td>
<td>4.88</td>
</tr>
<tr>
<td></td>
<td>6SPVAH 1,2</td>
<td>10.38</td>
<td>9.91</td>
<td>8.77</td>
<td>8.10</td>
<td>6.68</td>
<td>5.37</td>
<td>5.37</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>9.27</td>
<td>8.97</td>
<td>8.32</td>
<td>7.86</td>
<td>6.81</td>
<td>5.92</td>
<td>4.97</td>
</tr>
<tr>
<td>15</td>
<td>4SPVAH 1,2</td>
<td>7.83</td>
<td>7.08</td>
<td>6.17</td>
<td>5.09</td>
<td>4.46</td>
<td>3.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5SPVAH 1,2</td>
<td>7.62</td>
<td>7.14</td>
<td>6.46</td>
<td>5.50</td>
<td>3.98</td>
<td>3.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6SPVAH 1,2</td>
<td>7.37</td>
<td>6.88</td>
<td>6.52</td>
<td>5.41</td>
<td>4.20</td>
<td>4.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>7.61</td>
<td>7.03</td>
<td>6.38</td>
<td>5.33</td>
<td>4.21</td>
<td>3.91</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4SPVAH 1,2</td>
<td>4.38</td>
<td>4.16</td>
<td>3.85</td>
<td>3.41</td>
<td>3.14</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5SPVAH 1,2</td>
<td>3.92</td>
<td>3.85</td>
<td>3.71</td>
<td>3.60</td>
<td>3.29</td>
<td>2.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6SPVAH 1,2</td>
<td>3.93</td>
<td>3.89</td>
<td>3.81</td>
<td>3.57</td>
<td>2.90</td>
<td>2.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>4.08</td>
<td>3.97</td>
<td>3.79</td>
<td>3.53</td>
<td>3.11</td>
<td>2.37</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 8

Values of the Macromolecular Ratio \( \mu \) Derived From Tables 4 to 7

<table>
<thead>
<tr>
<th>% Reaction/ Ester Temp.</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1,2 25°</td>
<td>3.35</td>
<td>3.32</td>
<td>3.30</td>
<td>3.03</td>
<td>2.75</td>
<td>2.45</td>
<td>2.23</td>
<td>1.95</td>
</tr>
<tr>
<td>S1,2 25°</td>
<td>5.43</td>
<td>5.28</td>
<td>5.00</td>
<td>4.68</td>
<td>4.37</td>
<td>3.70</td>
<td>3.22</td>
<td>2.80</td>
</tr>
<tr>
<td>S1,2 20°</td>
<td>6.68</td>
<td>6.46</td>
<td>5.99</td>
<td>5.66</td>
<td>4.91</td>
<td>4.27</td>
<td>3.58</td>
<td>-</td>
</tr>
<tr>
<td>S1,2 15°</td>
<td>7.86</td>
<td>7.26</td>
<td>6.59</td>
<td>5.51</td>
<td>4.35</td>
<td>4.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S1,2 10°</td>
<td>6.08</td>
<td>5.92</td>
<td>5.65</td>
<td>5.26</td>
<td>4.63</td>
<td>3.53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G1,1 25°</td>
<td>5.30</td>
<td>4.29</td>
<td>3.37</td>
<td>2.38</td>
<td>2.13</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A1,1 25°</td>
<td>5.06</td>
<td>4.04</td>
<td>3.39</td>
<td>2.42</td>
<td>1.98</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

TABLE 9

Values of \( k \) in Aqueous Solution for Oxalate \( ^{14} \)NaOH runs at 25°

<table>
<thead>
<tr>
<th>Run No.</th>
<th>k ((\text{1 mole}^{-1}\text{ min}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Ox2 NaOH 2</td>
<td>42.8 (Non. arrested run)</td>
</tr>
<tr>
<td>2 Ox6 NaOH 4</td>
<td>48.9 &quot; &quot;</td>
</tr>
<tr>
<td>3 Ox7 NaOH 5 KHP 1</td>
<td>53.7 (Arrested run)</td>
</tr>
<tr>
<td>4 Ox7 NaOH 5 KHP 1</td>
<td>37.3 &quot; &quot;</td>
</tr>
<tr>
<td>5 Ox7 NaOH 5 KHP 1</td>
<td>50.2 &quot; &quot;</td>
</tr>
<tr>
<td>6 Ox8 NaOH 6 KHP 3</td>
<td>47.0 &quot; &quot;</td>
</tr>
<tr>
<td>7 Ox8 NaOH 7 KHP 3</td>
<td>46.5 &quot; &quot;</td>
</tr>
<tr>
<td>Mean</td>
<td>46.6 ± 4.31% ( \text{1 mole}^{-1}\text{ min}^{-1} )</td>
</tr>
</tbody>
</table>
TABLE 10

Values of $k$ (mole$^{-1}$ min$^{-1}$) and $\mu$ in Aqueous Solution for PVAH Runs at 25° At Increasing Values of % Reaction for the Oxalate Monoester

<table>
<thead>
<tr>
<th>% Reaction/Run</th>
<th>0</th>
<th>15</th>
<th>25</th>
<th>35</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Ox4 PVAH 1</td>
<td>77</td>
<td>73</td>
<td>69</td>
<td>66</td>
<td>62</td>
</tr>
<tr>
<td>2 Ox4 PVAH 1</td>
<td>99</td>
<td>92</td>
<td>87</td>
<td>82</td>
<td>74</td>
</tr>
<tr>
<td>3 Ox5 PVAH 2</td>
<td>86</td>
<td>79</td>
<td>75</td>
<td>68</td>
<td>61</td>
</tr>
<tr>
<td>4 Ox5 PVAH 2</td>
<td>125</td>
<td>120</td>
<td>116</td>
<td>116</td>
<td>110</td>
</tr>
<tr>
<td>5 Ox8 PVAH 3 KHP</td>
<td>120</td>
<td>118</td>
<td>116</td>
<td>109</td>
<td>108</td>
</tr>
<tr>
<td>Mean</td>
<td>101</td>
<td>96</td>
<td>93</td>
<td>88</td>
<td>83</td>
</tr>
<tr>
<td>$\mu$</td>
<td>2.17</td>
<td>2.06</td>
<td>2.00</td>
<td>1.89</td>
<td>1.78</td>
</tr>
</tbody>
</table>

TABLE 11

Values of the Standard Error S.E. for the PVAH Runs at 30% Reaction (35% for the Oxalate Ester) Expressed as a percentage of $k$

<table>
<thead>
<tr>
<th>Ester</th>
<th>Temp°</th>
<th>Standard Error(S.E.) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malonate</td>
<td>25</td>
<td>5.82</td>
</tr>
<tr>
<td>Succinate</td>
<td>25</td>
<td>2.50</td>
</tr>
<tr>
<td>Succinate</td>
<td>20</td>
<td>2.12</td>
</tr>
<tr>
<td>Succinate</td>
<td>15</td>
<td>2.36</td>
</tr>
<tr>
<td>Succinate</td>
<td>10</td>
<td>1.67</td>
</tr>
<tr>
<td>Glutarate</td>
<td>25</td>
<td>1.42</td>
</tr>
<tr>
<td>Adipate</td>
<td>25</td>
<td>2.86</td>
</tr>
<tr>
<td>Oxalate</td>
<td>25</td>
<td>11.76</td>
</tr>
</tbody>
</table>
The Precision of the Values of \( k \)

The reliability of the mean of a group is given in terms of a standard error (S.E.) \([82]\)

\[
\text{S.E.} = \pm \sqrt{\frac{\text{Variance}}{n}} = \pm \sqrt{\frac{\sum (x - \bar{x})^2}{n(n-1)}}
\]

The standard error of the determinations of \( k \) for the sodium hydroxide runs and the \( k_{30\%} \) values (\( k_{35\%} \) for oxalate) for the PVAH runs have been calculated and are expressed as a percentage of \( k \). The S.E. for PVAH runs are listed separately in Table 11.
THE ARRHENIUS PLOT

The Arrhenius activation energy \( E \) and the frequency factor \( A \) for the sodium hydroxide-succinate hydrolysis was derived from the data in Table 4/5 by means of the Arrhenius plot\(^{[83]} \) of \( \ln e^k \) against \( T^\circ K^{-1} \) (p.133, Fig.19). \( E \) for the reaction was obtained from the gradient of the straight line by the relation \( E = -R \times \text{gradient} \), where \( R \), the universal gas constant = 1.986 cal.deg\(^{-1}\)mole\(^{-1}\).

\( A \) was obtained from the relation \( \ln e^A = \ln e^k + \frac{E}{RT} \), \( T^\circ K^{-1} \) and \( \ln e^k \) being obtained from the abscissa and ordinate respectively of any convenient point on the Arrhenius plot (viz. \( 3.441 \times 10^{-3}, 0.150 \)).

The curved Arrhenius plot for the PVAH hydrolyses at successive 10% reaction values is shown in Figure 20 (p. 134).
Fig 19 Arrhenius plot for the hydrolysis of potassium ethyl succinate by NaOH.

\[
\begin{array}{|c|c|c|}
\hline
E & \text{cal mole}^{-1} & A_1 \text{mole}^{-1} \text{min}^{-1} \\
\hline
12.08 \times 10^3 & 1.40 \times 10^9 \\
\hline
\end{array}
\]
Each curve is successively displaced on the ordinate axis by 0.1 units. The values of $\ln k$ shown correspond to the 30% reaction curve.
DISCUSSION
Polystyrene and its chloromethylation

The polystyrene used in the present work had been prepared by radical chain polymerization at $80^\circ$ in xylene solution with benzoyl peroxide (1%) as initiator. It is now realised that conventional free radical-initiated polymers may contain stereoregular sequences in the polymer chain. The local description of a polymer chain is referred to as the microtacticity. Polymers in which there is a regularly alternating sequence of the steric configurations of successive carbon atoms along the vinyl chain are known as syndiotactic. Thus methyl methacrylate, polymerized under free radical initiation and particularly at low temperatures consists largely of the syndiotactic structure.\[87\]

The actual configuration of the polystyrene prepared does not affect any of the discussion which follows but, when constructing the molecular models, a syndiotactic structure was portrayed (p.178).

A unique property of high polymers is their ability, when in dilute solution to raise considerably the viscosity of the pure solvent. This leads to the most convenient method of characterizing a polymer and determining its
molecular weight. Viscosity measurements using an Ostwald U-tube viscometer gave a viscosity average molecular weight for the heterogeneous polymer of 26,100 (p. 44).

The introduction of chloromethyl groups into aromatic hydrocarbons is well known. It was first performed using paraformaldehyde and hydrogen chloride as the chloromethylating agent \[88\]. Since then dimethyl or diethyl formal and hydrochloric acid have been used. The third method involves the use of chloromethyl methyl or sym dichlorodimethyl ether. Generally the reaction is assisted by Lewis acids. Zinc chloride \[89\] has been used and stannic chloride \[90\] for more unreactive compounds. Glacial acetic acid \[91\] concentrated sulphuric acid \[92\] and mixtures of glacial acetic acid and syrupy phosphoric acid have also been used \[93\] as the catalyst.

In this work, chloromethylation of the polystyrene was effected by means of chloromethyl methyl ether in 16 fold excess in the presence of the Friedel-Crafts type catalyst zinc chloride. The method has the advantage that the polystyrene, the catalyst, and the product are soluble in the ether, even at the comparatively low temperature \(10^\circ\)
of reaction.

Chloromethylation can be accompanied by a side reaction in which diaryl methanes are produced. For polystyrene, monochloromethylation is represented.

\[
\begin{align*}
\text{H} + \text{ClCH}_2\text{OCH}_3 & \xrightarrow{\text{ZnCl}_2} \text{CH}_2\text{Cl} + \text{HOCH}_3 \\
\text{ClCH}_2\text{OCH}_3 + \text{ZnCl}_2 & \rightarrow \text{ClCH}_2 + [\text{CH}_3\text{O.ZnCl}_2]^-
\end{align*}
\]

The actual electrophilic reagents is presumably \( ^+\text{CH}_2\text{Cl} \), produced by \( \text{ClCH}_2\text{OCH}_3 + \text{ZnCl}_2 \rightarrow \text{ClCH}_2 + [\text{CH}_3\text{O.ZnCl}_2]^- \).

Alkylation which would result in cross-linking by methylene bridges, is represented by

\[
\begin{align*}
\text{H} + \text{CH}_2 & \rightarrow \text{CH}_2 + \text{ZnCl}_2 + \text{HCl} \\
\text{ZnCl}_3 & \rightarrow \text{ZnCl}_2 + \text{HCl}
\end{align*}
\]

as a result of the chloromethylated benzene rings competing with the ether for unreacted rings. The resulting polymer would be rendered insoluble by the cross-linkages before the reaction had progressed very far and high degrees of substitution would not be attainable. Under the reaction conditions used in this work, the polymer remained soluble throughout the reaction and since its logarithmic viscosity number (0.153) was close to that of the parent polystyrene (0.175), the evidence indicates there was no formation of
cross links. Analysis figures gave a mean chlorine content (23.13%) corresponding closely to that for complete chloromethylation (23.24%).

Jones[94] has prepared soluble products containing moderate proportions of chloromethylated polystyrene units by the use of zinc chloride as catalyst and a large excess of chloromethyl methyl ether as the solvent and chloromethylating agent. However, as the degree of chloromethylation increased and at the higher temperatures of reaction the tendency for cross-linking to occur became pronounced, so that the product was rendered insoluble with consequent gelation of the mixture. The reaction was stopped using aqueous dioxan.

Recently some Russian workers[95] have obtained non cross-linked chloromethylated polystyrenes of molecular weights from 5 to 250 thousand using a 7 fold excess of symdichlorodimethyl ether in the presence of zinc chloride for a reaction time of 12 hours at 60°. They found zinc chloride was a more efficient catalyst than stannous chloride.

Workers using stannic chloride as catalyst found that the secondary cross-linking reaction always occurred when complete monochloromethylation was approached (up to 22% Cl) for a reaction temperature between 25° and 58° and chloromethyl
methyl ether in 7 and 15 fold excesses.[96]

The chloromethylated polystyrene produced is believed to be mainly p substituted, as would typically result from an electrophilic attacking reagent, together with small proportions of o and m isomers.

This is supported by Alger's observation that depolymerization by dry distillation yielded mainly p chloromethyl styrene.[97]
Chloromethylated polystyrene and its quaternisation

The normal Menschutkin reaction between an organic halide and a tertiary amine was applied to the chloromethylated polystyrene to yield the water soluble polymeric quaternary ammonium chloride.

\[
\begin{align*}
\text{CH}_2\text{Cl} + \text{NR}_3 & \rightarrow \text{CH}_2\text{NR}_3\text{Cl} \\
\end{align*}
\]

The rate of reaction has been found to be higher in solvents of high dielectric constant, second order, and independent of the degree of polymerisation.

Some tendency for the quaternisation to be accompanied by cross-linking has been observed. In the present work, however, with quaternisation by triethylamine (1 fold excess) in dioxan:methanol solvent mixture at 60° for 48 hours, no such side reaction was found. The product in this work was a water soluble, hygroscopic, pale yellow powder with a chloride-ion content corresponding to 92.5% conversion of chloromethyl groups into quaternary ammonium groups.

Aminations of 90% have been obtained by other workers with a number of amines, trimethylamine, triethylamine, pyridine and triethanolamine using a 2 fold excess and reaction at 40° for 8 hours.
Use of ion exchange in the conversion of the polymeric quaternary ammonium chloride to the hydroxide.

Ion exchange resins may be regarded as insoluble acids or bases which also form insoluble salts. They consist of a cross-linked polymer network to which are attached ionized or ionizable groups. The resins swell in water but the cross links between the polymer chains prevent them from dissolving. This important fact distinguishes them from aqueous solutions of polyelectrolytes. The functional groups can ionize into counterions and fixed ions attached to the polymer chain. The counterions are mobile and can diffuse through the swollen resin and exchange with an ion of like charge in a surrounding solution. A particle of an ion exchange resin may thus be considered as two regions, one surrounded by a semipermeable membrane permeable to the exchangeable ion but impermeable to the ionic groups, the other, the rest of the solution accessible to the simple unfixed ions only. When in equilibrium with an electrolyte solution, the system therefore can be considered as a Donnan membrane equilibrium. Conditions of electroneutrality must apply on both sides of the membrane so that the first region will contain a high concentration
of the counterions to balance the charges on the polymeric network. Within the resin, the constrained polyions can be equivalent to a concentrated solution of 1 to 10N.\[^{100}\] In addition, in the presence of a simple electrolyte, simple ions of like charge to the fixed charges, accompanied by the equivalent amount of counterion can also enter the first region.

In general a resin in its A form (i.e., containing the anion $A$ for an anion exchange resin) can be converted into its B form even though it may have a greater affinity for $A$ by exposing the resin to a sufficiently large excess of electrolyte solution containing the anion $B$ and removing $A$ as it diffuses from the resin region. This is usually done by allowing a continual flow of the electrolyte containing $B$ down a column containing the resin.

The affinities of resins for different counterions is expressed in terms of a selectivity coefficient $K^B_A$ which applies to the system when in equilibrium. For the two univalent counterions $A$ and $B$

$$K^B_A = \frac{[B][A]}{[A][B]}$$

where $[\cdot]$ refers to the concentration of the counterions in the resin region and $[\cdot]$, in the external aqueous region.
respectively. When $k_B^e < 1$, the resin takes up $A$ more strongly than $B$.

Strongly basic anion exchange resins of the Amberlite IRA 401 type exhibit a greater affinity for chloride ions than for hydroxyl ions, the value of $k_{Cl^-}^{OH^-}$ being about 0.09 \[101\]. Thus the large volume of sodium hydroxide used to convert the resin to the hydroxide form from its chloride form is explained. Further, the conversion of a chloride solution to a hydroxide solution is favoured using the resin.

Polyelectrolytes in solution can be considered to consist of regions in which the counterions become concentrated near to it by the same Donnan membrane effect. In the presence of each other, the anion exchange resin and polymeric quaternary ammonium cation would compete for anions. The resin would have a stronger affinity for anions than the polycation due to the greater density of charge on the cross-linked network of the former. In the present work, poly(vinylbenzyltriethylammonium chloride) was completely converted into its hydroxide in aqueous solution by use of a molar ratio of resin to polyelectrolyte of 14.3:1. Jones\[94\] and Morley\[72\] using similar procedures obtained 96% and 98.5% conversions into the hydroxide.
Ester anions of a homologous series of aliphatic dicarboxylic acids: their hydrolysis and preparation.

(1) Mechanism of the basic hydrolysis of carboxylic esters.

Substitution reactions of carboxylic esters have been shown to be of two types involving acyl oxygen heterolysis and alkyl oxygen heterolysis. The two possible base catalysed bimolecular hydrolysis mechanisms are indicated below:

(a) Bimolecular acyl oxygen heterolysis $B_{AC}^2$

(b) Bimolecular alkyl oxygen heterolysis $B_{AL}^2$

The first mechanism (a) involves an initial reversible nucleophilic attack of the hydroxyl ion on the carbon atom of the carboxyl group which is followed by rapid reversible
elimination of alkoxyl ion \( R'0^- \). The reaction then goes to completion by the fast irreversible transfer of a proton from the carboxylic acid to the alkoxide ion. In this case, the carbonyl group, having a separation of charge would be liable to attack by the strong nucleophile \( -OH \). In the mechanism \( \text{BA}L^2 \), however, release of the \( R'0 \) bond electrons to the oxygen atom is required, which for simple aliphatic esters and ester anions is unlikely. Alkyl oxygen fission has been shown to be negligible for the simple ester \( n \) pentyl acetate by the use of the \( 0^{18} \) isotope.\(^{[102]} \) On hydrolysis in \( 0^{18} \) enriched aqueous alkali, the alcohol formed was found to be of normal isotopic constitution.

\[
\text{CH}_3\text{COO}{\overset{\text{18}}{\text{C}}}H_{11} + 0^{18}H \rightarrow \text{CH}_3\text{COO}^{18}H + C_5H_{11}OH.
\]

The oxygen must therefore have come from the original ester.

Unimolecular basic hydrolysis has been observed with alkyl-oxygen heterolysis in which a carbonium ion formed is stabilised by resonance, but since a unimolecular process is not relevant to this work, it will not be further considered.

From these considerations, and others, the \( \text{BA}L^2 \) mechanism is concluded to be the most common mechanism for the bimolecular basic hydrolysis of simple esters.
(2) **Ester anion hydrolysis**

The ester anion hydrolyses have an overall order of 2, being first order in ester and first order in base. The $B_{AC}^2$ mechanism shown below is operating in which the first slow step is the rate-determining step.

\[
\begin{align*}
\text{HO} & \xrightleftharpoons{\text{slow}} \text{C} - \text{OC}_2\text{H}_5 \xrightarrow{\text{fast}} \text{HO} - \text{C} \\
\text{CH}_2 \text{CH}_2 \text{CO}_2^- & \quad \text{CH}_2 \text{CH}_2 \text{CO}_2^- \\
\end{align*}
\]

(3) **Preparation**

The preparation of potassium ethyl esters by half saponification of the diethyl esters was first described by Walker. Using equimolar proportions of potassium hydroxide and diethyl succinate in alcohol, he obtained a crude product containing the dipotassium salt and some unreacted diester as impurities. After lengthy extraction procedures, he finally obtained the potassium ethyl monoester free from impurity.
No yields for the preparation were recorded. Walker found, however, that potassium ethyl adipate prepared and purified by the same method could not be obtained free from impurity. A number of workers since then have used this technique and variations on it with respect to temperatures, concentrations and times of reaction, obtaining products of varying purities.

Nielsen\textsuperscript{[76]} by a half saponification procedure using the diethyl ester in excess, and recrystallisation of the crude material from alcohol, was able to obtain the oxalate with no detectable dipotassium salt present. In the malonate monoester, however, there was a 1.5 mole\% of the dipotassium salt as impurity. Puente et al.\textsuperscript{[104]} using a similar procedure obtained the oxalate pure. Svirbely\textsuperscript{[105]} by fractional precipitation, using ether as precipitant and alcohol as solvent for the crude product, obtained the malonate 100\% 0.1\% pure. Westheimer et al.\textsuperscript{[106]} obtained the malonate with a saponification value of 100.6\% of the theoretical and the adipate 99.5\% pure. Hungarian workers\textsuperscript{[107]} obtained the malonate 100\% 0.15\% pure while Finnish workers\textsuperscript{[108]} obtained the oxalate and malonate 100\% 1\% pure. Hoppé and Prue\textsuperscript{[109]} using Nielsen's method obtained the oxalate and malonate 99\% pure and using Walker's method, the
adipate 99.6% pure. Indelli has obtained the oxalate pure,\cite{115} the malonate 98.9% pure\cite{110} and the adipate\cite{111} 99% pure. Purification was found to be very difficult.

We thus see that the purification procedures used were frequently not successful in removing all dipotassium salts. The final methods used in this work were a result of many experiments to determine the method giving optimum yields and high quality products.

The purity-factors, below, are the ratio:equivalent found/theoretical equivalent, expressed as a percentage.

Potassium ethyl esters of oxalic, malonic, succinic and glutaric acids were prepared in alcoholic media by the half saponification of the diethyl ester with potassium hydroxide. The oxalic and succinic esters, under the conditions used, were found to give directly products of sufficient purity, 99.55% and 100.0% purity factors respectively, (p. 74 ), for the kinetic work. For the malonic and glutaric ester preparations however, the dipotassium salt, the product of complete saponification was formed in too large amounts for use of the product in kinetic work.
For these esters, the crude product was treated with hydrochloric acid. The hydrogen ethyl esters, so released were then extracted and carefully titrated with potassium hydroxide to give almost pure products of 100.0 and 99.3% purity factors respectively.

Because of the excessive difficulty in purifying and obtaining in sufficient yield the potassium ethyl adipate by saponification, the monoester was prepared by another route.

Hydrogen ethyl adipate was prepared from a mixture of diethyl adipate, adipic acid, ethanol, and di-n-butyl ether as solvent, in the presence of hydrochloric acid as catalyst. Although the reactant concentrations used had no simple interrelationship,[112] the two steps probably involved are

1. Half-esterification of adipic acid by ethanol

\[
\begin{align*}
\text{CO}_2\text{H} & \quad \text{(CH}_2\text{)}_4 \quad H^+ & \quad \text{fast} & \quad \text{CO}_2\text{H} \quad \text{(CH}_2\text{)}_4 \quad C_2\text{H}_5\text{OH} \\
\text{H}_2\text{O} & \quad \text{C} & \quad \text{C}_2\text{H}_5 & \quad \delta^+ \quad \delta^+ \quad \text{C}_2\text{H}_5
\end{align*}
\]

2. Esterification of ethyl adipate by hydrochloric acid

\[
\begin{align*}
H^+ & \quad \text{(CH}_2\text{)}_4 \quad \text{fast} & \quad \text{CO}_2\text{H} \quad \text{(CH}_2\text{)}_4 \quad C_2\text{H}_5\text{OH} \\
\text{C} & \quad \text{OC}_2\text{H}_5 & \quad \text{C} & \quad + \text{H}_2\text{O}.
\end{align*}
\]
(2) Half hydrolysis of diethyl adipate (acid catalysed $A_{AC}^2$), by a mechanism similar to the reversal of the above process.

\[
\begin{array}{ccc}
CO_2\text{C}_2\text{H}_5 & H^+ & CO_2\text{C}_2\text{H}_5 \\
(\text{CH}_2)_4 & \rightleftharpoons & (\text{CH}_2)_4 + \text{EtOH} \\
\text{C} - \text{OC}_2\text{H}_5 & \downarrow & \text{C} - \text{OH} \\
0 & & 0
\end{array}
\]

Distillation of the hydrogen ethyl ester and titration with alcoholic potassium hydroxide gave potassium ethyl adipate of purity factor 100.0%.

(4) Kinetics of hydrolysis with sodium hydroxide.

In this work, for all esters, a plot of the second-order integral expression $\frac{1}{a-b} \ln \frac{b}{(a-b)}$ vs time gave good linear plots; the reaction was always followed to 40% and in some cases to 80% completion. The slopes of the straight lines gave the values of the rate constants $k$. Three or more runs were carried out for each condition (Table 4-10 p. 124); standard errors are recorded in Tables 4, 5, 9.

The hydrolysis of monoethyl esters of dicarboxylic acids effected by simple alkali have been carried out by a number of workers with different aims in view. The conditions
of concentration, ionic strength and dielectric constant that have been used, however, cover a wide range. Because of this, direct comparison of the results given in this work with that of others is not always possible. Values of \( k \) (converted to \( 1 \text{ mole}^{-1} \text{ min}^{-1} \) where necessary) from the literature, comparable with the present work on hydrolyses in salt-free aqueous solution, together with a statement of the monoester used and the temperature and concentration conditions, are summarised below (Table 12). All authors used titration techniques to follow the kinetics except where asterisked; for these cases conductivity methods were used.

Potassium ethyl monoesters are denoted by \( K \). The use of the sodium monoester is denoted by \( Na \).

The results in the literature, for the same concentrations, show some variance. An essential point is that these hydrolyses are reactions of the type subject to a positive salt effect: they are accelerated by increase in ionic strength. A variety of concentrations were used by the authors of Table 12, and almost all conducted the hydrolyses with equimolar concentrations of ester and alkali, whereas the majority of hydrolyses in the present work were effected with a 100% excess of alkali. In only once instance, the potassium ethyl adipate, are results recorded in the literature for the conditions used in the present work.
TABLE 12

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Ester</th>
<th>Alkali</th>
<th>Ester</th>
<th>Temp° in all cases close to the integral value given.</th>
<th>k exp. l.mole⁻¹min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>oxalate (K)</td>
<td>0.0008</td>
<td>0.0008</td>
<td>25</td>
<td>31.3</td>
</tr>
<tr>
<td>109</td>
<td>oxalate (K)</td>
<td>0.01</td>
<td>0.01</td>
<td>25</td>
<td>40.5</td>
</tr>
<tr>
<td>104</td>
<td>&quot; (K)*</td>
<td>0.025</td>
<td>0.025</td>
<td>25</td>
<td>22.3</td>
</tr>
<tr>
<td>108</td>
<td>&quot; (K)</td>
<td>0.01</td>
<td>0.01</td>
<td>25</td>
<td>38.4</td>
</tr>
<tr>
<td>108</td>
<td>&quot; (K)</td>
<td>0.025</td>
<td>0.025</td>
<td>25</td>
<td>40.1</td>
</tr>
<tr>
<td>This work.</td>
<td>*</td>
<td>0.006</td>
<td>0.003</td>
<td>25</td>
<td>46.6</td>
</tr>
<tr>
<td>109</td>
<td>malonate (K)</td>
<td>0.01</td>
<td>0.01</td>
<td>25</td>
<td>1.05</td>
</tr>
<tr>
<td>110</td>
<td>&quot; (K)</td>
<td>0.005</td>
<td>0.005</td>
<td>25</td>
<td>1.04</td>
</tr>
<tr>
<td>108</td>
<td>&quot; (K)</td>
<td>0.01</td>
<td>0.01</td>
<td>25</td>
<td>0.99</td>
</tr>
<tr>
<td>108</td>
<td>&quot; (K)</td>
<td>0.025</td>
<td>0.025</td>
<td>25</td>
<td>1.11</td>
</tr>
<tr>
<td>113</td>
<td>&quot; (Na) range 0.01-0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>25</td>
<td>1.08</td>
</tr>
<tr>
<td>This work.</td>
<td></td>
<td>0.02</td>
<td>0.01</td>
<td>25</td>
<td>1.214</td>
</tr>
<tr>
<td>114</td>
<td>succinate (Na)</td>
<td>0.01</td>
<td>0.01</td>
<td>25</td>
<td>1.06</td>
</tr>
<tr>
<td>113</td>
<td>&quot; (Na) range 0.01-0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>25</td>
<td>1.93</td>
</tr>
<tr>
<td>This work</td>
<td></td>
<td>0.02</td>
<td>0.01</td>
<td>25</td>
<td>1.998</td>
</tr>
<tr>
<td>113</td>
<td>succinate (Na)</td>
<td>0.009</td>
<td>0.045</td>
<td>20</td>
<td>1.25</td>
</tr>
<tr>
<td>113</td>
<td>&quot; (Na)</td>
<td>0.0019</td>
<td>0.0009</td>
<td>20</td>
<td>1.11</td>
</tr>
<tr>
<td>This work</td>
<td></td>
<td>0.02</td>
<td>0.01</td>
<td>20</td>
<td>1.388</td>
</tr>
<tr>
<td>109</td>
<td>adipate (K)</td>
<td>0.01</td>
<td>0.01</td>
<td>25</td>
<td>2.64</td>
</tr>
<tr>
<td>111</td>
<td>&quot; (K)</td>
<td>0.01</td>
<td>0.01</td>
<td>25</td>
<td>2.45</td>
</tr>
<tr>
<td>This work.</td>
<td></td>
<td>0.01</td>
<td>0.01</td>
<td>25</td>
<td>2.443</td>
</tr>
</tbody>
</table>
THE EFFECT OF THE POLYMERIC QUATERNARY AMMONIUM HYDROXIDE ON THE REACTION KINETICS

The velocities of hydrolyses of the five half esters studied, when conducted with sodium hydroxide and with poly(vinylbenzyltrimethylammonium hydroxide), cover a wide range and three separate concentration conditions were used in order that the kinetics of the reactions could be conveniently studied by the techniques adopted. Thus the malonate and succinate half esters were hydrolysed in the presence of a one-fold excess of alkali (0.02N in alkali), the glutarate and adipate were studied using equimolar concentrations of ester and alkali (0.01N respectively) while the oxalate was hydrolysed with a one-fold excess of alkali (0.006N) but at a considerably lower concentration. For each ester, however, exactly the same conditions were used for the monomeric and polymeric alkali so that the rate constants obtained were exactly comparable.

For all polymeric alkali runs, rate plots had the form of a smooth convex curve which indicated a decrease in rate as the reaction proceeded. Determination of the instantaneous rate constants by the manual
differentiation method described (p. 86) shows that the initial rate constants are in all cases higher by several fold for the polymer alkali, PVAH, than for sodium hydroxide (Tables 4-10).

A macromolecular ratio \( \mu \) defined as

\[
\mu = \frac{\text{rate constant in presence of PVAH}}{\text{rate constant in presence of NaOH under same concentration conditions}}
\]

was calculated for each 10% increment in reaction within the range of the experimental points obtained. This represents the fraction by which the reaction rate is increased due to the polycation. It is seen to be greatest at the beginning and to decrease as the reaction proceeds. Over the ranges of reaction conditions studied, the value of \( \mu \) is seen at all times to be greater than unity. We thus see that the polymeric nature of the macrocation of the polymeric strong base catalytically increases the rate of hydrolysis of these esters.
Discussion of the Polyelectrolyte Effect

The rate-determining step for these hydrolyses is the bimolecular collision of the ester anion and the hydroxyl ion as shown by the linear plots obtained using the monomeric alkali sodium hydroxide. The increase in reaction rate with the polymeric alkali can be interpreted in terms of the Morawetz model of a polyelectrolyte in which negatively charged species are retained in and near the polycation due to the high electrostatic potential existing in its neighbourhood (p. 16).

The negatively charged carboxyl group of the ester anions (viz. $\text{CO}_2^-$) together with the hydroxyl counterions also negatively charged, would be expected to be unevenly distributed throughout the solution because of their association with the polyanion domains. This association, at the same time, introduces the hydrolysable carbethoxy group ($\text{CO}_2\text{C}_2\text{H}_5$) into the same region. Because of this forced close proximity of the reacting species, an increased rate is to be expected.

A simple mathematical treatment can be used to illustrate this result quantitatively.
Consider a reaction $A + B \rightarrow \text{products}$ for which the rate equation has the form

$$\frac{d[A]}{dt} = -k[A][B]$$

where terms in square brackets are concentrations in moles litre$^{-1}$.

Let the total volume of solution, $V$ litres say, be arbitrarily divided into halves I and II, one containing the polyion domains, the other, the remainder of the solution.

Diagrammatically, the situation is represented below:

<table>
<thead>
<tr>
<th>Case</th>
<th>I $V/2$</th>
<th>II $V/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$[A][B]$</td>
<td>$[A][B]$</td>
</tr>
<tr>
<td>2</td>
<td>$[A][B+q]$</td>
<td>$[A][B-q]$</td>
</tr>
<tr>
<td>3</td>
<td>$[A+p][B+q]$</td>
<td>$[A-p][B-q]$</td>
</tr>
</tbody>
</table>

Case 1 represents the simple case for a monomeric alkali in which there is even distribution of reactants throughout the solution.

Case 2 represents the part of the solution of the polyelectrolyte which consists of the regions of polyions
with a high density of fixed charges creating the high
local electrostatic potentials, so that the counterions B
are powerfully attracted to them, while II represents the
remainder of the solution depleted in counterion
concentration.

Case 3 is that when both reactant A and the counterions
are unequally divided between the halves of the solution.
Electrostatic or hydrophobic interaction of the substrate
with the polion would cause this effect.

If $dA$ is the decrement (in moles per unit time) of
A, then for the total solution, the decrement is
\[ \frac{V}{2} (d[A]_I + d[A]_{II}) \]

Rate equations can now be formulated for cases 1, 2 and 3.

Case 1. \[ \frac{dA}{dt} = - k[A][B] \frac{V}{2} - k[A][B] \frac{V}{2} \]
Rate = \(- kV[A][B] \)

Case 2. \[ \frac{dA}{dt} = - k[A][B+q] \frac{V}{2} - k[A][B-q] \frac{V}{2} \]
Rate = \(- kV[A][B] \)

Case 3. \[ \frac{dA}{dt} = k[A+p][B+q] \frac{V}{2} - k[A-p][B-q] \frac{V}{2} \]
\[ = \frac{-kV}{2} [2AB+2pq] \]
Rate = \(- kV[AB+pq] \)
We thus have rate 3 $>$ rate 2 = rate 1.
We have shown that (provided any variations in activity coefficients of the counterion or substrate close to the polyion have been allowed for) a reaction in which the counterion participates as catalyst or reagent and the substrate or intermediate associates with the polyion is expected to undergo an increase in rate for reactions of first order in counterion and in substrate.

Of interest here are two other reactions studied by other workers using a similar PVAH reagent.

For the Cannizzaro reaction of glyoxal, effected by and second order in hydroxyl ion, the reaction mechanism proposed was one in which a rapid equilibrium reaction of a nucleophilic attack of the hydroxyl ion on a hydrated glyoxal unit took place, giving a negatively charged product (a) [117]

\[
\begin{align*}
\text{OH} & \quad \text{OH} - \quad \text{OH} - \quad \text{OH} - \quad \text{OH} - \\
\text{HO-C-H} & \quad \text{HO-C-H} \quad \text{O-C-H} \quad \text{O-C-H} \quad \text{OH} \\
\text{H-C-OH} & \quad \text{H-C-OH} \quad \text{H-C-OH} \quad \text{H-C-OH} \\
\text{OH} & \quad \text{OH} \quad \text{OH} \quad \text{OH}
\end{align*}
\]

The rate determining step is then a further reaction with a hydroxyl ion giving a divalent anion (b). This then rapidly irreversibly rearranges to give the reaction
product, the negatively charged anion of glycollic acid (c).

The rate determining step here involves the reaction of the hydroxyl ion and the reaction intermediate (a). Both are negatively charged and the increased reaction rate was partially attributed to their effective increased concentration in the neighbourhood of the polycation. In addition to this, however, a further effect was operating.

For this reaction, being second order in counterions, the rate equation is

\[
\frac{d[A]}{dt} = -k[A][B]^2
\]

Using the same notations as before, the following rate equations are formulated.

Case 4 Rate = \(-kV[A][B]^2\)
Case 5 Rate = \(-kV[A][B^2+q^2]\)
Case 6 Rate = \(-kV[A+p][B^2+q^2]\)

We now have rate 6/rate 4 = \(\frac{[A+p][B^2+q^2]}{[A][B]^2}\)
rate 5/rate 4 = \(\frac{[B^2+q^2]}{[B]^2}\)
rate 6/rate 5 = \(\frac{[A+p]}{[A]}\)

from which we see rate 6 \(\gg\) rate 5 \(\gg\) rate 4.

We see that non-uniformity in the spatial distribution of counter ions should not alter the rate of a reaction first order in these ions, i.e. rate 2 = rate 1, but should
for a reaction second order in these ions rate $5 >$ rate $4$. The 26 fold increase in rate at $25^\circ$ with PVAH for the glyoxal rearrangement was attributed to a combination of the "order-independent" effect which arises when both substrate and counterions associate with the polyion, and the effect which arises when the counterions participate as a second order term in the rate equation.

The catalytic decomposition of N nitrosotriacetonamine by PVAH shows further evidence for the preceding postulates. The reaction is first order in hydroxyl ion and it was found that the value of the ratio of the second order catalytic rate constants $\frac{k}{[\text{OH}^-]}$ for PVAH and sodium hydroxide was $1.72[66]$. This relatively small increase in rate was attributed to the increase in concentration in the region of the polycation of the hydroxyl counterion and of the N nitrosotriacetonamine molecules, which, having an appreciable dipole moment, interacted with the positive charge centres on the macrocation to a marked degree.

In the present investigation, the values of $\mu$ are seen to be in the range 2-8. These values are greater than that for the N nitrosotriacetonamine decomposition, where dipolar association with the polycation is postulated,
and less than the value for the glyoxal rearrangement for which the "second order" effect is present.

Recently work was done in this laboratory on the hydrolysis of simple uncharged aliphatic esters of monocarboxylic acids[115].

In the presence of the polycation, although the uneven distribution of counterions in the solution of the polyelectrolyte still holds, the uncharged esters would not be expected to experience any differential electrostatic effects and even distribution would result. It was found that the values of $\mu$ for these simple aliphatic esters were in the range 0.7-1.1, that is, the rates of hydrolysis for these simple esters are little different from that in sodium hydroxide solution.

The electrically neutral molecules are inferred to interact only weakly with the polycation.

The relatively small departures of these rates from unity may be accounted for by two minor influences coming into operation. Should the simple ester be partially excluded from the regions round the polycation by a salting out effect, then, with the hydroxyl ion concentration enhanced in this region and diminished in the intervening
parts of the solution, the ester molecules are subjected to an effectively lower hydroxyl ion concentration, and a $\mu < 1$ would result. On the other hand, hydrophobic interaction of the esters with the aliphatic main chain and ethyl groups of the polyion could account for an increase in $\mu$ above unity. In view of the values of $\mu$ for simple esters, it is considered that salting out and hydrophobic association are only minor influences on the hydrolyses of the ester anions, where they tend to be masked by the electrostatic effects arising from the unit negative charge on the substrate. The potassium ethyl esters, further, are very soluble in water.

The relevance of the activity coefficients to the reaction rates

For a second order reaction between two ions A and B, the first stage in the reaction path will be for the two ions to come together to form an activated complex AB which will be transformed into the final products. According to the Bronsted-Bjerrum theory, the rate of the reaction will be governed by the concentration of the complex and this, in turn, will depend upon the original reactants with which it is assumed to be in reversible equilibrium.
For this reaction, the dissociation constant $K^x$ of the activated complex or transition state is now defined as

$$K^x = \frac{C^x}{C_{OH}^x C_E} \frac{Y^x}{Y_{OH}^x Y_E}$$

where $C^x$, $C_{OH}^x$, $C_E$, $Y^x$, $Y_{OH}^x$, and $Y_E$ are the concentrations and activity coefficients of the activated complex, hydroxyl ion and ester anion respectively. From this, the rate of reaction is given by

$$\frac{-dC}{dt} = k C_{OH} C_E = k^x C^x = k K^x C_{OH} C_E \frac{Y_{OH} Y_E}{Y^x} \ldots$$

where $k$ is the observed second order rate constant and $k^x$ is the rate constant for the decomposition of the activated complex into products. For dilute solution and in low molecular weight alkali, the term $\frac{Y_{OH} Y_E}{Y^x}$ approximates to unity, so that the effect of the activity coefficients on the reaction rate is not very marked. For polymeric alkali solutions, however, we know that the mean counterion activity coefficients are markedly lower than in the corresponding simple electrolyte solution (see p.21). This is not due to incomplete dissociation of the strong polyelectrolyte, but to the high electrostatic potential existing on the polyion binding the counterions to it.
Experimental measurements of the mean hydroxyl ion activity coefficients in aqueous solutions of the polymeric quaternary ammonium hydroxide were done by Morley[72] via pH measurements using a glass electrode and a cell with liquid junction. Subject to the unavoidable limitations of the method which assumed the polycation in the polymeric hydroxide solution does not influence the response of the glass electrode to pH and that the liquid junction potential is not altered for the cell containing a standard reference or the polyelectrolyte solution, the mean hydroxyl ion activity coefficients were found to be less than those for the corresponding sodium hydroxide solutions. His results are reproduced below for a temperature of 25°

Evidence that liquid junction potentials are small in dilute solutions of the polyelectrolytes has been provided by Mock[119] who measured the activity coefficients of sodium ions of sodium polystyrene sulphonate solutions by cryoscopic methods and compared them with values from emf measurements by Kagawa[23]. The agreement between them was satisfactory in view of the experimental difficulties in both measurements.
TABLE 13

Mean Value of $\gamma_1$ at 25° for the Hydroxyl Ion in PVAH and NaOH Solutions

<table>
<thead>
<tr>
<th>Concentration (molality)</th>
<th>NaOH</th>
<th>PVAH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0100</td>
<td>0.87</td>
<td>0.51</td>
</tr>
<tr>
<td>0.0050</td>
<td>0.89</td>
<td>0.55</td>
</tr>
</tbody>
</table>

The lack of information concerning the activity coefficients of the ester anion and the activated complex in the presence of the polymeric anions prevents evaluation of the $\frac{Y_{OH}Y_e}{Y_e}$ term. Consequently further development of the determination of the effect of the activity coefficient term on the reaction rate according to equation 2. is prevented. Another approach, however, is more fruitful.

Ø The PVAH solutions used were derived from a parent polystyrene of DP = 410 whereas the PVAH solutions used in this investigation were derived from polystyrene of DP = 251. But, in view of the fact that electrochemical properties have been found to be independent of the chain length (p.24)[31], these activity coefficients are considered to be applicable to the arguments that follow.
According to the Debye-Hückel theory, the mean activity coefficient of an ion in terms of the ionic strength is given, for dilute solutions by the relation

\[-\log_{10} \gamma_+ = \frac{Z_n^2 \alpha \sqrt{I}}{1 + \beta_a \sqrt{I}}\]  \hspace{1cm} (3)

where $Z_n$ is the charge on the ion,

$a_n$ is the distance of closest approach of another ion to the $n^{th}$ ion and $\alpha$ and $\beta$ are constants for a given solvent and temperature. This approximates to

\[-\log_{10} \gamma_+ = \frac{Z_n^2 \alpha \sqrt{I}}{\beta a_n \sqrt{I}}\]  \hspace{1cm} (3a)

when $\beta a_n \sqrt{I} \ll 1$.

Defining the rate constant $k_0$ as that for dilute solution when the activity coefficients are all unity we obtain from (2) and (3)

\[\log_{10} \frac{k}{k_0} = \ln \gamma_{OH} + \ln \gamma_E - \ln \gamma \] \hspace{1cm} (4)

Finally substituting (3a) in (4).

\[\log_{10} \frac{k}{k_0} = 2Z_n^2 \alpha \frac{\sqrt{I}}{\beta a_n} \] \hspace{1cm} (5)

Equation (5) is general and shows how the ionic strength acting through the activity coefficient affects the rate
of reaction. This effect is known as a primary salt effect.

The ionic strength, first defined by Lewis and Randall[120] is given by the relation

$$I = \frac{1}{2} \sum c_n Z_n^2$$

where $Z_n$ is the valency and $c_n$ the molality of all the ionic species present. For the reaction

$$\text{OH}^- + 5_2 C(CH_2)_n CO_2 C_2 H_5 \xrightleftharpoons{\text{Transition state}}^{2-}$$

where the charge of the complex is the algebraic sum of the charges $Z_{\text{OH}}$ and $Z_E$ of the reactants, values of the formal, average, ionic strength $I$ of the solution can be calculated by substituting the mean ionic activity coefficients for the hydroxyl ion ($Z_n = -1$) from Table 13 into equation 3a. The value of $\alpha = 0.5092$ used is that given by Manov et al[121] for water at $25^\circ C$. Caution is required in interpreting the exact meaning of the ionic strength values calculated when polyions are present, but assuming some general meaning to the values of $I$, ratios of $k$ to $k_0$ have been calculated from equation 5. (concentrations on the molal scale, moles per litre of solvent, have been equated with the molar scale expressed in moles per litre of solutions).

Now, since $k_0$, the rate constant at infinite dilution, is the same for the monomeric and polymeric alkalis,
the value of \( \frac{k_{PVAH}}{k_{NaOH}} \) can be found. The value \( \varepsilon \) gives the factor by which the reaction rate is increased by the ionic strength effect only (i.e. assuming uniformity in the distribution of the ester anions).

A table showing the calculated values of I, \( \frac{k}{k_o} \) and \( \varepsilon \) for NaOH and PVAH is given.

TABLE 14.

<table>
<thead>
<tr>
<th>Alkali</th>
<th>Concentration</th>
<th>I</th>
<th>( \frac{k}{k_o} )</th>
<th>( \varepsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAH</td>
<td>0.010</td>
<td>0.3297</td>
<td>3.843</td>
<td>2.91</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.010</td>
<td>0.01411</td>
<td>1.321</td>
<td></td>
</tr>
<tr>
<td>PVAH</td>
<td>0.005</td>
<td>0.2599</td>
<td>3.306</td>
<td>2.62</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.005</td>
<td>0.009576</td>
<td>1.263</td>
<td></td>
</tr>
</tbody>
</table>

The values of \( \varepsilon \) are 2.91 and 2.62 at alkali concentrations of 0.01 and 0.005N respectively. The values of \( \mu \), the experimental value of the macromolecular rate ratio, have a maximum value at 25° of 5.43, and at 15°, of 7.86, so although the values of \( \varepsilon \) cannot be vigorously adhered to in view of the many assumptions made, it is reasonable to assume that an effect other than this ionic strength effect is operating, namely the electrostatic migration of the ester anions into the counter
ion layer of the domain of the polycation as already described.

The variation of the reaction rate with time

All the rate plots for PVAH indicated a decrease in reaction rate as time increased. As the reaction proceeds, the negatively charged dianion of the dicarboxylic acid is formed. This, itself, will become electrostatically associated with the polycation. The net result will be the exclusion of some of the hydroxyl ions or ester anions from the polyion domains resulting in the less close proximity of the reacting species and a falling off in rate as the reaction proceeds. The effect is equivalent to poisoning the counterion layer with a divalent ion of the same charge as the counterion.

It has been theoretically calculated by Wall [122] that where bivalent and univalent counterions (at the same equivalent concentration, i.e. when the molarity of the univalent ion is twice that of the bivalent ion) compete for association with a polyion, the bivalent ions prove more effective. Thus this poisoning of the counterion layer is enhanced by the bivalent nature of the dianion formed as the product of reaction and the fall-off in rate
is greater than would be the case for a neutral or univalent reaction product.

Further evidence for the idea of the packing of the counter ion layer by dicarboxylate anions is provided by ionic strength considerations. In the reaction

$$\text{OH}^- + \text{O}_2\text{C(CH}_2\text{)}_n\text{CO}_2\text{C}_2\text{H}_5 \rightarrow \text{O}_2\text{C(CH}_2\text{)}_n\text{CO}^-$$

there is no change in ionic strength due to the polycation and the potassium ions but for the left hand side of the equation (assuming equimolar concentrations for simplicity and again equating molarities with molalities)

$$I = \frac{1}{2}[m(-1)^2 + m(-1)^2] = m$$

For the right hand side of the equation

$$I = \frac{1}{2}[m(-2)^2] = 2m$$

There is thus an increase in ionic strength as reaction proceeds which would accelerate reactions of the type shown where the reactants A and B have like charges, i.e. a positive salt effect.

The observed fall in rate must therefore arise from blocking out of some of the reacting species from the polycation domain by the dicarboxylate anions.

The reason for using a 1 fold excess of PVAH for the malonate and succinate esters was to reduce this packing
in of the counterion layer by ensuring that an excess of polyion was always present. Thus at 50% reaction, in this case, there still remain 75% of the original hydroxyl ions, and hence of the original structure of the polymeric alkali. For the equimolar case, however, at 50% reaction, 50% of the original hydroxyl ions have been consumed and the percentate drop in rate would be expected to be greater since there remain at this point a smaller percentage of "unadulterated" charge sites on the polycation. Experimental evidence for this is provided by the following figures.

Taking the drop in $k$ over the range 0-40% reaction as unity, i.e. $k_0 - k_{40\%} = 100\%$ change (since a 40%- value of $k$ is available for the 4 esters), the differences in the value of $k$ for the ranges $k_{0-10\%}$, $k_{0-20\%}$, $k_{0-30\%}$ and $k_{0-40\%}$ have been calculated, for the malonate and succinate, and the glutarate and adipate monoesters at 25°, as percentages of the drop ($k_{0} - k_{40\%}$).

\[
\text{i.e. } \% \text{ drop} = \frac{k_p - k_0}{k_{40\%} - k_0} \times 100 \text{ where } p = \% \text{ reaction.}
\]
TABLE 15.

<table>
<thead>
<tr>
<th>Ester/% reaction p.</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Malonate</td>
<td>5.5</td>
<td>8.2</td>
<td>53.4</td>
<td>100</td>
</tr>
<tr>
<td>2 Succinate</td>
<td>13.8</td>
<td>40.5</td>
<td>70.5</td>
<td>100</td>
</tr>
<tr>
<td>3 Glutorate</td>
<td>32.0</td>
<td>60.9</td>
<td>91.9</td>
<td>100</td>
</tr>
<tr>
<td>4 Adipate</td>
<td>33.3</td>
<td>54.4</td>
<td>85.7</td>
<td>100</td>
</tr>
</tbody>
</table>

The percentages in rows 3 and 4 in the table are seen to be greater for the same increment in per cent reaction than for rows 1 and 2, and hence for esters 3 and 4 the polycation sites are more effectively rendered inactive by attraction of the ester anion into the counterion layer than for the esters 1 and 2, in accordance with the greater excess of PVAH in 1 and 2.

The effect of increasing the chain length of the ester anion

Observation on p. 129 shows the value of the macromolecular ratio $\mu$ for the five ester anions at 0% reaction. Comparing the values of $\mu$ under identical
concentration conditions, we see that for the malonate and succinate esters $\mu_{\text{succinate}}$ is greater than $\mu_{\text{malonate}}$ and for the glutarate and adipate esters, $\mu_{\text{glutarate}}$ is slightly greater than $\mu_{\text{adipate}}$. One might have held the view that $\mu$ would be inversely proportioned to the chain length of the ester anion, the latter being envisaged as having the anionic "head" close to the polycation and the methylene-carbethoxy "tail" extended approximately at right-angles to the main chain axis; $\mu$ would then be smallest for the longest ester anion, in which the carbethoxy group was furthest from the polyion domain and in a lower differential counterion concentration. This view is obviously an oversimplification and implies too compact an idea of the counterion layer packing round the polyelectrolyte.

A number of theoretical treatments have been given to the distribution of the counterion layer about a polyion, some using as a basis for calculation a spherical model of the polyion and others a chain model. No quantitative theory has yet been developed, though, to account for both long and short range electrostatic interaction and for the apparent ion binding observed for polyelectrolytes.
A small section of the macrocation in the syndiotactic conformation was constructed from scale molecular models (Courtqulds: by C. Robinson) to illustrate the steric relationships of the charge centres along the poly vinyl chain.

The model was constructed so that, within the flexibility of the structure, the distances between the centres of charge were a maximum as would result in dilute aqueous solution from the mutual repulsion of the charges (p. 17).

The axes of successive benzyl groups were arranged at 100° to each other since visually, this was the angle giving the largest separation of charge centres. As a result the charge groups were seen to space themselves in a spiral down the length of the polyvinyl backbone. The triethyl groups were seen to pack round the quaternary nitrogen with a result that the effective charge was diffused over a relatively large volume. Because of this, the possibility of specific site binding of the substrate with a charge centre is considered unlikely.

A further view held was that as the length of the ester anion was successively increased by one methylene
group, a critical length might be reached at which the spacing of the charge centres in the macrocation would correspond to the length of the ester anion.

Such a situation is represented below.

For this contingency, assuming the same reaction scheme as previously proposed (p. 147) we would expect the formation of the doubly charged intermediate (a) to be assisted by the two positive charge centres on the macroion, the whole entity being within the macroion domain with its increased counterion concentration; at the same time we would also expect some effect on its subsequent decomposition to products. Thus for an ester anion of this length, a striking effect on the overall reaction rate might reasonably be expected. Unfortunately, a study of the models showed that the longest ester anion used, the adipate ion, is not long enough to bridge the N-N charge centre distance ~13Å (see p. 182) so no experimental evidence for the operation of this effect can be offered.
In fact, no marked relationship of the chain length of the ester anion to values of $\mu$ is apparent.

Photographs of the scale models of the poly(vinyl-benzyltrimethylammonium) macrocation together with two ester anions, the oxalate and adipate, are included to show the relative sizes and spatial distribution of the reacting entities. Two hydroxyl ions (non solvated) are also shown.

Three complete units of the chain are shown, in which it is evident that the positively charged quaternary nitrogen atom is surrounded and shielded by the three triethyl groups.

A further six incomplete benzyl units are shown attached to the poly vinyl backbone giving an indication of the overall shape and steric relationships within the molecule.

The domain of the macro-ion is defined as the cylindrical envelope encasing the whole chain and its covalently-attached side groups.

Photographs P1 and P2 show a side view of the model with the oxalate and adipate anions within and near to the domain of the macroion. In this work in which the
parent polystyrene had D.P. = 251, the total length of the molecule (average) would be nearly 28 times the length of the portion of chain shown. Photographs P3 and P4 show the macrocation with the two anions viewed along the main chain axis. The spatial distribution of the charged groups (at $100^\circ$) is indicated together with the spiralling of the charge centres down the main chain. A scale is incorporated, each main division corresponding to 1Å. Measurements taken from the model with the angular specifications stated are shown in the next diagram.

Fig. 21.

View along the poly vinyl main chain. N1 is closest to viewer with the charge centres spiralling in an anticlockwise direction into the plane of the paper.

Mean distances (measured) from N apices:-

$N_1N_2 = 12.8\AA$; $N_2N_3 = 13.4\AA$; $N_3N_1 = 14.8\AA$

Length per unit charge, along main-chain axis $2.2\AA$
The effect of increase of temperature on the reaction rate

The temperature-studies were done on the succinate monoester since this gave the greatest value of $\mu$ and hence was considered to be the most valuable to study.

Figure 22 shows in a three dimensional plot the variation of the macromolecular ratio $\mu$ with per cent reaction $P$ and temperature $T$. Base plane axes are constructed at $30^\circ$. The figure is constructed from the results given in Table 8. In all cases, as previously described, $\mu$ decreases with increase in per cent reaction. The variation of $\mu$ with temperature is seen to be more complex. As the temperature is decreased from $25^\circ$ to $10^\circ$, the values of $\mu$ for $0\%$ reaction rise to a maximum at $15^\circ$ and then fall again.

The theoretical treatment by Wall[122] has shown that ion binding is not a sensitive function of temperature as far as electrostatic effects are concerned and since, in the dilute solutions used, the macro ion will be in its fully extended conformation (p. 18), the variation of $\mu$ with temperature can only be explained in terms of solvation effects occurring within the polyion domain in the aqueous solution.
Refractivity measurements on polyacrylic acids at various degrees of neutralisation indicate the presence of two regions of water around the polyanion, one more strongly bound than the other. It is considered that similar solvation regions round the PVAH polycation may exist and that the effects observed are a result of temperature changes on the different solvation regions. In the absence of physical data, no further development of this approach can be made.

A plot of \( \ln k \) v. \( \frac{1}{T^0_k} \) (p. 134), the plot for the integrated form of the Arrhenius equation for the PVAH hydrolysis of the succinate monoester, in contrast to the NaOH plot (p. 133) is not linear, but can be seen to be more steeply sloping at lower temperatures.

In this case we are obviously not measuring the simple activation energy \( E \) or the frequency factor \( A \) as for the monomeric alkali. In terms of the collision theory, \( A \) represents the number of collisions leading to a reaction which occur in unit time for unit concentration of reactants where as \( E \) is the energy which the molecule must absorb to become activated.
If we consider, for example, the rate constants for the four temperatures at 20% reaction and artificially calculate values for A and E assuming the three sections of the Arrhenius plot are linear, we obtain Table 16.

**TABLE 16.**

<table>
<thead>
<tr>
<th></th>
<th>PVAH</th>
<th>NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>E cal mole(^{-1})A 1 mole(^{-1}) min(^{-1})</td>
<td>E cal mole(^{-1})A 1 mole(^{-1}) min(^{-1})</td>
<td></td>
</tr>
<tr>
<td>25(^\circ)-20(^\circ)</td>
<td>6.354x10(^3)</td>
<td>4.531x10(^5)</td>
</tr>
<tr>
<td>20(^\circ)-15(^\circ)</td>
<td>8.911x10(^3)</td>
<td>3.662x10(^7)</td>
</tr>
<tr>
<td>15(^\circ)-10(^\circ)</td>
<td>16.909-10(^3)</td>
<td>12.08x10(^3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.40x10(^9)</td>
</tr>
</tbody>
</table>

These results would indicate the number of collisions leading to reaction increases with decreasing temperature, but that this is outweighed by the increase in activation energy which gives a decreasing specific rate constant with decreasing temperature. Also for the first two sections over the range 25\(^\circ\)-15\(^\circ\), the frequency factor is less than that for sodium hydroxide. This would be unexpected in view of the fact the average number of collisions per unit volume would be expected to be higher.
for PVAH where both reactants are increased in concentration round the polyions.

Because of these unexpected results for the derived activation parameters, reconsideration of the Arrhenius plot used is necessary.

The integrated form of the Arrhenius equation viz. \( k = Ae^{-E/RT} \) is derived from the differential form viz \( \frac{d \ln k}{dT} = \frac{E}{RT^2} \) (which has a firm statistical basis), on the assumption that the energy of activation does not vary with temperature.

In solution, two possible contributary terms to the total activation energy are (1) a term \( E_e \) from electrostatic interaction between the reactants and (2) a term \( E_s \) arising from the various degrees of solvation of the reactants and transition state.

For simple reactions, as for the sodium hydroxide-effected hydrolyses, probably the transition state is similar to the reactants so that the effect of temperature on their solvation is similar leading to a nearly constant \( E \).
For the hydrolyses effected by PVAH however in which an initially charged substrate is involved with a polyion in a medium (water) possibly exhibiting several layers about the polyion, $E_e$ and $E_s$ may well vary differently with temperature and it is reasonable to assume this accounts for the non linearity of the integrated Arrhenius plots.

It is thus not considered that there is any physical significance to the activation energies or frequency factors listed for the PVAH hydrolyses in Table 16 above.
PART II

THE EFFECT OF SOME WATER-SOLUBLE POLYMERS ON SOME CONDENSATION REACTIONS PERFORMED IN BUFFERED AQUEOUS SOLUTIONS

NOTE

The work to be described forming Part II of this thesis was carried out earlier than that of Part I, but further research on the lines adopted was not continued since the catalytic effects found were not large and the reaction situations encountered were complex.
INTRODUCTION

Maitland and his co-workers have published two papers\(^{[123,124]}\) containing a large number of organic condensation reactions performed in aqueous solution at room temperature. The purpose of their work was to extend general organic synthetic methods and in particular to broaden the field of synthesis under physiological conditions; with those views in mind, they used mild reagents, simple catalysts and a wide range of pH conditions. In order to allow simple detection and isolation of products, products of reaction were chosen having high crystallising power and sharp melting point.

In this work, a number of their reactions were selected for a kinetic investigation under more controlled temperature and concentration conditions. The pH values used being those found suitable by Maitland. The reactions were then conducted in the presence of three water soluble polymers with a view to investigating enhancements in the rate of reaction by macromolecular associative effects.
EXPERIMENTAL

All organic reagents used, which were of analytical grade, were redistilled or recrystallised using conventional Quickfit apparatus. Buffers were prepared from distilled water and AR grade B.D.H. reagents. The correct, approximate buffer strength solutions were prepared by the mixing of appropriate volumes of standard solutions of constituent reagents according to Britton[125]. The pH values of the buffers obtained were measured on a pH meter (E.I.L. Model 23A with glass and calomel electrodes) and finally standardised by accurate titration of one of the reagents to the required pH.

In the text are recorded the final pH values used together with the strength of each constituent reagent.

Preliminary Condensation Experiments

Seven experiments were performed; they were carried out in duplicate or triplicate, and a summary is given. Reactants were dissolved in an appropriate volume of buffer, mixed, and allowed to condense at room temperature in stoppered flasks for a certain time. In cases where an oil
was found which could not be made to solidify, a portion was withdrawn, cooled in solid carbon dioxide and scratched and the solid formed used to seed the other flasks (<0.001g.) In all runs the solid was filtered off at the pump, washed with water, dried over calcium chloride for 24 hours and weighed. The pH of the filtrate was checked and found to be within 0.5pH units of the buffer unless otherwise stated. The melting point of the product of each run was taken. Where an oil was formed, the melting point of the crystalline material was taken and not that of the solidified oil which, in most cases, melted over a further 2° range of temperature.

(1) Aniline (1.86g. bp 184-185° nD 25 1.5815) in buffer (150ml. N NaOH-N KH₂PO₄ pH 8.0) was added to acrylonitrile (1.06g. bp 74-78°) in buffer (50ml.). An oil was formed after 7 days

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>20</th>
<th>22</th>
<th>mp. 50-51°</th>
</tr>
</thead>
<tbody>
<tr>
<td>% yield</td>
<td>52</td>
<td>48</td>
<td></td>
</tr>
</tbody>
</table>

2 cyanoethylaniline

(2) Acrylonitrile (2.08g.) in buffer (40ml.) N NaOH-N KH₂PO₄ pH 10.7) added to methyl acetoacetate (2.32g. bp. 67-68° at 16mm. nD 25 1.4152) in buffer (10ml.). Final pH of filtrate was 7.5
methyl-αα di(2 cyanoethyl)acetoacetate.

(3) Thiourea (0.38g. recrystallised from 96% Ethanol mp. 170°) in buffer (10ml N NaOH-N KH₂PO₄ pH 5.6) added to N ethyl maleimide (0.63g. mp. 32°) in buffer (40ml.)

\[\begin{array}{c|cc|c}
\text{Time (days)} & 1 & 2 & \text{mp. 196-198°} \\
\% yield & 54 & 46 & \\
\end{array}\]

N ethyl α(2-imino-4-oxo-thiazolidin-5-yl)acetamide.

(4) Benzylamine (1.07g. bp. 184° nD 1.5402) in water (43ml.) added to acetonyl acetone (1.14g.) in water (11ml.). Buffer (150ml 0.2N NaOH-0.2N KH₂PO₄ pH 11.05) was added. Flasks were stored in the dark.

\[\begin{array}{c|cc|c}
\text{Time (days)} & 2 & 7 & \text{mp. 40-42°} \\
\% yield & 41 & 62 & \\
\end{array}\]

1-benzyl -2,5-dimethyl pyrrole

(5) Acetonyl acetone (4.56g. bp.190-192° nD 1.4228) in water (45ml) added to aniline (0.93g.) in water (109ml.) then pH was adjusted from 6.9 to 5.0 with acetic acid (10ml. 1.03N) finally buffer (49ml.) N NaO₂C₃H₇-N CH₃CO₂H pH 5.0 added giving an opalescent solution. Flasks were stored in the dark.
Product was a brown waxy solid sensitive to aerial oxidation.

2,5-dimethyl-1-phenyl pyrrole

\[
\text{mp} \quad 43-44 \quad 43-44 \quad 46-47^\circ
\]

(6) Acetyl acetone (1.00g.) was added to furfural (0.96g. bp. 160-161° \( n_D^{25} 1.5207 \)) in buffer (20ml \( \text{NaO}_2\text{CH}_3 \)-\( \text{N CH}_3\text{CO}_2\text{H} \) pH 5.0). A yellow oil was formed.

\[
\begin{array}{c|ccc}
\text{Time (days)} & 7 & 8 & 9 \\
\% \text{ yield} & 68 & 71 & 75 \\
\end{array}
\]

2-acetyl-1-\( \alpha \)-furyl-but-1-en-3-one

\[
\text{mp.} \quad 56-58 \quad 57-61 \quad 57-59^\circ
\]

(7) Diethyl acetone dicarboxylate (2.02g. bp. 140-143° at 13-15mm. \( n_D^{25} 1.4401 \)) in buffer (180ml \( \text{KH}_2\text{PO}_4 \)-\( \text{NaOH} \) pH 7.5) added to acetyl acetone (1.00g.) in buffer (20ml.). Oil was formed.

\[
\begin{array}{c|cc}
\text{Time (days)} & 2 & 6 \\
\% \text{ yield} & 64 & 82 \\
\end{array}
\]

diethyl-2-hydroxy-4,6dimethyl isophthalate

**Selection of condensation reactions**

Since yields were to be obtained gravimetrically in order to be suitable for the proposed investigation, the condensation reactions needed to have the following characteristics:
the condensation reactions needed to have the following characteristics:-

(1) Good yield gradations with time, with complete reaction time of at least 1 day.

(2) Products giving consistent melting points.
With these in mind, reactions 5, 6 and 7 were selected for a kinetic investigation.

(3) Buffer strengths and volumes of convenient values.

Recrystallisation of condensation products

In order to have pure specimens to seed the reaction mixtures, quantities of the crude products obtained above were purified by crystallisation to constant melting point. The following solvents for trial recrystallisations were used: hexane, heptane, cyclohexane, CHCl₃, CH₂Cl₂, CCl₄, CH₃CO₂C₂H₅, CH₃CO₂CH₃, ethanol, methanol.

2-acetyl-1-α-furyl-but-1-en-3-one

The pure compound was obtained as a pale yellow, crystalline powder by recrystallisation from boiling cyclohexane, mp. 57.5-58°.

Diethyl-2-hydroxy-4,6-dimethyl isophthalate

The pure compound was obtained as white plates from aqueous methanol, mp. 42.5-43.5°.
2,5 dimethyl-1-phenyl pyrrole

The brown compound was first distilled under reduced pressure in a semimicro apparatus bp. 72-76° 0.2mm. and then recrystallised from aqueous methanol by adding water dropwise to a boiling methanolic solution to incipient precipitation and allowing to cool.

The product was pale brown crystalline solid, mp. 49-49.5°.

Selection of polymers for the catalytic study

Three water-soluble polymers were selected two of which were available commercially and were not further purified poly(vinyl alcohol) and poly(vinylpyrrolidone). The third, poly(methacrylic acid) was prepared from the monomer.

Polymerisation of methacrylic acid

Methacrylic acid monomer was distilled under nitrogen at reduced pressure from a 100ml. flask through a water condenser with water circulating at 20°C to prevent solidification of the monomer (mp. 16°). The fraction having bp. 86° 60-61mm was collected.

The monomer (30g.) was poured via a drawn out funnel onto the initiator azobisisobutyronitrile (0.31g.) mp.98-98.5°,
recrystallised from aqueous acetone) contained in a long soft glass boiling tube (int. diameter 18mm.). The soft glass tube had been previously necked, allowing 40% space above the monomer. The tube was alternately evacuated to 75mm. and filled with nitrogen three times, and then rapidly but carefully sealed. The tube was shaken to dissolve the initiator in the monomer then heated for 2 hours in an oven at 70° when the monomer polymerised. When cool the tube was cooled in solid carbon dioxide, split open and the hard rod of white polymethacrylic acid withdrawn. It was ground to a white powder in a percussion mortar and stored over CaCl₂.

**Solubility measurements on the polymeric compounds in buffer solutions**

Two buffer solutions were prepared.

(1) pH 5.0 0.4N CH₃CO₂Na-0.4N CH₃CO₂H

(2) pH 7.5 0.4N KH₂PO₄-0.4N NaOH and trial solubility measurements performed. It was found \[ \frac{N}{20} \frac{N}{10} \frac{N}{5} \] solutions of each polymer based on the molecular weight of the repeating unit, could be prepared by vigorous shaking after heating to 60°. Poly(vinylpyrrolidone) was the most
soluble of the three. The pH of the resulting solutions were measured and found to be the same as that of the buffer except for polymethacrylic acid in pH 7.5 buffer. Here the final pH was found to be 5.8; this circumstance, therefore, applies to the experiments 3 below.

Time-Yield data for the three condensation reactions alone and in the presence of $\frac{N}{10}$ homogeneous polymer solutions.

Suitable, precalculated weights of reactants were dissolved in turn in preprepared buffer (400ml.) and the volume made up to 500ml. with buffer. Eight 50ml. portions were pipetted into preweighed centrifuge tubes of 100ml. capacity which served as reaction vessels. The tubes were sealed with rubber caps and set gently agitating on a rocking device immersed in a water thermostat bath kept at 25°C. The time between mixing the reactants and setting in the thermostat bath did not exceed 20 minutes and was hence negligible compared with the total reaction time. After 1 hour each tube was seeded with a small portion of pure product ($<0.001g$). This served as a nucleus around which the product formed and so prevented an oil from forming.
For runs in the presence of polymer, the calculated weight was dissolved in the buffer before dissolving the reactants.

After appropriate reaction times a tube was removed from the thermostat and the solid on the walls of the tube scratched into the liquid. The mixture was centrifuged (2,500 rpm.), the aqueous layer pipetted off and further 20ml. washing water added. The procedure was repeated and finally the product was dried under vacuum over CaCl$_2$ for 24 hours. The tube with product, was then weighed, and the weight of product obtained by difference. Seed weights were not taken into consideration since they were less than 0.001g.

**Polymer solutions**

Poly(vinyl alcohol) basic unit weight 44.05

\[ -\text{CH}_2\text{CH-} \uparrow \text{CH} \]

\[ \text{N} \text{I}_{10} \text{ solution given by } 2.202\text{g./500ml} \]

Poly(vinylpyrrolidone) basic unit weight 111.15

\[ -\text{CH}_2\text{CH-} \uparrow \text{N} \text{ CO} \text{CH}_2 \text{CH}_2 \]

\[ \text{N} \text{I}_{10} \text{ solution given by } 5.557\text{g./500ml} \]
Poly(methacrylic acid) basic unit weight 86.09

\[
\begin{align*}
\text{CH}_3 \\
\text{-CH}_2\text{-C-} \\
\text{CO}_2\text{H}
\end{align*}
\]

\( \frac{N}{10} \) solution given by 4.304 g./500 ml. solution

(1) Furfural-acetyl acetone yield-time runs

\[
\begin{align*}
\text{CHO} \\
\text{CHO} \\
+ \text{CH}_3\text{COCH}_2\text{COCH}_3 \rightarrow \text{CH}==\text{C(}\text{COCH}_3\text{)}_2
\end{align*}
\]

2-acetyl-1-α-furyl-but-1-en-3-one

Concentration of reactants used: \( \frac{\text{mole}}{10} /500 \text{ml} \)

Furfural (9.600 g.) and acetyl acetone (10.000 g.) were dissolved in buffer 0.4 N pH 5.0 CH\(_3\)CO\(_2\)Na-CH\(_3\)CO\(_2\)H, and the run commenced as described in presence of the three polymers and with no polymer. When no polymer was present, reseeding after 4 hours was necessary since the first seed dissolved.

**TABLE 1**

(a) No Polymer

<table>
<thead>
<tr>
<th>Hours</th>
<th>28</th>
<th>48</th>
<th>72</th>
<th>96</th>
<th>120</th>
<th>168</th>
<th>216</th>
<th>264</th>
<th>480</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (g.)</td>
<td>0.218</td>
<td>0.300</td>
<td>0.531</td>
<td>0.561</td>
<td>0.722</td>
<td>0.602</td>
<td>0.681</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>% yield</td>
<td>0</td>
<td>12</td>
<td>17</td>
<td>30</td>
<td>32</td>
<td>41</td>
<td>34</td>
<td>38</td>
<td>58</td>
</tr>
</tbody>
</table>
(b) **Poly(vinyl alcohol)**

<table>
<thead>
<tr>
<th>Hours</th>
<th>49</th>
<th>72</th>
<th>97</th>
<th>166</th>
<th>190</th>
<th>213</th>
<th>237</th>
<th>333</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (g.)</td>
<td>0.447</td>
<td>0.542</td>
<td>0.608</td>
<td>0.708</td>
<td>0.700</td>
<td>0.760</td>
<td>0.771</td>
<td></td>
</tr>
<tr>
<td>% yield</td>
<td>25</td>
<td>31</td>
<td>34</td>
<td>40</td>
<td>39</td>
<td>44</td>
<td>43</td>
<td>43</td>
</tr>
</tbody>
</table>

(c) **Poly(vinylpyrrole)**

<table>
<thead>
<tr>
<th>Hours</th>
<th>27</th>
<th>47</th>
<th>71</th>
<th>143</th>
<th>167</th>
<th>191</th>
<th>215</th>
<th>243</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (g.)</td>
<td>0.177</td>
<td>0.421</td>
<td>0.537</td>
<td>0.777</td>
<td>0.763</td>
<td>0.720</td>
<td>0.798</td>
<td>0.885</td>
</tr>
<tr>
<td>% yield</td>
<td>10</td>
<td>24</td>
<td>30</td>
<td>44</td>
<td>43</td>
<td>40</td>
<td>45</td>
<td>50</td>
</tr>
</tbody>
</table>

(d) **Poly(methacrylic acid)**

<table>
<thead>
<tr>
<th>Hours</th>
<th>47</th>
<th>71</th>
<th>167</th>
<th>191</th>
<th>217</th>
<th>240</th>
<th>266</th>
<th>335</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (g.)</td>
<td>0.381</td>
<td>0.510</td>
<td>0.777</td>
<td>0.771</td>
<td>0.723</td>
<td>0.856</td>
<td>0.818</td>
<td>0.858</td>
</tr>
<tr>
<td>% yield</td>
<td>21</td>
<td>29</td>
<td>44</td>
<td>43</td>
<td>41</td>
<td>48</td>
<td>46</td>
<td>48</td>
</tr>
</tbody>
</table>

Theoretical yield 1.78g. per tube.

The results are shown in figure 22, which shows the relationship of % yield with time.

(2) **Aniline-acetonyl acetone yield-time runs**

\[
\begin{align*}
\text{NH}_2 + \text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3 & \rightarrow \text{CH}_3\text{N} \quad 2,5\text{-dimethyl-1-phenyl pyrrole} \\
\end{align*}
\]

Concentration of reactants used: \( \frac{\text{mole}}{500\text{ml}} \).
Aniline (4.650g.) in water (136ml.) was added to acetonyl acetone (5.700g.) in water (56ml.), then acetic acid 1N was added to pH 5.0, and finally buffer (0.2N pH 5.0 CH₃CO₂Na-CH₃CO₂H) was added to 500ml. The general procedure was repeated.

It was found the organic solid 'crept' onto the outside of the tube when under vacuum <20mm so the desiccator was not evacuated below this pressure. A melting point of the white solid adhering to the outside of the tube confirmed it to be the pyrrole. The crystals inside the tube were brown, however, as in the preliminary experiments.

### TABLE 2

(a) No Polymer

<table>
<thead>
<tr>
<th>Hours</th>
<th>Yield (g.)</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>0.118</td>
<td>14</td>
</tr>
<tr>
<td>72</td>
<td>0.237</td>
<td>28</td>
</tr>
<tr>
<td>120</td>
<td>0.320</td>
<td>37</td>
</tr>
<tr>
<td>144</td>
<td>0.336</td>
<td>39</td>
</tr>
<tr>
<td>168</td>
<td>0.368</td>
<td>43</td>
</tr>
<tr>
<td>192</td>
<td>0.394</td>
<td>46</td>
</tr>
<tr>
<td>215</td>
<td>0.418</td>
<td>49</td>
</tr>
<tr>
<td>287</td>
<td>0.459</td>
<td>54</td>
</tr>
</tbody>
</table>

(b) Poly(vinyl alcohol)

<table>
<thead>
<tr>
<th>Hours</th>
<th>Yield (g.)</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>0.117</td>
<td>14</td>
</tr>
<tr>
<td>42</td>
<td>0.189</td>
<td>22</td>
</tr>
<tr>
<td>65</td>
<td>0.277</td>
<td>32</td>
</tr>
<tr>
<td>98</td>
<td>0.383</td>
<td>45</td>
</tr>
<tr>
<td>168</td>
<td>0.413</td>
<td>48</td>
</tr>
<tr>
<td>190</td>
<td>0.431</td>
<td>50</td>
</tr>
<tr>
<td>216</td>
<td>0.555</td>
<td>65</td>
</tr>
<tr>
<td>262</td>
<td>0.686</td>
<td>80</td>
</tr>
</tbody>
</table>
(c) Poly(vinylpyrrolidone)

<table>
<thead>
<tr>
<th>Hours</th>
<th>26</th>
<th>93</th>
<th>101</th>
<th>117</th>
<th>143</th>
<th>165</th>
<th>198</th>
<th>259</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (g.)</td>
<td>0.091</td>
<td>0.240</td>
<td>0.232</td>
<td>0.258</td>
<td>0.291</td>
<td>0.358</td>
<td>0.478</td>
<td>0.470</td>
</tr>
<tr>
<td>% yields</td>
<td>11</td>
<td>28</td>
<td>27</td>
<td>30</td>
<td>34</td>
<td>45</td>
<td>56</td>
<td>55</td>
</tr>
</tbody>
</table>

(d) Poly(methacrylic acid)

<table>
<thead>
<tr>
<th>Hours</th>
<th>31</th>
<th>56</th>
<th>71</th>
<th>143</th>
<th>170</th>
<th>188</th>
<th>212</th>
<th>307</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (g.)</td>
<td>0.25</td>
<td>0.331</td>
<td>0.412</td>
<td>0.513</td>
<td>0.519</td>
<td>0.537</td>
<td>0.566</td>
<td>0.514</td>
</tr>
<tr>
<td>% yield</td>
<td>29</td>
<td>39</td>
<td>48</td>
<td>60</td>
<td>61</td>
<td>63</td>
<td>66</td>
<td>60</td>
</tr>
</tbody>
</table>

Theoretical yield 0.855g. tube. Results are shown in figure 23.

(3) Diethyl acetone dicarboxylate – acetyl acetone yield-time runs

\[
\text{C}_2\text{H}_5\text{O}_2\text{C} + \text{CH}_3\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5 + \text{CH}_3\text{COCH}_2\text{COCH}_3
\]

Diethyl-2-hydroxy-4,6-dimethyl isophthalate

Concentration of reactants used: \(\frac{\text{mole}}{400}\) /500ml

Diethyl acetone dicarboxylate (5.050g.) and acetyl acetone (2.500g.) were dissolved in buffer (0.4N pH 7.5 KH₂PO₄-NaOH) and the mixture vigorously shaken and made up to 500ml.
The procedure for the run was adopted as before. The reaction times were much shorter for this run but since the time elapsing between removing the reaction tube from the thermostat and centrifuging off the product was not more than 10 minutes, it was not considered necessary to stop the reaction by freezing. Trial experiments showed this to be permissible.

**TABLE 3**

(a) **No Polymer**

<table>
<thead>
<tr>
<th>Hours</th>
<th>8</th>
<th>23</th>
<th>30</th>
<th>47</th>
<th>57</th>
<th>71</th>
<th>103</th>
<th>192</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (g.)</td>
<td>0.243</td>
<td>0.407</td>
<td>0.443</td>
<td>0.505</td>
<td>0.518</td>
<td>0.509</td>
<td>0.521</td>
<td>0.530</td>
</tr>
<tr>
<td>% yield</td>
<td>37</td>
<td>61</td>
<td>67</td>
<td>76</td>
<td>78</td>
<td>77</td>
<td>78</td>
<td>80</td>
</tr>
</tbody>
</table>

(b) **Poly(vinylalcohol)**

<table>
<thead>
<tr>
<th>Hours</th>
<th>8</th>
<th>23</th>
<th>28</th>
<th>33</th>
<th>46</th>
<th>50</th>
<th>53</th>
<th>119</th>
<th>143</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (g.)</td>
<td>0</td>
<td>0.392</td>
<td>0.419</td>
<td>0.456</td>
<td>0.477</td>
<td>0.493</td>
<td>0.463</td>
<td>0.466</td>
<td>0.515</td>
</tr>
<tr>
<td>% yield</td>
<td>0</td>
<td>59</td>
<td>63</td>
<td>69</td>
<td>72</td>
<td>74</td>
<td>70</td>
<td>70</td>
<td>77</td>
</tr>
</tbody>
</table>

(c) **Poly(vinylpyrrolidone)**

<table>
<thead>
<tr>
<th>Hours</th>
<th>16</th>
<th>19</th>
<th>22</th>
<th>40</th>
<th>43</th>
<th>46</th>
<th>64</th>
<th>∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (g.)</td>
<td>0.374</td>
<td>0.453</td>
<td>0.432</td>
<td>0.450</td>
<td>0.474</td>
<td>0.479</td>
<td>0.490</td>
<td>0.523</td>
</tr>
<tr>
<td>% yield</td>
<td>56</td>
<td>68</td>
<td>65</td>
<td>68</td>
<td>71</td>
<td>72</td>
<td>74</td>
<td>79</td>
</tr>
</tbody>
</table>
TIME-YIELD GRAPHS

Fig. 22 Furfural-acetyl acetone condensations
Fig. 23 Aniline-acetonyl acetone condensations
Fig. 24 Diethylacetone dicarboxylate-acetyl acetone condensations.
Fig. 22 Furfural-acetyl acetone condensations. Time-yield plot.

Curves 2, 3, 4 have been drawn at 10, 20 and 30 units respectively above the ordinate values shown.

1. No polymer
2. poly(vinyl alcohol)
3. poly(vinylpyrrolidone)
4. poly(methacrylic acid)
fig. 23 Aniline-acetonyl acetone condensation.  
Time-yield plot.

1. No polymer.  
2. poly(vinyl alcohol).  
3. poly(vinyl pyrrolidone).  
4. poly(methacrylic acid).
fig. 24 Diethylacetone dicarboxylate-acetyl acetone condensations. Time-yield plot

1. No polymer
2. poly(vinylalcohol)
3. poly(viny1pyrrolidone)
4. poly(methacrylic acid)

For the sake of clarity, curves 2, 3, 4 have been drawn staggered at 10, 20 and 30 units respectively below the ordinate values shown.
(d) Poly(methacrylic acid)

<table>
<thead>
<tr>
<th>Hours</th>
<th>14</th>
<th>18</th>
<th>22</th>
<th>34</th>
<th>38</th>
<th>42</th>
<th>70</th>
<th>∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (g.)</td>
<td>0.365</td>
<td>0.401</td>
<td>0.430</td>
<td>0.470</td>
<td>0.478</td>
<td>0.478</td>
<td>0.507</td>
<td>0.553</td>
</tr>
<tr>
<td>% yield</td>
<td>55</td>
<td>60</td>
<td>65</td>
<td>71</td>
<td>72</td>
<td>72</td>
<td>76</td>
<td>83</td>
</tr>
</tbody>
</table>

Theoretical yield 0.665g per tube.

Only in run (a) was any product visible before 8 hours reaction time.

Results are shown in figure 24.

Discussion of catalytic effects looked for in the condensation reactions performed

It is well known that many organic reactions are catalysed by $\text{H}^+$ or $\text{OH}^-$ ion. The particular condensation reactions selected for study involving activated methylene groups were known to be pH dependent. The first, the condensation between furfural and acetyl acetone is known to occur in reasonable yields in the pH range 3.6-6.5, that is the acid pH values $[^{123}]$. The condensation between acetonyl acetone and aniline has similarly been shown to occur in the pH range 3.5-5.5 to give reasonable yield $[^{123}]$. Finally the condensation between acetyl acetone and diethyl acetone dicarboxylate is known to occur over
the pH range 5.6-9.2, the highest yield occurring in
the range pH 7.3-7.6\(^{124}\).

Specific mechanisms for the above reactions have
not been proposed, but generally, acid catalysed reactions
may be expressed by

\[
RCHO + H^+ \rightleftharpoons R^+CHOH \rightleftharpoons RCH(OH)CHR'COR'' + H^+ \\
\text{RCH} = \text{CR'COR''} + H_2O
\]

Similarly, base catalysed reactions may be expressed by

\[
B + CH_2R'COR'' \rightleftharpoons BH^+ + "CHR'COR" \\
RCHO + "CHR COR" \rightleftharpoons RCH CHR'COR'' \rightleftharpoons RCH(OH)CHR'COR'' + B \\
\text{RCH} = \text{CR'COR''} + H_2O.
\]

It was hoped that, by performing the condensation
reactions in buffered solutions in the presence of a
macromolecule, a difference in rate could be detected.

It has been demonstrated that polyelectrolytes
with acidic or basic groups on the main chain, exert in
solution, a catalytic effect on acid and base catalysed
reactions different from that of their low molecular weight
analogues (p. 30).

Thus in any reaction where the reactants can
associate in some way with the polion, an increase in rate
can be expected since the reactants are brought closer together. Furthermore, for reactions catalysed by the counterion, increases in rate can again be expected. Two of the three polymers selected did not have essentially acid or basic groups attached but it was still hoped that some catalytic effect would be exhibited by these by some associative effect. Thus a hydrophobic interaction was demonstrated by Sakurada in the hydrolysis of esters by polymeric sulphonic acids[68] (see p. 36).

Interpretation of time-yield graphs

(1) Furfural - acetyl acetone (Fig. 22).

Observation of the graph indicates that a small increase in rate occurs with the polymeric compounds but no one polymer can be said to be superior in this respect. By the addition of the 0.4N buffer, it is possible that additional catalytic effects are swamped out in the presence of the added electrolytes since more even distribution of the reactants throughout the solution may occur. Any electrostatic association of the reactants with the polyion giving rise to large catalytic effects would not be expected, but some associative effect may be operating.
The irregular array of the experimental points of the curve can only be explained in terms of an irregular course of crystallisation from the solution.

(2) The condensation between aniline and acetonyl acetone is known to be catalysed by $H^+$ and from the experimental results it can be seen that a definite acceleration in rate in the presence of poly(methacrylic acid) is indicated. If one of the reactants, most likely the aniline, becomes associated with the negatively charged carboxyl groups on the main chain, then, in terms of the explanation already given, the localised large concentration of counterion, i.e. $H^+$, causes the increase in rate of this hydrogen ion catalysed reaction.

Interpretation of the other curves is not so easy, however. Certainly the rate in the presence of poly(vinyl alcohol) increases considerably as the reaction time increases; this may be due to association of both of the reactants with the main chain.

No explanation is offered for the apparent sudden increase in rate at 180 hour reaction time for poly(vinyl alcohol).
(3) Curves of the acetyl acetone-diethyl acetonedicarboxylate condensation are more difficult to satisfactorily interpret for although a difference in rate is indicated using the three polymers, the effect is slight. The reaction is really too fast to follow by the gravimetric procedure used.

During the first 8 hours of reaction when no product was precipitated in the polymer runs, presumably the product was building up to precipitation point.
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