BASE- AND ACID-CATALYSIS

BY

ORGANIC MACROMOLECULES

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

by

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ABSTRACT

The strongly basic poly(vinylbenzyltriethylammonium hydroxide) has been prepared, as an aqueous solution, from chloromethylated polystyrene, and has been used as a catalyst for the decomposition of nitrosotriacetonamine in aqueous solution.

The first-order rate constants, determined by measurements of rates of nitrogen-evolution, observed in the presence of the polymeric hydroxide solution are higher than the corresponding values in the presence of sodium hydroxide and benzyltriethylammonium hydroxide (which are nearly identical) by a factor of 1.7 at a hydroxyl-ion concentration of 0.01N. A marked decrease in the rate constant of the polymeric hydroxide-catalysed reaction is produced by the addition of sodium chloride and of sodium sulphate, and also by the incorporation of 1,4-dioxan. Evaluation of the activation parameters shows that the higher catalytic efficiency of the polymeric hydroxide is reflected in a higher entropy of activation.

The products of the above decomposition have been investigated. Acetone, mesityl oxide, phorone, semiphorone and, probably, 2,6-dimethyl-1,5-heptadiene-4-one have been identified.
A mechanism has been proposed for the reaction, and the higher catalytic efficiency of the polymeric hydroxide has been attributed to an increase in the concentrations of both nitrosotriacetonamine molecules and hydroxyl ions in the regions of solution in and around the polymeric cations, under the influence of the electrostatic fields created by these poly-cations.

The rate constants of the isomerisation of cinchonine into cinchotoxine have been measured, with acetic acid and poly(methacrylic acid) as the catalysts. This investigation (commenced before the work described above) was discontinued because of the experimental difficulties encountered.
The investigations described in this thesis were conducted in the Organic Research Laboratories, recently named the "Joseph Kenyon Research Laboratories", of the Battersea College of Technology.

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Two reactions have been studied. The first, the hydroxyl-ion catalysed decomposition of 1-nitroso-2,2,6,6-tetramethyl-4-piperidone (nitrosotriacetonamine) into phorone, was investigated in solution with sodium hydroxide, benzyltriethylammonium hydroxide and a polymeric quaternary ammonium hydroxide, respectively, as catalysts. This investigation forms Part I of the thesis.

The second reaction, the isomerisation of cinchonine into cinchotoxine, which is catalysed by weak acids, was examined in aqueous 1,4-dioxan solutions, with acetic acid and poly(methacrylic acid), respectively, being used as catalysts. Owing to experimental difficulties, this latter investigation could not be brought to a satisfactory conclusion; it forms Part II of the thesis, but was carried out earlier than the work of Part I.
PART I

The Hydroxyl Ion-Catalysed Decomposition of

Nitrosotriacetonamine
INTRODUCTION
The Catalytic Decomposition of Nitrosotriacetonamine

The alkali-catalysed decomposition of nitrosotriacetonamine (1-nitroso-2,2,6,6-tetramethyl-4-piperidone) in aqueous alkali into phorone, water and nitrogen:

\[
\begin{array}{c}
\text{H}_2\text{C} \\
\text{Me}_2\text{C} \\
\text{N} \\
\text{NO} \\
\end{array}
\quad \text{CO} \\
\quad \text{CH}_2 \\
\quad \text{C} \quad \text{Me}_2 \\
\quad \rightarrow \quad \text{Me}_2\text{C} \\
\quad \quad \text{OH}^{-} \\
\quad \quad \text{H}_2\text{O} + \text{N}_2,
\end{array}
\]

was first described by Heintz [1] who used warm concentrated aqueous sodium or potassium hydroxide solutions to effect the conversion. The phorone was isolated, after extraction with ether, by fractional distillation and was purified by crystallisation. Clibbens and Francis [2] found that Heintz's method gave poor yields and that the phorone was accompanied by at least one other product. They were however able to achieve a nearly quantitative conversion into phorone in alcoholic solution at room temperature, with a small quantity of potassium ethoxide as catalyst. Even so, the presence of some impurity was observed.

Reaction Kinetics

The kinetics of the reaction have been investigated from
a number of aspects. Clibbens and Francis [2] and Francis and Geake [3] followed the reaction by measurement of the volume of nitrogen evolved, and established that in aqueous solution at temperatures in the region of 30° the rate showed first-order dependence on the substrate concentration for sodium hydroxide solutions of less than 0.05N. They further showed that, when the sodium hydroxide concentration was less than 0.05N, the rate also exhibited first-order dependence on the concentration of the hydroxyl ions, the observed first-order constant increasing linearly as the alkali concentration was increased. In fact, Clibbens and Francis [2] and Francis and Geake [3] calculated the hydroxyl ion "concentrations" from conductivity data, on the assumption that there was incomplete dissociation of the sodium hydroxide. However, for the dilute alkali solutions, equally good linearity exists in graphs of rate constant against sodium hydroxide concentration, and later workers have preferred the rate equation in which the rate constant is related to the total hydroxyl ion concentration arising from the complete dissociation of sodium hydroxide. For these reactions in dilute alkali "initial irregularities" in the rates of the evolution of nitrogen have been observed [2].

At concentrations of hydroxyl ions in excess of about 0.05N and less than 0.5N, Clibbens and Francis [2] and Francis
and Geake [3] found that the rate in aqueous solution, although relatively fast, ceased to conform to any simple order, the rate "constant" increasing throughout the reaction. The presence of ethanol caused this deviation from first-order behaviour to begin at lower concentrations of alkali, viz. about 0.03N [2].

Finally, these authors [2,3] observed that for hydroxyl-ion concentrations greater than 0.5N, in aqueous solution, the first-order dependence of the rate on substrate concentration was re-established and also that the first-order constants then decreased as the hydroxyl-ion concentration was increased. This decrease was sharp at first but levelled off until the rate constant attained a steady, small finite value at sodium hydroxide concentrations in excess of about 3.5N. Although the first-order relationship had re-emerged, it was noted [2] that there was always an initial stage during which the reaction was slow, the rate "constant" increasing until it attained its steady value.

Despite these changes in kinetic behaviour, the reaction was observed to proceed to completion at all hydroxyl-ion concentrations [2]. No reaction occurred in the absence of alkali.

Francis and Geake [3] demonstrated that the linear
variation of the first-order rate constant with hydroxyl-ion "concentration" was independent of the cation of the hydroxide which was used. In this case also the hydroxyl-ion "concentrations" were estimated from conductivity data, so that the increase of the first-order rate constant with the stoichiometric concentration of the alkali (i.e. with the hydroxyl-ion concentration from complete dissociation), although linear, varied slightly with different hydroxides. The differences, however, are very slight for hydroxyl-ion concentrations of less than 0.02N and it is clear that it is the hydroxyl ion and not its cation which is the catalytically active component of the hydroxides. The discrepancies between the stoichiometric alkali concentrations and the hydroxyl-ion "concentrations" deduced from conductivity measurements became more marked for the higher concentrations of alkali. Thus, 5.70N sodium hydroxide solution was thought to have a hydroxyl-ion concentration of 1.482N [3].

Francis, Geake and Roche [4] were able to obtain more accurate results for the rate constants by changing the volumetric method, which had been used previously to follow the evolution of nitrogen, to a manometric technique; the error was reduced from ca. 3% to ca. 0.7%. They also showed that the rate of reaction could be used for the determination of hydroxyl-ion concentrations up to 0.05N by utilising the first-
order dependence of the rate on hydroxyl-ion concentration. These concentrations again were those calculated from conductivity measurements.

Colvin [5] investigated the reaction rate in low concentrations of sodium hydroxide (less than 0.05N) taking the activities of the reactants into account, and concluded that the reaction was first-order with respect to the hydroxyl-ion activity rather than the hydroxyl-ion concentration.

Goodall and Lewis [6] extended their investigations into the regions of higher hydroxyl-ion concentrations, and demonstrated that the reaction rate, at alkali concentrations in excess of 0.5N, could be first-order with respect to the hydrogen-ion activity. They proposed that the nitrosotriacetonamine decomposition was composed of two consecutive reactions, one catalysed by hydroxyl ions and the other by hydrogen ions. It was considered that in dilute alkali solution, less than 0.05N, the hydrogen ion-catalysed reaction proceeded so rapidly, relative to the hydroxyl ion-catalysed step, that the latter was rate-controlling, while in more concentrated alkali, higher than 0.5N, the opposite situation arose and the slower hydrogen ion-catalysed reaction was then rate controlling. Goodall and Lewis [6] showed that the kinetic behaviour of the reaction in the intermediate range of alkali concentrations (0.05 to 0.5N), where no simple order
obtained, could be satisfactorily accounted for by the expression for two consecutive first-order reactions:

\[
\frac{a - x}{a} = \frac{k_1}{k_1 - k_2} \exp(-k_2 t) - \frac{k_2}{k_1 - k_2} \exp(-k_1 t),
\]

where \( k_1 \) and \( k_2 \) are the first-order constants for each of the component steps, \( a \) is the initial quantity of nitrosotriacetonamine and \( x \) is the quantity of nitrogen evolved after a time \( t \).

The justification for the use of activity terms in the rate equations does not appear to be fully established. However, the results of Goodall and Lewis [6] definitely demonstrate the existence in the nitrosotriacetonamine decomposition of two consecutive steps which appear to be dependent on the catalytic actions of hydroxyl and hydrogen ions respectively.

**Salt Effects**

Brönsted and King [7], using sodium chloride as the added salt, found a negative primary salt effect to be operative in the reaction. In 0.01N aqueous sodium hydroxide solution at 15° the rate was found to decrease by about 7% as the sodium chloride concentration was raised from zero to 0.1M. These authors [7] also observed secondary salt effects when weakly basic systems such as a piperidine–piperidinium chloride buffer solution were used as catalysts. Kilpatrick
[8] also conducted similar investigations.

The results of Brönsted and King [7] revealed a linear relationship between rate constant and ionic strength, and King and Marion [9] found that, for dilute sodium hydroxide solutions up to 0.05N, at 24.9°, the relationship was of the general form

$$k_2 = \frac{\text{observed rate constant}}{\text{alkali concentration}} = 1.209 + 0.479 \mu 1.\text{mole}^{-1}\text{min}^{-1},$$

where $\mu$, the ionic strength, was varied from 0.01 to 0.25 with sodium chloride. Such a salt effect is that expected to operate in a reaction between an ion and a neutral molecule [10], and is in contrast to that observed for two ionic reactants, when the logarithm of the rate constant bears a linear relationship to $\mu^2$ [11].

French [12] investigated the salt effects at 25° in 0.014N potassium hydroxide solution for higher ionic strengths, up to $\mu = 3$, and found that different uni-univalent salts depress the rate constant to different extents, the order of effectiveness in retarding the reaction being KI > LiCl > KBr > NaCl > KCl.

A decrease in the rate constant, for small concentrations of alkali, was also observed by Francis and Geake [3] when various sodium salts were included in the reaction mixture, but an increase in the rate constant occurred when the alkali concentration was higher, viz. 1N.
The Effect of Dielectric Constant on Reaction Rate

The effect of a change in the dielectric constant, $D$, of the solvent on the rate constant, $k$, was investigated by King and Lionetti [13], who used 1,4-dioxan to lower the dielectric constant of the aqueous solvent. They observed that $\log_{10} k$ varied only slightly with $D^{-1}$, at a given temperature, and did not exhibit the linearity expected from the simplified Laidler-Eyring equation [14]. King and Lionetti [13] also found that the entropy of activation, $\Delta S^\neq$, in an entirely aqueous solvent at $25^\circ C$ is $-12.4 \text{ cal.mole}^{-1}\text{deg.}^{-1}$, while in a medium containing 40% of 1,4-dioxan (v/v) it is $-1.1 \text{ cal.mole}^{-1}\text{deg.}^{-1}$. This effect was counterbalanced by a corresponding increase in the activation energy, to produce the observed insensitivity of $k$ towards $D$. 
Properties of Polyelectrolyte Solutions

Linear polymers containing ionic groups possess the ability to conduct electricity in solution in the same way as solutions of simple electrolytes. For this reason, the polymers are called polyelectrolytes.

The presence of these charged groups confers properties on a polyelectrolyte which distinguish it in many respects from its uncharged counterpart. These differences arise as a result of the strong electrostatic forces established by the charged groups.

The constraint imposed upon the ionic substituents by the fact that they are held covalently in the polymeric molecule results in the establishment of a high charge density in the macro-ion. In polyelectrolyte solutions, therefore, the electrostatic potential is high in the region occupied by the poly-ions and falls off as the distance from the poly-ions increases. This causes an uneven distribution to be imposed upon the counterions, which become more concentrated within, and near, the poly-ions. In a corresponding simple electrolyte solution the ions could be distributed more evenly throughout the medium to minimise the electrostatic repulsive forces between ions of like charge.

Another consequence of the presence of the charged
groups is a conformation of the poly-ion chain which differs appreciably from that of its uncharged analogue. The conformation of an uncharged flexible polymer chain is determined by the energetic interactions between polymer segments and the solvent molecules, and by relatively weak nearest-neighbour interactions of the groups on the chain. As a result of this, an uncharged flexible polymer chain usually adopts a randomly coiled conformation in solution, the tightness of the coiling depending upon the magnitude of these relatively weak interactions. In the case of poly-ions, however, the long-range mutual repulsions of the ionic groups, although partially screened by the counterions, cause the polymer chain to adopt a far more extended conformation in solution than it would have without the ionic substituents. In an alternative explanation for the expanded dimensions of poly-ions [15], which is in fact equivalent to the one just given, it is pointed out that since many of the counterions are retained, as if by a membrane, in the poly-ion domain, the osmotic pressure to which they give rise would cause the poly-ion to expand.

For polyelectrolyte solutions at high concentrations (and free from added simple electrolyte) the poly-ion domains occupy the whole volume of the solution, so that the counterions are confined completely to them. Dilution of the solution creates regions into which some of the counterions can escape.
However, as already mentioned, the net charges (or alternatively, the osmotic forces) produced in the poly-ion domains by the loss of these counterions cause the poly-ions to expand and re-occupy much of these newly-formed regions in the solution. Eventually, on continued dilution, the poly-ions reach the limiting extensions beyond which they cannot expand further. The escape of more counterions with further dilution increases the net charge on a poly-ion, but since the energy of the resulting additional repulsions cannot be used for the expansion of the poly-ion, this escape of counterions becomes progressively more difficult. It has been estimated [16] that a net poly-ion charge equivalent to about one electronic charge for ten repeating units in the chain would produce a nearly fully-extended configuration. A poly-ion with a high density of charged groups in the chain should therefore be nearly fully extended well before it has lost many of its associated counterions [15].

It has also been pointed out [15] that the addition of simple electrolyte would cause the difference between the counterion concentrations on the two sides of the 'membrane' to diminish, with the result that the tendency of counterions to diffuse out of the poly-ion region is suppressed. This, in turn, would lessen the effective charge of the poly-ion and cause the poly-ion to contract.
Osmotic Pressure

Measurements of the osmotic pressure ($\pi$) of polyelectrolyte solutions at different concentrations ($c$) provide evidence for the partial retention of counterions by poly-ions. Strauss and Fuoss [17] compared the values of $\pi/c$ for poly(4-vinylpyridine) and poly(4-vinyl-N-butylpyridinium bromide) in ethanol, the latter polyelectrolyte having been prepared from the former polymer. Values of $\pi/c$ for the polymer increased linearly with $c$, but for the polyelectrolyte these values were much higher and decreased as $c$ increased. This was attributed to the greater proportion of osmotically active entities in the more dilute polyelectrolyte solution, due to the escape of counterions from the poly-ion regions, the counterions associated with the poly-ion being osmotically inactive. The addition of 0.6N lithium bromide both to the polyelectrolyte solution and to the ethanol, on the two sides of the osmometer membrane, resulted in a variation of $\pi/c$ with $c$ which resembled that of the original poly(4-vinylpyridine). In the presence of the added bromide anions the counterions no longer tended to leave the regions occupied by the poly-ions. Therefore, after the automatic allowance for the contribution of the added electrolyte, the only osmotically active components in the solution were the poly-ion-counterion units, which produced an osmotic
pressure similar to that of the poly(4-vinylpyridine) at the same concentration. Theoretical treatments [18] also lead to the conclusion that the proportion of counterions held within or near a poly-ion will decrease on dilution of the solution.

**Counterion Association**

The powerful attraction exerted by a poly-ion on some of its counterions has been demonstrated experimentally by various techniques. Electrolytic transference studies on partially-neutralised poly(acrylic acid) solutions containing radio-active sodium counterions [19] revealed that a proportion of the counterions moved with the poly-anion towards the anode compartment. The fraction of the total number of sodium counterions associated with the poly-anion in this way increased as the degree of neutralisation was increased; at 25% neutralisation the fraction was about one-quarter and at 100% neutralisation it was about two-thirds. Similar results for the fractions of associated sodium counterions in this system have been obtained from steady-state diffusion studies [20] and refractivity measurements [21], respectively. The steady-state diffusion method, applied to poly(ethyleneimine hydrochloride) solutions with radioactive chloride counterions [22], showed that the fraction of chloride counterions associated with the poly-cation was about one-half.
It was also found [19] that the fraction of the total current carried by the poly-anions during electrolytic transfer in sodium polyacrylate solution, over a range of degree of neutralisation from 25 to 100%, was unexpectedly high and nearly constant at 0.4 to 0.5, thus indicating that the net charge on the poly-anions was high under these conditions. Further investigation of the system [23] revealed that the fraction of associated sodium ions decreased as the polymer concentration increased, at a constant degree of neutralisation. In this latter respect the behaviour of sodium polyacrylate solutions is contrary to that expected from the generally-held view (see p. 21) that dilution of a polyelectrolyte solution would cause a smaller proportion of the counterions to be retained in the regions of the poly-ions.

The rate of exchange of sodium counterions in polyacrylate solutions, measured by radio-active tracer techniques, indicated that there were two distinct rates: a fast exchange between the sodium ions outside of the poly-ion regions, and a slow exchange involving those inside the poly-ion regions [24].

A polarographic technique has been used [25] to estimate the fraction of free cadmium ions in aqueous cadmium polystyrene-sulphonate solutions. This fraction was obtained from the ratio of the diffusion current in the solution containing only
polyelectrolyte to that in an excess of supporting electrolyte. The results indicated that a large proportion of the cadmium counterions was retained in the poly-anion domains, over the concentration range investigated (9.8 x 10^{-5} to 1.9 x 10^{-2}equiv.l.^{-1}).

Cathers and Fuoss [26] found that the conductance of poly(4-vinyl-N-butylpyridinium bromide) solutions increased as the dielectric constant of the medium increased. This is attributed to the greater proportion of bromide counterions able to escape from the electrostatic influence of the poly-cations when the dielectric constant is high.

**Viscosity**

Evidence for the expansion of poly-ion dimensions on dilution of the polyelectrolyte solutions is obtained from measurements of reduced viscosities, $\frac{\eta_{sp}}{c}$, where $\eta_{sp}$ is the specific viscosity of the solution at a concentration $c$. When $c$ is about 1 g.dl.^{-1} the poly-ions are in contact with each other and not expanded to any large degree. The reduced viscosity is then about the same as those encountered for solutions of uncharged polymers. As the solution is diluted the values of the reduced viscosity increase and become very large as $c$ approaches zero. This large value reflects the expansion of the poly-ions which occurs as the solution is diluted.
empirical expression for the reduced viscosity in terms of the concentration has been formulated [27]. This is

$$\frac{\eta_{sp}}{c} = \frac{A}{1 + B\sqrt{c}}$$

where $A$ and $B$ are constants. The addition of simple electrolyte in sufficient excess to the polyelectrolyte solution completely suppresses the increase of reduced viscosity with dilution, and produces instead a linear increase of $\frac{\eta_{sp}}{c}$ with an increase in $c$, which behaviour resembles that of uncharged polymers (see p.167). This is readily explained in terms of the retention of counterions by the poly-ions on dilution, when simple electrolyte is present, since under these conditions the poly-ions would not expand appreciably.

**Activity Coefficients of Counterions**

The thermodynamic property of polyelectrolyte solutions which has received a considerable amount of experimental attention is the mean activity of the counterions. It is generally found that the mean counterion activity coefficient of a polyelectrolyte solution is markedly lower than the corresponding value in a simple electrolyte solution, and is independent of the degree of polymerisation [28,29]. Although no theoretical treatment exists to prove that the counterions retained near a
poly-ion by the high electrostatic potential have activity coefficients lower than those of the counterions further away from the poly-ion, it is generally accepted that this situation does exist [30] and that the observed low counterion activity coefficients in polyelectrolyte solutions result from it.

Kern[31] found that the activity coefficients of sodium ions, measured potentiometrically in aqueous sodium polyacrylate solutions, were lower than those in sodium butyrate solutions. The depressed activity coefficient of sodium ions was also observed in the presence of various poly-anions in solution by Nagasawa and Kagawa [28] who also found that the activity coefficient showed a marked dependence on the charge density of the poly-anion, the activity coefficient tending to zero as the charge density increased. Both Nagasawa and Kagawa [28] and Kern [31] found that the activity coefficients of sodium counterions in aqueous polyelectrolyte solutions decreased when the solutions were diluted. Such behaviour is in contrast to that expected, since dilution would normally cause a greater proportion of counterions to leave the poly-ion, with the result that the observed mean counterion activity coefficient should increase. An investigation of the activity coefficients of sodium counterions of linear poly-anions with different spacings of the charged groups along the chains
revealed [29] that when the spacing was less than a certain value the mean activity coefficient of the counterion was particularly low, and almost independent of the concentration. For larger spacings the activity coefficient was higher, and approached the values observed in simple electrolyte solutions. It was also found [29] that the increase in the reduced viscosity of the solutions with dilution was not accompanied by an increase in the mean activity coefficient of the sodium counterions. In this respect, polyelectrolyte solutions containing sodium counterions again show an unexpected behaviour, since the expansion of the poly-anions on dilution, as revealed by the increase in reduced viscosity, would be expected to result in an increase in the mean activity coefficient of the sodium ions, due to a smaller proportion of them being retained by the poly-ions.

The activity coefficients of silver counterions in silver carboxymethylcellulose solutions are low, and dilution results in the expected increase of the activity coefficient [32]. Potassium ions in solutions of potassium poly(p-styrenesulphonate) also possess the low activity coefficient of about 0.25 over a concentration range of about 0.02 to 0.36M [33]. The mean activity coefficients of anions in the presence of polycations in solution are also lower than the values in the corresponding simple electrolyte solutions. For example,
the chloride-ion activity coefficients in aqueous solutions of poly(ethyleneimine hydrochloride) are lower than those in solutions of the analogous low molecular weight salts, increasing from 0.298 to 0.562 as the polyelectrolyte molality is decreased from 1 m to 0.001 m [22].

Simultaneous measurements of the activity coefficients of counterions and by-ions in polyelectrolyte solutions [34,35] indicate that the activity coefficient of a by-ion is not depressed relative to the value in a corresponding simple electrolyte solution. This conclusion has been reiterated by Nagasawa and Rice [36] and Katchalsky and Alexandrowicz [37].

A simple additivity rule has been found to hold approximately for the activity of a univalent counterion in an aqueous solution containing a mixture of a polyelectrolyte and a simple electrolyte [35]. In this relationship, the observed counterion activity in the mixture is given by the sum of the activities of that ion in separate pure solutions of the two components, at the same concentrations as they had in the mixture. Thus, the mean activity coefficient, $\gamma_M$, of the univalent counterion M in a solution containing concentrations $c_p$ and $c_g$ equiv. l$^{-1}$ of the polyelectrolyte and simple electrolyte, respectively, is given approximately by:

"by-ion", "co-ion" or "nebenion" is the term applied to the ionic species with a charge of the same sign as the poly-ion.
where \( \gamma_M^{(P)} \) and \( \gamma_M^{(S)} \) are the activity coefficients of \( M \) in pure aqueous solutions of polyelectrolyte and simple electrolyte (at \( c_P \) and \( c_S \)) respectively. Similarly, the osmotic pressure of such a mixture is given approximately by the sum of the osmotic pressures of the corresponding solutions of the pure components [37].

The electrostatic nature of the force exerted by the poly-ion on its counterions has been demonstrated in aqueous solutions of poly(p-styrenesulphonic acid) [38]. This polyelectrolyte appears to be only partially dissociated in solution, but proton magnetic resonance studies revealed that all of the protons from the sulphonic acid groups were in an ionic state and in no way bound covalently to the sulphonate groups.

Summary

The observed properties of polyelectrolyte solutions, described above, together with theoretical treatments of the electrostatic potential around poly-ions [18, 39], have led to the view that a linear poly-ion in a solution free from simple electrolyte possesses an extended, coiled configuration, the extension increasing as the charge density of the poly-ion
increases and as the solution becomes more dilute. Poly-ions containing a high density of charged groups retain a high proportion of their counterions within the regions occupied by their extended, coiled structures. Even when the solution is very dilute and the tendency for the counterions to escape from the highly extended poly-ion is greater, an appreciable proportion of the counterions is still concentrated near the poly-ion. In the regions outside the volume occupied by the poly-ion, the counterion concentration is lower and continues to decrease as the distance from the poly-ion increases.

When simple electrolyte is also present in the solution, the extension of the poly-ion is less than that of the poly-ion in pure polyelectrolyte solution at the same concentration. The counterion concentration within the poly-ion region is, however, again higher than that in the external solution.

This association of counterions with the poly-ions is the result of electrostatic attractive forces, but no specific ion-pair formation between charged groups on the poly-ion and the counterions is considered to occur [22].

Theoretical considerations [39] indicate that the proportion of counterions associated with poly-ions should be greater for bivalent counterions than for univalent ones at the same equivalent concentration, i.e., when the molarity of the univalent ions is twice that of the bivalent ions. It has
also been concluded theoretically [39] that the extent of counterion association should not be very sensitive to change of temperature.

The observed low values for the mean activity coefficients of counterions in polyelectrolyte solutions are thought to be due to the circumstance that those counterions which are held in and near the poly-ion region have very low activity coefficients. In some cases the counterion activity coefficients increase as the solution is diluted, in agreement with the concept that a greater proportion of the counterions leave the poly-ion regions on dilution. The activity coefficients of sodium counterions in the presence of poly(vinyl sulphate), polystyrenesulphonate, cellulose sulphate and carboxymethyl-cellulose poly-anions, however, have been observed to exhibit the opposite trend [28], with the values decreasing as the solution was diluted. This behaviour also occurs with sodium polyacrylate solutions [31] and is reflected in the electrolytic transference studies [23] which showed that a greater proportion of the sodium ions were associated with the polyacrylate poly-anion in the more dilute solution. Presumably, in this particular case, the expansion of the poly-anion on dilution results in a greater proportion of sodium counterions coming under the attractive electrostatic influence of the poly-anion. Other observations [29] have revealed that when the poly-anion charge
density is high, the activity coefficient of sodium counterions is low and almost independent of concentration, despite the expansion of the poly-anion which occurs on dilution of the solution.

The activity coefficient of a by-ion in a polyelectrolyte solution is not markedly affected by the presence of the poly-ions.

In common with the other properties arising from the electrostatic association of the counterions with the poly-ions in polyelectrolyte solutions, counterion activity coefficients are independent of the degree of polymerisation of the poly-ion [28, 29].

When a polyelectrolyte solution contains simple electrolyte having the same ion as the counterion, the observed mean activity coefficient of that ion assumes a value between its separate values in the pure polyelectrolyte and simple electrolyte solutions respectively. This supports the simple qualitative picture in which the counterions within and near the poly-ions possess very low activity coefficients, while the counterions in the external solution have higher activity coefficients approximating to the "normal" values.
Polyelectrolyte Effects on Reaction Rates

Attention was drawn, by Morawetz and Westhead [40] in 1955, to the possibility that the rates of chemical reactions in polyelectrolyte solutions could differ from those in the corresponding simple electrolyte solutions. These authors pointed out that studies of such "polyelectrolyte effects" in the kinetics of a reaction involving an ionic species could provide information on the electrostatic interaction between the polymeric ion (poly-ion) and the simple reactant ion, and could also prove a useful aid to the understanding of the related phenomenon of catalysis by ion-exchange resins. Furthermore, they considered that the use of polyelectrolytes as model systems might provide information which would assist in explaining some aspects of the complicated processes of enzyme catalyses.

Morawetz and Westhead [40], from a consideration of mean ionic activity coefficients, which are known to be lower in polyelectrolyte solutions than in simple electrolyte solutions (see p. 26), concluded that a small uncharged molecule undergoing a hydroxyl ion - or hydrogen ion -catalysed reaction should do so in polyelectrolyte solution at a rate different from that in simple electrolyte solution at the same pH. In the case of the hydrogen ion-catalysed decomposition of ethyl
diazoacetate, in low-molecular-weight buffer solutions and poly(methacrylic acid) solutions, respectively, the rate was expected to be greater in the polyelectrolyte solution at a given pH. This expectation was not substantiated, and in fact slower rates were observed in the polymeric-acid solution [41]. To explain this result, it was suggested [40, 41] that ethyl diazoacetate was partially excluded from the regions around the poly-anions so that, with the hydrogen-ion concentration enhanced in these regions and diminished in the intervening parts of the solution, the ethyl diazoacetate molecules were subjected to an effectively lower hydrogen-ion concentration in the polymeric acid solution than they would be in a simple electrolyte solution of the same pH.

A number of investigations by Kern and co-workers [42, 43, 44], using the strong polymeric acid, poly(vinylsulphonic acid), as catalyst, also revealed differences between the catalytic powers of polymeric and simple strong acids, respectively. Thus, for the hydrogen ion-catalysed hydrolysis of various peptides, e.g. glycylglycine, in aqueous solution the polymeric acid, in low concentrations, produced a rate constant of from three to five times that obtained in sulphuric acid of the same hydrogen ion-concentration [42]. These results were attributed to the existence of an enhanced concentration of both hydrogen ions and basic peptide molecules in the vicinity
of each poly-anion, such a distribution giving a greater rate of reaction than that for evenly-distributed reactants. When a neutral substrate, sucrose, was employed, its rate of inversion was approximately the same in both poly(vinylsulphonic acid) and sulphuric acid at the same hydrogen-ion concentration [42], while with hydrochloric acid the corresponding rate constant was higher than that for the polymeric acid by about 52%. The sucrose molecule, being an electrically-neutral entity, interacted far less strongly with the electrostatic field of the poly-anion and so remained evenly distributed, with little consequent modification of the rate of inversion.

The catalytic rate constant for the glycylglycine hydrolysis, i.e. the observed pseudo first-order rate constant divided by the acid concentration, whilst remaining constant as the acid concentration varied in the cases of sulphuric acid and hydrochloric acid, decreased with increasing concentration of the polymeric acid [43]. The polymeric enhancement of the rate was therefore more pronounced for dilute solutions of the acid.

Poly(styrenesulphonic acid) was also found to be more effective than simple acids, but less effective than poly(vinylsulphonic acid), for peptide hydrolyses [44]. This was taken as an indication that a higher density of anionic sulphonic acid groups on the poly-ion backbone, as in
poly(vinylsulphonic acid), gave a greater enhancement of reaction rate.

No dependence of the rate of peptide hydrolysis on the degree of polymerisation of the poly-anion was detected [44]. Poly(vinylsulphonic acid) also catalysed the hydrolysis of proteins more rapidly than did hydrochloric acid [42, 44]. The possibility of the polymeric acid providing a model for some enzymes was also suggested [43, 44].

Similar effects have been reported by Painter and Morgan [45] in the hydrolysates of polysaccharides. Thus, for example, methyl-2-amino-2-deoxy-β-D-glucopyranoside hydrochloride was hydrolysed in 0.04N poly(styrenesulphonic acid) at a rate thirty times as rapid as in 0.04N hydrochloric acid, while methyl-2-acetamido-2-deoxy-β-D-glucopyranoside, where the basic amino group has been replaced by a neutral acetamido group, was hydrolysed with only equal efficiency in the presence of each of these two acids, respectively.

Poly(styrenesulphonic acid) has been used as a catalyst for the hydrolysis of ethyl acetate [46] and has proved more effective than the monomeric analogue, p-toluenesulphonic acid, at the same acid concentration. The increased rate constant observed for the polymeric acid was again explained in terms of an increase in concentration of hydrogen ions near the poly-anions in solution, together with a corresponding increase
in activity coefficient of these ions in the same regions.

The use of measurements of the rates of reactions between low molecular weight species, in solutions containing poly-electrolytes, to furnish information about the distribution of electrostatic potential around the poly-ions in solution was proposed by Morawetz [47]. It has been demonstrated both theoretically and experimentally (see p. 19) that, in solution, polymeric ions bearing high densities of ionised groups can establish high electrostatic potentials in their immediate vicinities, and consequently can impose uneven distributions on the counterions, which become more concentrated as their distance from the poly-ions decreases. Morawetz's treatment was applied to bimolecular reactions between ionic reactants in the presence of poly-ions. When both ionic reactants carried charges of the same sign, whether the same or opposite to that of the poly-ion, it was predicted that reaction would proceed more rapidly than in the presence of simple electrolyte, while if the reactants were of opposite sign the rate would be less than in the presence of simple electrolyte. The derivation of these predictions can be expressed in simple pictorial terms in the following way. When both reactants have charges of the same sign, which is opposite to the charge of the poly-ion, they will be concentrated around the poly-ion, giving a greater effective concentration of both reactants, and
therefore a greater reaction rate, than if they were distributed evenly in a simple electrolyte solution. In a similar manner, when both reactants bear charges of the same sign as the poly-ion they will be repelled from the regions occupied by the poly-ions, again giving rise to greater effective reactant concentrations, and a higher reaction rate, than in simple electrolyte solution. When, however, the reactants carry charges of different sign, then one will be attracted to, and the other repelled from, the poly-ion, with the result that partial separation of the reactants takes place and the reaction rate becomes less than in simple electrolyte solution, because of the lowering of the effective reactant concentrations.

Morawetz and Shafer [48] has applied these principles in an investigation of the rates, in solution, of the hydroxyl ion-catalysed hydrolyses, in the presence of polymeric anions, of phenyl esters containing cationic groups. An ester ion with one unit of positive charge, the N,N,N-trimethyl-N-(phenoxycarbonylmethyl)ammonium cation \((\text{CH}_3)_3\text{N} \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{Ph})\), was found to undergo hydrolysis at a rate slower in partially-neutralised aqueous polymeric acid solution than in simple electrolyte solution at the same pH, as expected. This retardation was expressed in terms of an "inhibition factor", \(k'\), where \(k\) and \(k'\) were the rate constants in the presence of the simple electrolyte and the polyelectrolyte, respectively.
The hydrolysis of a doubly-charged cationic ester, the ethylene bis-[N,N-dimethyl-N-(phenoxy carbonylmethyl)ammonium] cation (\textit{Ph}O\textit{2}C\textit{CH}_{2}\tilde{\textit{N}}(\textit{CH}_{3})_{2}\cdot\textit{CH}_{2}\tilde{\textit{N}}(\textit{CH}_{3})_{2}\cdot\textit{CH}_{2}\cdot\textit{CO}_{2}\cdot\textit{Ph}) also exhibited the expected retardation in the presence of polymeric anions, and gave an inhibition factor greater than that for the singly-charged ester under the same conditions. This latter effect was not surprising since the doubly-charged cation was expected to undergo a more pronounced interaction with the electrostatic field of the poly-anion than did the singly-charged ion.

The inhibition factor for the doubly-charged ester was increased when the density of anionic sites on the poly-anion was increased, but showed a decrease when the counterion concentration was enhanced by the addition of neutral simple salt.

Uncharged p-nitrophenyl acetate gave a value of unity for \( \frac{k^{+}}{k} \), indicating that the uncharged ester remained evenly distributed in the presence of the poly-anion.

Using a simple model for the polymeric ion, Morawetz and Shafer concluded that in solutions of a two-thirds-neutralised poly(acrylic acid-maleic acid) copolymer, at a "bulk-average" concentration of poly-anion groups of about 0.01N, the actual concentration of these poly-anion groups in the poly-ions was about 0.2 to 0.3N, for "bulk-average" counterion concentrations of 0.0184N and 0.0367N.
It has also been found that ion-exchange resins catalyse some reactions in solution at rates which differ significantly from the rates in the corresponding homogeneous low-molecular-weight systems. Thus, Whitaker and Deatherage [49] demonstrated that the poly(styrenesulphonic acid) ion-exchange resin Dowex-50 brought about rapid hydrolysis of glycylglycine in aqueous systems, while the corresponding hydrolysis of acetylglycine was slow. This was contrasted with the rates in hydrochloric acid, which exhibited the reversed order. It was proposed that the amino-group present in the glycylglycine molecule caused it to interact with the anionic sulphonate groups of the resin, leading to a more facile reaction.

Letsinger and Savereide [50] have observed that the rates of solvolysis of anionic nitrophenyl esters in poly(4-vinylpyridine) show a dependence on the degree of neutralisation of the polymer such that there is an optimum pH for the rate of each reaction. This was explained by proposing that the protonated pyridinium groups of the partially-neutralised polymer attract the anionic substrates to the polymer, where the catalytic tertiary-amine groups are able to effect the solvolyses readily. Similar results were obtained by Overberger, St. Pierre, Vorchheimer and Yaroslavsky [51] with poly(4(5)-vinylimidazole).
Some examples of the enhancement of reaction rates by the existence of micelles in solution have been reported. For example, Motsavage and Kostenbauder [52] have found that the rate of the hydrogen ion-catalysed hydrolysis of sodium dodecyl sulphate is greater when the substrate is present in concentrations in excess of the critical micelle concentration. These authors consider [52] that the catalytic hydrogen ions are attracted to the large, highly-charged anionic micelle of the substrate to give a rate faster than that for the evenly-distributed substrate in solutions below the critical micelle concentration.
EXPERIMENTAL

NOTE

All melting points determined in this investigation have been corrected.

Reagents and solvents were "laboratory grade" unless otherwise stated.
The Preparation of 2,2,6,6-Tetramethyl-4-piperidone
Monohydrate (Triacetonamine Hydrate)

This preparation was based on the one reported by Francis[53].

Formulation

<table>
<thead>
<tr>
<th>Substance</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>1000 g.</td>
</tr>
<tr>
<td>Calcium chloride</td>
<td>320 g.</td>
</tr>
<tr>
<td>Ammonia (gaseous)</td>
<td></td>
</tr>
</tbody>
</table>

The acetone was purified by successive addition to it of small quantities of AR potassium permanganate [54], while it was boiling under reflux, until the purple permanganate colour of the solution no longer faded (12 hours). A dark brown precipitate developed during the treatment. After it had been dried for 20 hours over anhydrous potassium carbonate, the mixture was filtered and the filtrate distilled using a lagged ten inch fractionating column packed with 3-4 mm. Fenske helices. The column was allowed thirty minutes for equilibration before the distillate was collected. The first portion, b.p. 55.8°, was rejected and the second fraction, b.p. 55.8°, uncorrected, \( n_D^{25} 1.3558 \), was retained for the preparation.

The calcium chloride (anhydrous, B.D.H. reagent, "contains
not greater than 1% alkali") was ground, quickly to a powder and stored in a desiccator.

The gaseous ammonia was obtained from a cylinder of liquid ammonia (I.C.I.) and was dried by potassium hydroxide pellets which were included in the gas-train leading to the reaction vessel.

Procedure

The preparation consisted of two stages. Stage 1 involved the actual condensation reactions, and included the removal of unreacted acetone; stage 2 was the isolation of the desired product as the monohydrate.

Stage 1: This was carried out in a fume-cupboard. The acetone was weighed into a 3 litre three-necked "Quickfit" round bottom flask fitted with a double-surface condenser, thermometer, gas-delivery tube and electrically-powered stirrer. A "Teflon" stirring gland with felt packing was used instead of a mercury seal, since ammonia is reported to form explosive compounds with mercury[55]. The calcium chloride powder was then added slowly over a period of ten minutes, whilst the acetone was being stirred, to give a white dispersion. An increase in the temperature of the acetone from 20° to 30° was noted.

After twenty minutes, the passage of a steady stream of ammonia was commenced, the gas being delivered at about 4 cm.
beneath the surface of the reaction mixture. The rate of flow of ammonia was found to control the temperature of the reaction mixture, and accordingly it later became necessary to reduce this flow to prevent the temperature from becoming too high. For most of the time the temperature during this stage was maintained between 30 and 40°, except that the ammonia was turned off overnight, when the temperature fell to that of the room.

As the reaction progressed the calcium chloride powder assumed a sticky consistency and eventually most of it disappeared, to be replaced by a second cloudy liquid phase. At the same time, the mixture became more viscous and its colour deepened to amber. The total time for which ammonia was passed was 28 hours, but the overall time for this stage, including the overnight periods when no ammonia was passed and the stirring stopped, amounted to 76 hours.

The ammonia delivery tube was then replaced by a stopper and the reaction mixture was left at room temperature for a further 112 hours, during which period it separated into a clear dark amber upper layer and a clear colourless lower layer, with some white solid at the bottom. The stirring was then recommenced and the reaction mixture heated gradually to a temperature of about 60° in a water bath, the temperature of which was
held between 60 and 70°. Ammonia was evolved and a slight reflux of acetone occurred in the condenser, while the mixture became darker, and sticky pale yellow solid was gradually deposited. After 8 hours of this treatment the heating and stirring were discontinued, and the mixture allowed to separate into a dark red-amber liquid and a slightly sticky sediment. After it had stood a further 16 hours the deep red, pungent smelling, slightly viscous liquid was decanted as completely as possible from the sediment. This solid varied from yellow to red in colour, but on removal of the adhering liquid with acetone it became nearly white. It was insoluble in cold or hot water but dissolved in cold hydrochloric acid, and the resulting solution gave a white precipitate when ammonium chloride, ammonia and ammonium carbonate solution were added, indicating that the solid was a calcium compound.

The decanted liquid (880 g.) was filtered, with slight suction, to remove the small amount of solid in it and the residual acetone was removed by distillation into a tared receiver. Initially, a water bath was used to heat the liquid. Ammonia was evolved and tended to carry the distillate over prematurely, the first of the distillate passing over at a still-head temperature of 39°. The distillation-temperature rose steadily as the water bath was heated and the condensing liquid developed a yellow colour. To achieve distill-
ation temperatures in excess of $65^\circ$ it was necessary to replace the water bath by an oil bath. Distillation was then continued until the distillation-temperature reached $75^\circ$ (oil bath temperature $136^\circ$), whereupon the heating was discontinued. The distillate was a clear yellow liquid with a pungent ammoniacal smell (119.5 g.) and the residue was a dark yellow mobile liquid containing some dark hard solid (about 20 g.) which had accumulated during the distillation. This solid was removed by filtration with suction and, in contrast to that removed before the distillation, was soluble in cold water, releasing some insoluble red oil as it dissolved. The resulting aqueous solution gave a white precipitate with nitric acid and silver nitrate solution, indicating the presence of chloride, while the addition of ammonium chloride, ammonia and ammonium carbonate solution to another portion also yielded a white precipitate, indicative of the presence of calcium.

Stage 2: The weight of acetone which had reacted was obtained from the difference between the weight of acetone in the initial charge (1000 g.) and the weight of the distillate (119.5 g.). Some acetone, however, was lost through the stirrer gland during Stage 1. This difference came to 880.5 g. The quantity of water required for the formation of the monohydrate was then calculated, assuming a 28% conversion of acetone into triacetonamine, as recommended by Francis [53]. The molecular weights
of water and acetone were taken as 18 and 58 respectively, and
since three acetone molecules are required to form one tri-
acetonamine molecule the amount of water required was given by:

\[ \text{Weight of water} = \frac{880.5}{3} \times \frac{28}{100} \times 18 = 25.5 \text{ g}. \]

The filtered residue, contained in a beaker, was chilled
in a sodium chloride-ice mixture (1 part to 3 parts respective-
ly) and stirred mechanically. When the temperature of the
residue had fallen to 1°, distilled water (25.5 g.) was added
drop-wise from a funnel at such a rate as to keep the tempera-
ture of the vigorously stirred liquid between 1° and 2°. After
all this water had been added, the temperature of the liquid
fell, and at -4.5° the liquid became more viscous as small
crystals began to develop. At this point the temperature also
rose spontaneously to +2° before falling again. The liquid was
held at -8° for 30 minutes and was then filtered with suction
to yield a slightly sticky mass of small dark yellow crystals.
This was pressed down in the Buchner funnel and then pressed
between filter papers and left overnight in the air. This
cased the liquid sticking to the outside of the mass of
crystals to turn a deep red-brown colour, although the inside
of the mass remained yellow. The weight of this impure tri-
acetonamine monohydrate was 155 g., which represented a yield
of 17.7% based on the acetone which had reacted.
To the mother liquor from the crystallisation was added more water (16 g.). The liquid was "seeded" with some triacetonamine monohydrate crystals and chilled to -10°. No crystals developed, nor did they when the liquid was left in a refrigerator at 4° for 11 days.

The crude crystalline product (155 g.) was twice crystallised from wet diethyl ether (50 ml.), which had been left in contact with water for two weeks. In the first crystallisation the solution was also boiled under reflux with animal charcoal (3 g.) for one hour. The monohydrate was obtained as white platelets, with a slight brown tint (94 g.), m.p. 58°, sintering commences at 53°; literature: 58°[56]. A further small quantity (3 g.) was obtained by concentration and cooling of the mother-liquor, m.p. 58°, sintering commences at 53°.

The melting point was constant after the two crystallisations.

The triacetonamine monohydrate was dried in a desiccator over paraffin wax and anhydrous calcium chloride at atmospheric pressure for two days. It was found that drying under reduced pressure (13 mm.) for two days resulted in the dehydration to the free amine, m.p. 37.5 - 38°; literature: 34.6°[56].

Another batch of the monohydrate was also prepared and corresponded closely in its appearance and m.p. (58.5°) to the one described above.
The Preparation of 1-Nitroso-2,2,6,6-tetramethyl-4-piperidone

(Mitrosotriacetonamine)

This was based on Heintz's method [57].

Formulation

A

(Triacetonamine monohydrate (0.5 mole) 86.5 g.

(Water (distilled) 115 g.

(Hydrochloric acid (36% solution) 44 ml.

B

(Potassium nitrite 1 (0.53 mole) 45.1 g.

(Water (distilled) 45.1 g.

C

Hydrochloric acid (36% solution) 14 ml.

Potassium nitrite 2 (0.53 mole) 45.1 g.

The triacetonamine monohydrate was the material, the preparation of which is described above.

The potassium nitrite was obtained from B.D.H. ("not less than 89% as nitrite").

Procedure

Solution A was prepared by the addition of the hydrochloric acid gradually to the amine-water mixture, with cooling. The resulting clear solution had a dark brown colour, and pH about 2, estimated from indicator papers.
Solution B was added to solution A with manual stirring to give a clear red-brown solution, pH about 7.

Preliminary experiments showed that no material separated from such a neutral solution within five hours, although Heintz [57] was able to obtain the nitrosamine in this way.

Hydrochloric acid, C, was added in small amounts, as required, to give a pH of about 4. At this pH value, yellow solid began to separate and some gas was evolved, while the pH tended to rise. However, as already mentioned, the pH was returned to 4 by the careful addition of 'extra' acid. After 2½ hours, 5 ml. of acid having been added, the yellow solid was separated by filtration under suction, and washed with ice-chilled water (20 ml.) to give a pale yellow crystalline solid (about 50 g.). The filtrate and washings (pH about 7) were treated with a further portion of acid (1 ml.) and left overnight. The crystalline solid (about 20 g.) which had separated was isolated and washed in the same manner as before. The procedure was then continued and, in addition, potassium nitrite 2 was dissolved in the reaction mixture to compensate for the nitrous acid lost through side reactions. After a further 4½ hours, a total of 14 ml. of 'extra' acid having been added, the solid was again isolated and washed. Thereafter no more precipitate was obtained by this method. The combined yellow crystalline product was dried in a desiccator over anhydrous
calcium chloride at 14 mm. for two days (91 g., 99% yield).

The melting point of the crude product obtained from a preliminary preparation was 56.5°C. This preliminary preparation also revealed that recrystallisation was not very successful in removing a dark oily contaminant from the crystals. Separation was effected, however, by sublimation.

Purification was therefore performed by an initial sublimation of the material under reduced pressure followed by recrystallisation of the sublimate to constant melting point. The apparatus used for sublimation was a 1 litre, thick-glass vessel with a wide side arm connected to a water pump. The lid, which carried the cold finger, was joined to the vessel by a greased ground-glass flange. Heating was applied to the base of the vessel from a steam bath and the whole apparatus was enclosed in a protective wire-mesh cage. The crude material was added to a Petri dish in batches of about 20 g. each and melted by gentle heating on a hot plate. The Petri dish was then placed on the heated base of the sublimation chamber and, after the lid had been placed in position, the vessel was evacuated to 11 to 20 mm. using a water pump. The sublimate developed slowly on the cold finger as very pale yellow needle-like crystals, which gradually merged together. When most of the solid had sublimed, the sublimate was chipped from the cold finger, the next batch of material added to the
Petri dish and the process repeated. Eventually, after a total time of 40 hours, all of this pale yellow solid had been collected (80.0 g.), m.p. 69.5 - 70°. The residue was a dark brown, slightly sticky solid (1.5 g.).

The sublimate was then crystallised to constant melting point from a water-methanol mixture (2:1v/v) to give very slightly yellow, small needles, m.p. 70 - 70.5°. Reported values: 72-73°[58] and 70-71°[59]. Found: N, 15.38, 15.40; calculated for C_9H_16N_2O_2: 15.21%.

Another batch of nitrosotriacetonamine was similar in its properties. It had m.p. 70-70.5°; found: N, 14.84%.
The Preparation of Polystyrene

Standardisation of the Benzoyl Peroxide Initiator

The benzoyl peroxide (B.D.H.) contained (for safety) added water; it was therefore dried at 18° under vacuum (0.01 mm.) over phosphorus pentoxide for a total of four hours, by which time no further loss in weight occurred. The proportion of water removed in this way amounted to 17% of the original weight of wet benzoyl peroxide.

The standardisation was carried out iodometrically according to the method of Nozaki [60]. The centinormal solution of AR sodium thiosulphate was prepared, and standardised following Vogel [61].

Samples of the benzoyl peroxide (0.05 - 0.06 g.) were weighed accurately into 250 ml. conical flasks fitted with rubber bungs, and to each was added acetic anhydride (10.00 ml.) from a pipette, and powdered sodium iodide (1 g.). When the sodium iodide had completely dissolved (15 minutes) carbon dioxide-free distilled water (50 ml.) was added and the flasks swirled vigorously for half a minute before the liberated iodine was titrated against the standard thiosulphate solution, the starch indicator (0.5 ml.) being added just before the end-point. Blank titrations were carried out, to allow for the presence of other oxidising agents in the system, by
repeating the titrations in the absence of the benzoyl peroxide. The small correction was deducted from the titre values for the benzoyl peroxide.

The data and calculations for the titrations are given in Appendix 1. The average benzoyl peroxide content, from three determinations, was 97%.

The Purification of Xylene

Laboratory grade reagent, presumably a mixture of the o-, m- and p-isomers (1 l.) was dried for 20 hours over anhydrous calcium chloride and then distilled using a six-inch Vigreux column. The second fraction, b.p. 139-140°, (750 g.) was dried over sodium wire and used as the solvent for the polymerisation.

The Removal of Inhibitor from Styrene

Styrene (300 g.) containing t-butylcatechol inhibitor was shaken with 2N aqueous sodium hydroxide solution (200, 200, 150, 100 ml.) to remove this inhibitor, which passed into the aqueous alkaline phase. The styrene was then washed with distilled water (200, 200, 150, 100 ml.) and dried over anhydrous calcium chloride for 48 hours at 5° in a refrigerator.

The dried monomer was distilled under reduced pressure, with a lagged six-inch Vigreux column, while a fine stream of dry nitrogen was drawn through the boiling liquid. The
distillate (280 ml.), b.p. 41.5°/16 mm. \( n_D^{25} 1.5437 \), was used without delay for the preparation of the polystyrene.

The Polymerisation of Styrene to Polystyrene S-2

The purified monomer (100 g.) and benzoyl peroxide (0.515 g.) were weighed into a 1 litre "Pyrex" round bottom flask. This quantity of initiator corresponded to 0.500% of pure benzoyl peroxide based on the monomer charge. The dry distilled xylene (300 g.) was added, giving a clear solution. The flask was then alternately evacuated to a pressure of 20 mm. and filled with nitrogen five times by means of a two-way tap, to de-gas the solution and provide an inert atmosphere. After it had been sealed with a ground-glass stopper, the flask was left in an oven at 80.5° for 24 hours to effect the polymerisation.

The polystyrene was isolated by adding the resulting clear mobile solution slowly from a dropping-funnel to distilled methanol (3 l.), with vigorous mechanical stirring, whereupon the polymer was precipitated in a finely divided form. The polystyrene was collected by filtration with suction and washed thoroughly with distilled methanol (300 ml.). It was then left in distilled methanol (500 ml.) for 20 hours before being filtered and washed again. Drying to constant weight at room temperature and 0.5 mm. pressure over calcium chloride and
paraffin wax shavings, yielded polystyrene S-2 as a finely divided white powder (55 g.).

Another batch of polystyrene (S-3) was obtained in a similar manner, 2.06 g. of initiator (2.00% of pure benzoyl peroxide on the monomer) being used; the yield was 80 g. A batch (S-1) of half the scale of S-2 and S-3 was also made, 1.00% of benzoyl peroxide on monomer being used; 33 g. of polymer were obtained. The percentage yields of the three polymers are given in Table 1, p. 61.
The Viscosity-Average Molecular Weights of the Specimens of Polystyrene

Portions of the different polystyrene batches were each dried to constant weight at room temperature in a drying-pistol, containing phosphorus pentoxide and paraffin wax shavings, at 0.25 mm. pressure.

The relative viscosity, $\eta_r$, of a solution of each sample in sodium-dry, distilled AR toluene (b.p. 109°) was then determined at a known concentration, c (about 1 g. dl.$^{-1}$), with an Ostwald U-tube capillary viscometer (No.1, British Standards Specification No.188-37). The viscometer was immersed in a thermostat bath at 25.00 ± 0.02° and was held in an accurately adjusted support (Townson and Mercer X 294 Universal) so that the capillary portion of the viscometer was truly vertical, as checked with a plumb-line. Furthermore, the solutions or solvent, as they were added to the viscometer, were filtered through a freshly burned-off 100 mesh Monel-metal gauze cone.

Flow times for solvent and solution, $t_o$ and $t$ respectively, were measured with a stop-watch which had proved consistent and accurate when checked against an accurate electric clock. At least 5 readings were taken for each flow-time and were consistent to within 0.2 sec. of each other. The flow-time measurement of the solution of S-1 was repeated after 4 hours and was found to have remained unaltered over this period. The determinations
for batches S-2 and S-3 were carried out in duplicate. For flow-times in excess of about 100 seconds, as were obtained in the measurements described here, \( \eta_r \) is given, to a good approximation, by

\[
\eta_r = \frac{t}{t_0}
\]

The intrinsic viscosity, \([\eta]\), for each sample was then evaluated from the Huggins equation [62] modified in accordance with Kraemer's definition of \([\eta]\) [63]:

\[
\frac{2.303 \log_{10} \eta_r}{c} = [\eta] - (0.5 - k')[\eta]^2 c,
\]

where \( c \) is in g.dl.\(^{-1}\) and \( k' \) is the Huggins constant. The value of \( k' \) employed (0.38) was that given by Fox and Flory [64] for a temperature of 30°.

The viscosity-average molecular weight \( (\overline{M}_v) \) was evaluated from the relationship [65]

\[
[\eta] = K \overline{M}_v^a
\]

The values of \( K \) and \( a \) used (1.16 x 10\(^{-4}\) and 0.72 respectively) were those obtained by Green [66] who used polystyrene samples of known weight-average molecular weights for the calibration.

The results for the three polystyrene batches (S-1, S-2 and S-3) are presented in Table 1. The degree of polymerisation (D.P.) was obtained by dividing \( \overline{M}_v \) by the monomolecular
weight of polystyrene, which is 104.

**TABLE 1**

Viscosity-average Molecular Weights, from Measurements in Toluene at 25.00°C.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Percentage of Benzoyl Peroxide on Monomer</th>
<th>Yield (%)</th>
<th>$\eta_r$ ($c=1g.\cdot dl^{-1}$)</th>
<th>Calculated $[\eta]_\eta$ (dl.g.)</th>
<th>$10^{-4}M^\eta$ D.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-2</td>
<td>0.500</td>
<td>55</td>
<td>1.276</td>
<td>1.276</td>
<td>0.2508</td>
</tr>
<tr>
<td>S-1</td>
<td>1.00</td>
<td>66</td>
<td>1.200</td>
<td></td>
<td>0.1866</td>
</tr>
<tr>
<td>S-3</td>
<td>2.00</td>
<td>80</td>
<td>1.138</td>
<td></td>
<td>0.1312</td>
</tr>
</tbody>
</table>
The Chloromethylation of Polystyrene

The method was based on that developed by Alger[67].

Formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
<th>Mole Equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene S-2</td>
<td>18.0 g</td>
<td>(0.173 monomoles)</td>
</tr>
<tr>
<td>Chloromethyl methyl ether</td>
<td>236.0 g</td>
<td>(2.93 moles)</td>
</tr>
<tr>
<td>Zinc chloride (anhydrous)</td>
<td>70.5 g</td>
<td>(0.517 moles)</td>
</tr>
</tbody>
</table>

These quantities represent a molar ratio of approximately 1 : 17 : 3 respectively.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,4-Dioxan)</td>
<td>120 ml</td>
</tr>
<tr>
<td>Distilled water</td>
<td>120 ml</td>
</tr>
</tbody>
</table>

The chloromethyl methyl ether was fractionally distilled through a lagged 9" column, packed with 3-4 mm. Fenske helices, and a double-surface condenser. A slow stream of dry nitrogen was passed into the boiling liquid and the apparatus was protected from the incursion of atmospheric moisture by a calcium chloride guard tube. Because chloromethyl methyl ether vapour and the fumes it produces in moist air are very unpleasant and harmful [68] the distillation was carried out carefully in a fume cupboard.

Three fractions were taken, of which the middle one was retained for the chloromethylation; it had b.p. 57-60°, \( n_D^{25} 1.3915 \); literature values [69] b.p. 58-60°, \( n_D^{25} 1.3940 \).
The zinc chloride obtained in an anhydrous granular state (B.D.H. Laboratory Reagent, "not less than 95%, as Zn; ZnO not greater than 4%") was fused in a porcelain basin and held in its molten state for twenty minutes to ensure complete removal of any water. Drops of the molten compound were then allowed to fall into a mortar, where they were quickly ground to a powder, and stored in a desiccator. The anhydrous zinc chloride thus obtained was a fine white powder.

The 1,4-dioxan was distilled under nitrogen (b.p. 100-101°).

Procedure

To the chloromethyl methyl ether, contained in a 1 litre round bottom three-neck flask fitted with a condenser and electrically-powered stirrer, and cooled to 10° in an ice-water bath, the polystyrene was added slowly with stirring to give a clear pale yellow slightly viscous solution. A mercury seal was incorporated in the stirring system and a calcium chloride guard tube was placed on the condenser.

The flask containing the powdered zinc chloride was connected to one neck of the reaction vessel by a short length of rubber tube (diameter 1 cm.) and the zinc chloride was transferred through this tube to the reaction vessel in four approximately equal portions at intervals of 20 minutes each.
The reaction mixture was stirred continuously and its temperature held between 13 and 15° by the appropriate additions of ice to the cooling bath, the temperature of which was found to vary between 10 and 13° (the reaction being exothermic).

As the successive portions of zinc chloride were added the mixture became cloudy and its colour gradually changed from yellow-brown to pale red-violet. The cloudiness was presumably due to the presence of undissolved zinc chloride.

After the last portion of zinc chloride had been added, the reaction mixture was stirred for another two hours, during which time evolution of heat ceased and the internal and external temperatures assumed the same value, viz. 14-15°. The reaction was then stopped by the slow addition of the 1,4-dioxan-water mixture A from a dropping funnel with vigorous stirring, and with the bath temperature lowered to 0°. Much heat was generated during this stage and the internal temperature was prevented from exceeding 15° by the cooling and by regulation of the rate of addition of the dioxan-water mixture. As this mixture was added, the cloudiness of the reaction mixture gradually disappeared and the pale red-violet colour slowly faded, until finally a sticky pale yellow-brown resin separated, leaving a nearly colourless liquid phase.

The resin was extracted from the mixture with distilled
benzene (170 ml.), and the pale yellow benzene solution then washed with water (16 x 200 ml.). In spite of this thorough washing the aqueous layers were persistently acidic.

The polymer contained in the benzene solution was isolated by adding the solution drop-wise to vigorously-stirred distilled methanol (2 l.). After filtration and washing with distilled methanol (200 ml.), the precipitated polymer was obtained as a white powder. This was reprecipitated twice more, using distilled benzene (250 ml.) as solvent and distilled methanol (2.5 l.) as precipitant each time. Although the benzene solutions were pale yellow in colour, the solid polymer was white. Drying to constant weight under vacuum (0.01 mm.) over phosphorus pentoxide and paraffin wax shavings yielded the polymer as a finely divided white powder (22 g.). This batch was designated C-2.

The chlorine content (22.87, 23.03%, mean 22.95%) corresponded closely to that (23.23%) required for complete monochloromethylation of the phenyl groups of the polystyrene.

An earlier batch of chloromethylated polystyrene, C-1 (17 g.), was obtained from polystyrene S-1 (15 g.) by the same method.
The Intrinsic Viscosities of the Chloromethylated Polystyrenes

These measurements were conducted under the same conditions as those used for the viscosity-average molecular weight determinations of polystyrene (p. 59).

Relative viscosities, $\eta_r$, were measured for solutions of dry polymer in toluene at 25.00 ± 0.02°C at four accurately known values of $c$ (about 1.2, 0.8, 0.6 and 0.4 g. dl.⁻¹ respectively). Extrapolation of the straight line, obtained by plotting $2.303 \log_{10} \eta_r$ against $c$, see Fig. 1, to $c = 0$ enabled the value of the intrinsic viscosity, $[\eta]$, to be read from the intercept on the $\frac{2.303 \log_{10} \eta_r}{c}$ axis.

No variation in the flow times of the polymer solutions was observed over a period of 4 hours.

The results are given in Table 2.

<table>
<thead>
<tr>
<th>Batch of Chloromethylated Polystyrene</th>
<th>$[\eta]$ (dl.g.⁻¹)</th>
<th>$10^{-4}M_n$ of Parent Polystyrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>C - 1</td>
<td>0.155</td>
<td>2.8</td>
</tr>
<tr>
<td>C - 2</td>
<td>0.230</td>
<td>4.3</td>
</tr>
</tbody>
</table>
Fig. 1 Intrinsic viscosity determinations for chloromethylated polystyrenes.
The Quaternisation of Chloromethylated Polystyrene with Triethylamine

Formulation

A
Chloromethylated polystyrene C-2 (0.14 monomoles)
1,4-Dioxan
80 ml.

B
Triethylamine (0.28 moles)
1,4-Dioxan
40 ml.

C
Methanol
52 ml.

D
Methanol
94 ml.

The 1,4-dioxan was purified by boiling it under reflux in the presence of sodium pellets with a slow stream of dry nitrogen passing through it [70] until the surfaces of the rounded pellets of sodium became shiny (12 hours). The 1,4-dioxan, which by this stage contained a yellow-brown resinous solid in addition to the sodium, was then fractionally distilled through a lagged column, 12 inches long, packed with 3-4 mm. Fenske helices. Dry nitrogen was passed slowly through the boiling liquid and a calcium chloride guard tube ensured that the distillate remained dry. The fraction boiling between 101.5 and 102° was collected ($n_D^{25} 1.4199$).

* calculated for complete mono-chloromethylation of the polystyrene.
The triethylamine was dried with chips of sodium and fractionally distilled (10" column, 3-4 mm. Fenske helices), the distillate being protected from moisture by a calcium chloride guard tube. The fraction boiling at 90° was collected (n_D 1.3980) and stored over sodium wire.

The methanol was also distilled b.p. 65°.

Procedure

The reaction was conducted under dry nitrogen in a 500 ml. round bottom flask fitted with a stirrer, mercury seal and a condenser.

Solution A was prepared in the reaction vessel and to it was added solution B. Methanol, C, was also added slowly with stirring. Chloromethylated polystyrene was precipitated locally as the methanol was added, but it redissolved quickly to give a clear, pale yellow solution. The flask was flushed out with dry nitrogen and the apparatus left for 48 hours in a thermostatically controlled water bath at 60°. Throughout this period the reaction mixture was stirred gently and a stream of dry nitrogen was passed over the top of the condenser to maintain the nitrogen atmosphere in the flask.

The ionic polymeric quaternary ammonium chloride groups produced by the reaction rendered the polymer insoluble in 1,4-dioxan, and it was found that the solution became cloudy
within 15 minutes of the flask being placed in the thermostat. The addition of methanol, D, caused the reaction mixture to become clear again, and prevented the formation of any further cloudiness.

After the 48 hours had elapsed the clear, slightly yellow solution was cooled and added to distilled diethyl ether (2.5 l.), with manual stirring. The polymeric quaternary ammonium chloride separated as a soft, white sticky mass which wrapped itself round the stirrer. This stirrer, with the polymer adhering to it, was then removed from the precipitant, and the excess liquid allowed to drain off. The soft polymer was cut from the stirrer and dried over calcium chloride and paraffin wax shavings under reduced pressure (15 mm.) for eighteen hours. By this time the polymer was sufficiently brittle to be ground to a powder, which was then further dried at 0.05 mm. pressure for two hours (weight 37 g.).

The product was then dissolved in distilled water (300 ml.) to give a clear, slightly alkaline solution, which was dried at 40–60° in a rotary film evaporator. The transparent, very slightly yellow, brittle film obtained from this treatment was ground to a white hygroscopic powder and dried over phosphorus pentoxide at 0.03 mm. (14 periods of one hour each) until constant weight was attained (32.9 g.). Aqueous
solutions of the polymeric quaternary ammonium chloride were clear, colourless and neutral. This batch of polymeric quaternary ammonium chloride was designated Q-3.

Two earlier batches, Q-1 and Q-2, were prepared from chloromethylated polystyrene C-1 in a similar manner, but with a reaction time of only 24 hours in each case, and without the rotary film evaporation stage.
The Determination of the Chloride-Ion Contents of the Polymeric Quaternary Ammonium Chlorides

Preliminary investigations, with specimens Q-1 and Q-2, into the gravimetric method of determining the chloride ion by precipitation as silver chloride revealed that the presence of the polymeric cation prevented the coagulation of the precipitate, which remained as a colloidal dispersion capable of passing through a number 4 sintered-glass crucible. Coagulation of the precipitate was effected when the dispersions were boiled for 10 minutes and then left for 20 hours, the operations being performed in a dark cupboard. Even so, some silver chloride particles passed through the sintered-glass crucible, requiring the filtrate to be re-cycled several times.

This procedure gave chloride-ion contents for specimens Q-1 and Q-2 of 12.9 and 12.6% respectively, corresponding to 87.8 and 84.7% of the chloromethyl groups having been quaternised, respectively.

The chloride-ion content of Q-2 was also estimated by the Volhard method [71]. It was found that the end-point was difficult to detect and that the colour at the end-point faded quickly. The chloride-ion content obtained by this method was 12.1%, which corresponds to 79.3% of the chloromethyl groups being quaternised. This is a lower value than
that obtained by the gravimetric procedure. The poor end-point was probably due to the inability of the nitrobenzene to form a protective coating around the silver chloride particles [71], which remained in the colloidal state under the protective colloid-action of the polymeric cation. Since the exposed silver chloride could react with the thiocyanate ion ($\text{AgCl} + \text{CNS} \rightarrow \text{AgCNS} + \text{Cl}^-$), the end-point would fade and also give low chloride-ion contents.

Although preferable to the Volhard method, the gravimetric technique was tedious and subject to some doubt, since it is possible that the boiling of the acidic solution (nitric acid being present) might cause hydrolysis of residual chloromethyl groups on the polymer to occur, thus releasing further chloride ions.

Accordingly, the chloride-ion content of batch Q-3 was estimated by means of the Mohr method with potassium chromate as indicator [72]. The end-point colour did not fade and could be detected with reasonable ease. Blank titrations were also carried out with AR calcium carbonate suspensions. The silver nitrate solution used for the titrations was standardised, by the same method, with AR sodium chloride which had been dried at 300°.

By this method batch Q-3 was estimated to contain
13.6% of chloride ion, which corresponded to a 95.5% conversion of chloromethyl groups into quaternary ammonium groups. The data and calculations are given in Appendix 2. Since the titration was performed at room temperatures in a neutral medium there is very little chance that any of the residual chloromethyl groups had been hydrolysed.

The value obtained for the chloride-ion content of this batch of polymeric quaternary ammonium chloride (Q-3) by use of the Volhard method was 13.1% (90.4% conversion).
The Conversion of the Polymeric Quaternary Ammonium Chloride into the Hydroxide, in Aqueous Solution

The main batch of chloride, Q-3, was converted into its corresponding hydroxide in solution by means of an anion-exchange resin.

Unless stated otherwise, the water referred to in this Section was saturated with nitrogen and free from carbon dioxide. To obtain this, distilled water was boiled for 30 minutes in a conical flask (5 l.) and then, as the water began to cool, the flask was stoppered with a rubber bung into which had been inserted a T-piece and a long glass tube, the latter nearly reaching the bottom of the flask, while at the top it was connected to a length (3 feet) of clean polyvinyl chloride tube with a glass tap (closed) on the end. Nitrogen was passed through the T-piece so that only nitrogen could enter the flask and dissolve in the water. The flow of this gas was indicated by a bubbler containing distilled water, at the open end of the gas-train. When the water had cooled to room temperature the gas flow was discontinued and the bubbler at the open end of the gas-train was sealed off, thus isolating the system from the atmosphere. To draw off the water, the nitrogen flow was re-commenced and a syphon was established in the tube, the flow of water being controlled by the glass-tap.
Preparation of the ion-exchange column

The anion-exchange resin, Amberlite IRA-401, was a strongly basic, lightly cross-linked polymer, based on polystyrene, with a capacity of 3 milliequivalents per g. of wet resin. The small pale yellow beads of resin (500 g. wet weight, 1.5 g. equivalents) were loaded into a water-filled long glass tube (90 x 4.8 cm.) with an outlet tube (diameter 0.5 cm.) at its lower end. A length of clean polyvinyl chloride tube, attached to the outlet, was taken up alongside the column and connected to an inverted U tube, so positioned that the open end was level with the liquid in the column. This ensured that the column would not run dry. In the top of the column was inserted a large rubber bung bearing a tap funnel (600 ml.), and on this was attached a tube of soda-lime to exclude carbon dioxide. The liquid to be passed through the column was poured into this funnel and thence allowed to pass drop-wise into the column.

The resin, as supplied, was in its chloride form. It was "conditioned" by the passage of 2N aqueous sodium hydroxide (600 ml.), distilled water (1 l.) and 2N hydrochloric acid (600 ml.) respectively. Then, after the column had been washed with more distilled water (2 l.), the column of beads was converted to the hydroxide form by means of 2N and then 1N aqueous sodium hydroxide (8.4 and 11.4 l. respectively). The
eluent was tested for the presence of the displaced chloride ions with nitric acid and silver nitrate solution. Eventually, such tests produced only an extremely faint turbidity which did not diminish when a further quantity (3 l.) of 1N sodium hydroxide was passed through the column. The resin was then considered to have been virtually completely converted. Water (7.2 l.) was used to wash the excess alkali from the column until 100 ml. portions of eluent produced no pink colour on the addition of phenolphthalein indicator solution.

Preparation of the polymeric quaternary ammonium hydroxide solution (approximately 0.1N)

Polymeric quaternary ammonium chloride, batch Q-3 (29.0g, 0.11 g. equivalents) was dissolved in water (nitrogen-saturated, 140 ml.) and the solution allowed to pass down the column, followed by more water (nitrogen-saturated). The eluent became alkaline after about 60 ml. of this water had been added, whereupon the eluent was collected in a clean 1 litre polythene bottle previously flushed out with nitrogen and fitted with a soda-lime tube to exclude carbon dioxide.

The flow of solution was noticeably slow at first, presumably due to the higher viscosity of the polyelectrolyte solution. In addition, the progress of the polyelectrolyte front down the column could be observed, owing to its darker
colour. 1 litre of the eluent was collected. The solution was a clear, pale yellow, slightly viscous liquid with a slight "fishy" smell, which had developed previously in the eluent from the column when the resin was converted to its hydroxide form. The polymeric quaternary ammonium hydroxide obtained in this aqueous solution was designated H-5.

Batches Q-1 and Q-2 of the polymeric quaternary ammonium chloride were also converted in a similar manner but on a smaller scale (3 g. polymeric quaternary ammonium chloride, 20 g. wet resin). The hydroxides were designated H-3 and H-4 respectively.

Conversion with moist silver oxide

Batches Q-1 and Q-2 were also converted to their hydroxides (H-1 and H-2 respectively) by the use of moist silver oxide suspensions, which had been prepared by the action of excess aqueous sodium hydroxide solution on silver nitrate solutions. Aqueous solutions of the polymeric chlorides, contained in stoppered flasks, were stirred magnetically in a dark cupboard with an excess (18% for H-1 and 25% for H-2) of moist silver oxide for one hour. The resulting hydroxide solutions, separated from the solids by centrifugation, were both clear, but brown in colour. Batch Q-3 was also found to give a brown solution after this treatment.
A portion (2 ml.) of the solution of Q-2 was treated with concentrated nitric acid (1 ml.) and evaporated to dryness in a weighed crucible. The solid was then "ashed", to give a trace of a light brown powdery residue (0.0006 g.), which was dissolved in water (1 ml.) and 1N nitric acid (1 ml.). The solution (1 drop) on a filter paper was treated with 1N nitric acid (1 drop) and a solution (1 drop) of 0.03% p-dimethylamino-benzylidene-rhodanine in acetone. A red-mauve stain was produced revealing the presence of the silver cation [73]. The original polymeric quaternary ammonium hydroxide solution did not produce this coloration, neither did the 1N nitric acid in the absence of the test solution. Silver nitrate solutions of known concentration were tested in the same way, and from a comparison of the intensities of the stains, the original polymeric quaternary ammonium hydroxide solution was estimated to contain approximately $10^{-4}$ M silver.
The Analysis of the Polymeric Quaternary Ammonium Hydroxide Solutions

Hydroxyl-ion contents

The hydroxyl-ion contents of the solutions were obtained by potentiometric titration with standard 0.1N AR hydrochloric acid. This acid had itself been standardised potentiometrically with 0.1N carbonate-free sodium hydroxide solution, the normality of which had been determined by potentiometric titration with dried (120°C) recrystallised AR potassium hydrogen phthalate. The water employed for the preparation of the reagents and for the titrations was free of carbon dioxide and saturated with nitrogen (see p. 75).

In the potentiometric titration, the alkali was contained in the burette, protected from carbon dioxide by a tube of soda-lime. Aliquots (10.00 ml.) of the standard 0.1N hydrochloric acid were each added to a 250 ml. beaker containing carbon dioxide-free water (50 ml.), and a steady stream of nitrogen was maintained over the surface of the liquid. Moderate stirring was provided by a magnetic stirrer. The alkali was added carefully to this stirred solution. An E.I.L. pH-meter (Model 23A) with a calomel/saturated potassium chloride half-cell and a glass electrode (E.I.L. type GHS23)
were used to measure the pH of the system. The pH meter was buffered, prior to the titrations, at a value of 4.00 with 0.05M potassium hydrogen phthalate solution. The setting of the instrument was also checked with a 0.05M borax solution (pH 9.18) and was found to give the correct reading.

The polymeric quaternary ammonium hydroxide behaved as a strong base, giving a sharp change of pH at the equivalence point, which was detected graphically. A typical graph of the titration of H-5 is given in Fig. 2.

It was also noted that the polymeric quaternary ammonium hydroxide solutions obtained by the anion-exchange method could be accurately standardised with phenolphthalein as the indicator. On the other hand, the brown coloration of the solutions obtained from the silver oxide method obscured the colour change and prevented the use of this indicator for their standardisation.

The hydroxyl-ion contents of the polymeric quaternary ammonium hydroxide solutions are given in Table 3.

**Chloride-ion contents**

The polymeric quaternary ammonium hydroxide solutions contained some residual chloride ions. In the cases of the solutions of batches H-1 to H-4, these chloride ions were estimated gravimetrically (see p.72), while the chloride content of H-5 was determined by the Mohr method (see p.73). Since the
Fig. 2 Potentiometric titration of aqueous polymeric quaternary ammonium hydroxide solution, batch E-5, with 0.09869N hydrochloric acid (10.00ml.), at 17°.
latter method was applicable only to neutral solutions, the aliquots (10.00 ml.) were first accurately neutralised by chloride-free 0.1N nitric acid with phenolphthalein as the indicator. The results are given in Table 3.

**TABLE 3**

Analysis of Polymeric Quaternary Ammonium Hydroxide Solutions.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Hydroxyl Ion (g. equivalents l.⁻¹)</th>
<th>Chloride Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>0.08630</td>
<td>0.0079</td>
</tr>
<tr>
<td>H-2</td>
<td>0.1491</td>
<td>0.027</td>
</tr>
<tr>
<td>H-3</td>
<td>0.1975</td>
<td>0.025</td>
</tr>
<tr>
<td>H-4</td>
<td>0.2281</td>
<td>0.0096</td>
</tr>
<tr>
<td>H-5</td>
<td>0.09618</td>
<td>0.0015</td>
</tr>
</tbody>
</table>
The Preparation of Benzyltriethylammonium Chloride

This compound was prepared by the method of Ladenburg and Struve [74].

**Formulation**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (g)</th>
<th>Mole (0.3 mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl chloride</td>
<td>38.0</td>
<td>(0.3 mole)</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>30.4</td>
<td>(0.3 mole)</td>
</tr>
</tbody>
</table>

Benzyl chloride was fractionally distilled under nitrogen with a 6" Vigreux column; it had b.p. 178°/750 mm., \( n_D^{25} 1.5363 \).

The purification of the triethylamine has already been described (p.69).

**Procedure**

The two reactants were mixed together and sealed, under nitrogen, in two "Pyrex" glass tubes (14 x 2 cm.) with thick walls (1.5 mm.). The mixture became cloudy almost immediately, as the insoluble ionic product formed. The tubes were then left in a steam bath (100°) for 6½ hours, the reaction mixture solidifying completely to a white mass in this time.

After they had been left at room temperature overnight (15 hours) the tubes were again heated in a steam bath (100°) for a further 8 hours, during which time a few brown patches developed in the solid. In retrospect, therefore, it is felt
that this second heating stage was not only unnecessary but also slightly detrimental to the purity of the product.

The tubes were then allowed to cool before they were broken open and the solid product chipped out. This product was a deliquescent white powder with a yellow tint. It was dried over phosphorus pentoxide at 14 mm. pressure (66.0 g.).

The crude material was crystallised from chloroform solution. It was found necessary to chill the solution in solid carbon dioxide to bring about this crystallisation. The crystals were quickly collected by filtration under suction while the mixture was still cold, and chloroform, which had also been chilled in solid carbon dioxide, was used to wash the crystals. The deliquescent white needles and prisms so obtained were dried at 65° under reduced pressure (18 mm. and then 0.5 mm.) to constant weight.

Chloride-ion determinations were carried out on the product by the Mohr method (see p. 73) and a constant value (15.6%) was attained after two crystallisations (calculated for $C_{13}H_{22}ClN$: Cl⁻, 15.57%).
The Conversion of Benzyltriethylammonium Chloride into Benzyltriethylammonium Hydroxide in Aqueous Solution

This was effected by means of the column of Amberlite IRA-401 resin, following the same procedure as that used for the preparation of the polymeric hydroxide H-5 (see p. 77).

Benzyltriethylammonium chloride (25.0 g., 0.11 g. equivalents), dissolved in nitrogen-saturated carbon dioxide-free water (50 ml.), was added to the column and the eluent (1 l.) collected as soon as it became alkaline. The resulting clear colourless solution was tested with nitric acid and silver nitrate and found to be completely free from chloride ions.

Standardisation by standard 0.1N hydrochloric acid with phenolphthalein indicator showed the hydroxyl-ion content to be 0.1056N.
The Investigation of the Reaction Kinetics of the Hydroxyl Ion-Catalysed Decomposition of Nitrosotriacetonamine

The kinetics of this reaction were investigated from four main aspects, viz.

(a) Comparison between the rate constants obtained with the polymeric quaternary ammonium hydroxide and low molecular weight hydroxides (sodium hydroxide and benzyltriethylammonium hydroxide) in aqueous solution at 25.00°C.

(b) Comparison between the effects of added neutral salts on the rate constants obtained with polymeric quaternary ammonium hydroxide and sodium hydroxide in aqueous solution at 25.00°C.

(c) Comparison between the effects of changing the macroscopic dielectric constant of the aqueous solvent (with 1,4-dioxan) on the rate constants obtained with the polymeric quaternary ammonium hydroxide and sodium hydroxide at 25.00°C.

(d) Comparison between the effects of changing the temperature on the rate constants obtained with the polymeric quaternary ammonium hydroxide and sodium hydroxide in aqueous solution. In other words, the activation parameters for the two catalyses were compared.
Reagents and Solvents

A stock solution of carbonate-free 0.1N sodium hydroxide solution in nitrogen-saturated water was prepared from AR sodium hydroxide according to Vogel [75]. The solution was standardised by potentiometric titration with dry AR potassium hydrogen phthalate and stored under nitrogen in a polythene bottle.

The batch of polymeric quaternary ammonium hydroxide used for the main sequence of kinetic runs was H-5 (see p. 77).

The benzyltriethylammonium hydroxide solution was that described on p. 86.

Nitrosotriacetonamine (see p. 51) was dried to constant weight at room temperature and 0.01 mm. pressure over phosphorus pentoxide, and stored in a dark glass bottle.

The water was free from carbon dioxide and saturated with nitrogen (see p. 75).

The AR sodium chloride was dried at 300° for 4 hours. It was stored in a bottle over phosphorus pentoxide.

The sodium sulphate was prepared by the dehydration of AR sodium sulphate decahydrate to constant weight with a carefully controlled Bunsen burner flame. The loss in weight accompanying the dehydration was 55.9%; the theoretical weight-loss was also 55.9%. This material was stored in a bottle over
phosphorus pentoxide.

The hygroscopic polymeric quaternary ammonium chloride, Q-3, was dried to constant weight at room temperature over phosphorus pentoxide at 0.03 mm. pressure and stored in a bottle over phosphorus pentoxide.

The 1,4-dioxan was purified in the same way as was that used in the quaternisation reaction (see p. 68), b.p. 100.5-101°, \( n_D^{25} 1.4194 \). It was stored under dry nitrogen in a dark glass bottle.

**Thermostat Bath**

This was a glass tank, 35 x 33 x 32 cm., containing water (30 l.) and provided with a constant-level device to compensate for losses by evaporation. The water was stirred efficiently by means of an electric motor and a stirrer with large propeller-like blades. Temperature control was achieved by the use of a "Sunvic" hot-wire vacuum switch relay, type F 102/4, in conjunction with a mercury-toluene regulator in the form of a helix made from 5 feet of glass tube, of 1 cm. bore, with glass capillary tube, 2 mm. bore, containing the mercury thread. The electrical contact wires in this regulator were made of platinum. A 200 watt immersion heater provided the heating. It was found necessary to provide the bath with a cooling coil through which tap water was passed on warm days.
if required. The system gave a maximum variation of $\pm 0.02^\circ$ from the required temperature. Two 0 to 40° mercury-in-glass thermometers divided in 0.1° and readable to 0.02° were placed at opposite sides of the thermostat bath to provide a check on the temperature. These thermometers were immersed to a standard depth of 100 mm. and had been calibrated against an N.P.L.-standardised set of thermometers at 25°, 30°, 35° and 40° respectively. The temperatures quoted for the kinetic runs are the corrected values. Both the thermometers in the bath were found to register the same corrected temperature.

**Reaction Vessel (see Fig. 3)**

Constructed from "Pyrex" glass, this consisted of a conical lower compartment of approximately 90 ml. capacity (made from a 100 ml. flask), above which was a spherical chamber of 25 ml. capacity, displaced to one side of the axis of the lower compartment. The tap was a good quality vacuum stopcock.

The lower compartment, in which the reaction occurred, was provided with a stirrer, consisting of a polythene-covered magnetised follower, 5 cm. long, with an external electric motor fitted with a magnet. This motor was contained in a water-tight copper box resting on the bottom of the water bath,
Fig. 3 Reaction vessel (actual size).
immersed in the water. The lower compartment of the reaction vessel stood on the flat top of this box, while the electrical leads for the motor passed down to the box through a copper tube, the upper end of which protruded well above the level of the water. A second, vacant, copper tube was also attached to the box to permit the free access of air to the motor. Two symmetrically-opposed indentations, 1 cm. deep, in the walls of the lower chamber of the reaction vessel acted as baffles to provide effective turbulence when the liquid was being stirred. The agitation of the reaction mixture is of great importance, since if it is insufficiently vigorous, the nitrogen is not released from solution as quickly as it is formed by the reaction [8]. The circle swept out by the magnetised follower virtually covered the base of the lower chamber completely. The rate of stirring was controlled by a "Variac" variable transformer which was always set at the same output voltage to provide reproducible stirring conditions. This rate was such that the vortex in the reaction mixture extended down to the magnetised follower at the bottom of the vessel, causing many small bubbles to be beaten into the mixture.

When it was standing on the copper box, the reaction vessel was completely immersed in the water of the thermostat, except for the B14 joint on the top, which was connected to
the gas burette.

Both the side arm in the lower chamber and its B14 stopper carried hooks so that the stopper could be secured with helical springs. All the ground-glass joints and taps were lubricated with "Vaseline".

Some preliminary experiments were conducted with a larger reaction vessel, the lower and upper compartments of which had capacities of 150 ml. and 100 ml. respectively. It was found that the volume of gas occupying the free space in this vessel was sufficiently great to cause the slight oscillations in the temperature of the thermostat to be detected in the burette readings. Consequently, the smaller reaction vessel was used to minimise this free volume.

Gas Burette (see Fig. 4)

This was constructed from a Grade A 25 ml. borosilicate glass burette, graduated in 0.1 ml. and readable to 0.01 ml. From the top of the burette, to which it was joined by a short length of rubber pressure tube, thick-walled glass capillary tube (2 mm. bore) descended towards the copper box in the water bath, terminating above it in a two-way ground-glass tap with a B14 cone on the lower end. It was to this cone that the upper socket of the reaction vessel was connected.

The bottom of the burette was joined to the base of a
**Fig. 4 Apparatus used for the investigation of the reaction kinetics.**
tube of internal diameter equal to that of the actual burette. This tube, open to the atmosphere at the top, was positioned alongside the burette so that when the menisci in the burette and the tube were level it was known that the gas in the burette was at atmospheric pressure. The equality of the internal diameters of the burette and the tube was necessary since their dimensions (1 cm.) were small enough for capillary effects to be appreciable. The burette and blank tube were enclosed in a water jacket through which water from the thermostat was circulated at 2.5 l. min.\(^{-1}\) by means of an electrically-powered centrifugal pump. The thick-walled capillary tube connecting the burette to the reaction vessel was, over its vertical length, similarly enclosed in a water jacket. In this way the system was maintained at a constant temperature, thus preventing fluctuations in the ambient temperature from affecting the burette reading.

The base of the gas burette was also connected to a reservoir by a length of rubber pressure tube. The reservoir, open to the atmosphere, was used to bring the gas in the burette to atmospheric pressure. It was held by a clamp which could be moved along a smooth vertical rod and clamped at any desired height. Fine adjustment to the level of the reservoir was obtained by means of a screw thread (pitch: 0.05") incorporated in the clamp.
The complete assembly is represented diagrammatically in Fig. 4.

The burette system, after it had been flushed out with nitrogen, was filled with nitrogen-saturated water. On those occasions when the apparatus was not in use it was sealed off from the atmosphere to prevent the nitrogen being replaced by air.

It was ascertained that the system was free from leaks by holding the nitrogen under a pressure of 60 cm. of water, with the burette full of the gas and the reservoir raised to its full height, for 6 hours at 25.00°, and confirming that the burette reading, after correction for a change in atmospheric pressure, had remained constant.

Some preliminary kinetic runs were carried out with a 100 ml. gas burette graduated in 0.2 ml. and readable to 0.05 ml. The change to a smaller burette was made to obtain a higher degree of accuracy.

Procedure

The following account applies in general to all the kinetic runs which were conducted. The quantities recorded are those used for the main sequence of runs, except when deliberate variations were made. The preliminary runs differed only in scale and not in procedure from those of the main sequence.
Care was taken throughout the series of runs to prevent atmospheric carbon dioxide entering the reactant solutions, by the appropriate use of soda-lime guard tubes and by flushing the vessels thoroughly with nitrogen.

The alkali solution to be used was prepared with nitrogen-saturated water in a standard Grade A "Pyrex" flask to a concentration exactly 3.5 times that of the value required for the kinetic run. This solution was immersed in the thermostat bath for one hour before it was finally made up to the mark, so that the concentration would refer to the temperature at which the run was conducted.

The reaction vessel was flushed out with nitrogen, and the nitrosotriacetonamine (0.206 \pm 0.001 g.) weighed into the lower compartment. Nitrogen-saturated water (50.00 ml.), which had been pre-heated in the thermostat bath for one hour to bring its temperature to that at which the run was to be carried out, was also added by means of a Grade A pipette to the lower chamber. The previously prepared alkali solution (20.00 ml.), at the temperature at which the reaction rate was to be measured, was then added to the upper chamber of the reaction vessel from a Grade A "Pyrex" pipette, the tap between the two chambers being closed.

The solutions of the polymeric quaternary ammonium hydroxide were slightly more viscous than the corresponding low
molecular weight alkali solutions. The drainage time quoted on the pipette was therefore accordingly increased for the polymeric hydroxide solutions by the ratio of the times taken by the polymeric and simple alkali solutions respectively to flow from the pipette.

With the side arm of the lower compartment securely sealed with the B14 stopper, the vessel was placed in the thermostat bath and connected to the gas burette (see Fig. 4). The two-way tap in the burette system was turned so that the gas in the reaction vessel was connected with that in the burette. Next, by adjustment of the reservoir height, the gas was brought to atmospheric pressure, and the stirring was commenced. Within one hour the nitrosotriacetonamine had dissolved in the water and the temperature of the system had reached that of the thermostat (determined by preliminary trials). It was assumed that the water vapour pressure had developed fully in this time.

The burette reading, which had increased on account of the expansion of the gas in the reaction vessel, was brought back to a value of about 0 ml. at atmospheric pressure by means of the two-way tap. This operation was performed gradually by allowing small successive quantities of nitrogen to be expelled. At no stage was the reverse flow of gas, from the atmosphere to the burette, permitted to occur.
The steady burette reading at atmospheric pressure was recorded, together with the actual value of the atmospheric pressure which was obtained from a Fortin barometer. Time was measured with a stopwatch which had been checked against an accurate electric clock, and had been found to be accurate over the maximum period (3 hours) for which the reaction was followed.

At a known time the tap between the two compartments of the reaction vessel was quickly opened to admit the alkali solution to the nitrosotriacetonamine solution. The dilution, 20.00 ml. to 70.00 ml., of the alkali was such that the alkali concentration acquired the desired value.

The burette readings, taken at atmospheric pressure, were recorded at fixed intervals of time, the duration of which depended upon the rate of the reaction (see below, p.103). The value of the atmospheric pressure was also measured at various times during the progress of the reaction. A white card with a black square on it was held behind the burette to accentuate the meniscus so that it was easier to obtain a reading.

When the effects of added neutral salts on the reaction rate were investigated, the salts were dissolved in the alkali solution beforehand, at a concentration exactly 3.5 times that required in the final reaction mixture. Therefore, when the alkali solution was added to the nitrosotriacetonamine solution
the salt concentration attained the desired value.

When the effect of the inclusion of 1,4-dioxan in the solvent was examined, all the 1,4-dioxan was added, in admixture with the appropriate amount of water, to the lower chamber of the reaction vessel; the alkali solution in the upper compartment contained only water as solvent.

The compositions of the 1,4-dioxan-water mixtures were evaluated on a weight basis since the dielectric constant data were presented in this way in the literature. The required volume, 14.00, 28.00 and 42.00 ml. respectively, of 1,4-dioxan was added from a burette to a tared standard 100 ml. flask and the weight of the added 1,4-dioxan ascertained. Nitrogen-saturated water was next added and the solution made up to the mark at 25.00°. The weight of the mixture was then determined so that when the aliquot (50.00 ml.) was added to the nitrosotriacetonamine in the lower chamber of the reaction vessel both the weight of the mixture and the weight of the 1,4-dioxan in it were known. In like manner, when the alkali was made up to the required concentration in a standard flask, the weight of the solution was also determined. Consequently, when the aliquot of the alkali solution (20.00 ml.) was mixed with the nitrosotriacetonamine solution, both the weight of the 1,4-dioxan and the total weight of the solvent were known, if the insignificant weight of the dissolved alkali was ignored.
The macroscopic dielectric constants at 25.00° were evaluated by graphical interpolation of the data given by Åkerlöf and Short [76]. The values obtained are given in Table 4.

<table>
<thead>
<tr>
<th>%, w/w of 1,4-Dioxan in Solvent</th>
<th>Macroscopic Dielectric Constant, 25.00°</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>78.5</td>
</tr>
<tr>
<td>10.25</td>
<td>69.4</td>
</tr>
<tr>
<td>20.35</td>
<td>60.4</td>
</tr>
<tr>
<td>30.33</td>
<td>51.6</td>
</tr>
</tbody>
</table>

The normalities of the sodium hydroxide and polymeric quaternary ammonium hydroxide stock solutions were checked once every two weeks by titration against standard hydrochloric acid, with phenolphthalein as indicator. The hydroxyl-ion concentrations were found to remain unchanged.

The Evaluation of Rate Constants

The observed first-order rate constants were evaluated
by the method of Guggenheim [77]. This method was adopted since it gave good first-order plots and because the times of half reaction for most of the runs were of the order of 1 hour, which required that the reaction be allowed to proceed for at least 10 hours before an infinity reading could be taken. In this method, the first-order rate constant, $k_1 (\text{sec}^{-1})$, was calculated from the gradient of the straight line obtained when $\log_{10}(r_{t+\Delta} - r_t)$ was plotted against $t$, where $t$ is time (min.), $r_t$ is the burette reading (ml.) at time $t$, and $r_{t+\Delta}$ is the burette reading at time $t + \Delta$, $\Delta$ being a constant interval of time for a given run. If the gradient of this line is $S$ min.$^{-1}$, the first-order rate constant is given by:

$$k_1 = -\frac{2.303S}{60} \text{ sec}^{-1}.$$  

The derivation of this expression is given in Appendix 3.

For one of the runs in aqueous solution at 25.00°, with 0.01N polymeric quaternary ammonium hydroxide, the infinity burette reading was calculated from the rate constant. The value obtained, 27.12 ml. at 759.8 mm. partial pressure, was in close agreement with that, 27.07 ml. calculated from the weight of nitrosotriacetonamine used (0.2074 g.), at the same partial pressure.

When the solvent used for the reaction was water alone
there was a short induction period and the rate of reaction was slow over the first 1 or 2 minutes (see Fig. 16). Consequently, the corresponding points on the graph of $\log_{10}(r_{t+\Delta} - r_t)$ against $t$ deviated below the straight line. When aqueous 1,4-dioxan was used, the burette reading actually decreased when the aqueous alkali was added to the water-1,4-dioxan mixture, the more so as the proportion of 1,4-dioxan increased. Thus, when the reaction mixture contained 10% of 1,4-dioxan the reading decreased by about 0.2 ml., and when the 1,4-dioxan content was 30% the decrease was about 0.6 ml. Within 1 minute of the mixing of the solutions the burette reading was increasing again. This reduction in volume could have been caused by the contraction of the liquid when the two solutions were mixed, or by an increase in the solubility of nitrogen in the mixture. However, the reaction settled down quickly and good first-order constants were obtained.

In order that $(r_{t+\Delta} - r_t)$ should be large enough to give reasonably accurate values for $k_1$, $\Delta$ was made greater than the time for half-reaction, $t_{0.5}$. Therefore, for the more rapid reactions, as $t_{0.5}$ became smaller, $\Delta$ could be made smaller also. This in turn required that the readings should be taken more frequently to obtain a reasonable number (20 - 30) of them. The intervals between readings, $I$, and the values of $\Delta$ employed for different values of $t_{0.5}$ are given.
in Table 5. Ideally, the period for which the reaction is observed should be greater than $2 \times \Delta$, since then all the readings could be included in the evaluation of $k_1$, and none would be wasted. This practice was followed as often as was possible.

**TABLE 5**

<table>
<thead>
<tr>
<th>$t_{0.5}$ (min.)</th>
<th>$I$ (min.)</th>
<th>$\Delta$ (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>0.5</td>
<td>17</td>
</tr>
<tr>
<td>15</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>35</td>
<td>2</td>
<td>50</td>
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<td>45</td>
<td>5</td>
<td>60</td>
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<td>50</td>
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<td>70</td>
</tr>
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<td>55</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>65</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>70</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>120</td>
<td>5</td>
<td>130</td>
</tr>
</tbody>
</table>
The complete details of a typical run, in which the polymeric quaternary ammonium hydroxide (0.0100N) was used as catalyst in an aqueous solution without added salt, are given in Appendix 4.

The residual chloride ion in the polymeric quaternary ammonium hydroxide stock solution (see p.81) gave rise to small chloride-ion concentrations in the reaction mixtures when this hydroxide was used. The concentrations of chloride ion from this source at all the different concentrations of hydroxyl ion which were used are given in Table 6.

**TABLE 6**

<table>
<thead>
<tr>
<th>$10^2 \times$ Concentration of Hydroxyl Ion (N)</th>
<th>$10^4 \times$ Concentration of Chloride Ion (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.80</td>
</tr>
<tr>
<td>0.75</td>
<td>1.2</td>
</tr>
<tr>
<td>1.00</td>
<td>1.6</td>
</tr>
<tr>
<td>1.50</td>
<td>2.4</td>
</tr>
<tr>
<td>2.00</td>
<td>3.2</td>
</tr>
</tbody>
</table>

The results of the main series of runs are given in Tables 7 to 18.
Key:  
NTAA: nitrosotriacetetamine.
OH\(^-\): hydroxyl ion.
P-OH: polymeric quaternary ammonium hydroxide.
P-Cl: polymeric quaternary ammonium chloride.
NaOH: sodium hydroxide.
NaCl: sodium chloride.
Na\(_2\)SO\(_4\): sodium sulphate.
\([\text{ ]}\): concentration of.
D: macroscopic dielectric constant.
T: absolute temperature.
k\(_1\): observed first-order rate constant.

### TABLE 7

Values of k\(_1\) in aqueous sodium hydroxide solutions

\[25.00 \pm 0.02^\circ\text{C.} \quad \text{No added salt.}\]

<table>
<thead>
<tr>
<th>Run no.</th>
<th>(10^2[\text{NTAA}]) (M)</th>
<th>(10^2[\text{OH}^-]) (N)</th>
<th>Mean (10^4k_1) (sec.(^{-1}))</th>
<th>Mean (10^4k_1) (sec.(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>1.61</td>
<td>0.500</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>78</td>
<td>1.61</td>
<td>0.500</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>35</td>
<td>1.60</td>
<td>1.00</td>
<td>2.03</td>
<td>2.03</td>
</tr>
<tr>
<td>36</td>
<td>1.60</td>
<td>1.00</td>
<td>2.04</td>
<td>2.04</td>
</tr>
<tr>
<td>44</td>
<td>1.60</td>
<td>1.00</td>
<td>2.06</td>
<td>2.06</td>
</tr>
<tr>
<td>58</td>
<td>1.60</td>
<td>1.00</td>
<td>2.04</td>
<td>2.04</td>
</tr>
<tr>
<td>93</td>
<td>1.60</td>
<td>1.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>127</td>
<td>1.60</td>
<td>1.00</td>
<td>2.03</td>
<td>2.03</td>
</tr>
<tr>
<td>129</td>
<td>1.60</td>
<td>2.00</td>
<td>4.07</td>
<td>4.07</td>
</tr>
<tr>
<td>130</td>
<td>1.60</td>
<td>2.00</td>
<td>4.01</td>
<td>4.01</td>
</tr>
</tbody>
</table>
TABLE 8

Values of $k_1$ in aqueous benzyltriethylammonium hydroxide solutions ($[OH^-] = 1.00 \times 10^{-2}N$), at 25.00 ± 0.02°C. No added salt.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$10^2[NTAA]$ (M)</th>
<th>$10^4.k_1$ (sec.⁻¹)</th>
<th>Mean $10^4.k_1$ (sec.⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>139</td>
<td>1.60</td>
<td>2.06</td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>1.60</td>
<td>2.07</td>
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</tr>
<tr>
<td>141</td>
<td>1.60</td>
<td>2.10</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 9

Values of $k_1$ in aqueous solution containing a mixture of sodium hydroxide ($[OH^-] = 0.500 \times 10^{-2}N$) and polymeric quaternary ammonium hydroxide ($[OH^-] = 0.500 \times 10^{-2}N$), at 25.00 ± 0.02°C. No added salt.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$10^2[NTAA]$ (M)</th>
<th>$10^2[OH^-]$ (N)</th>
<th>$10^4.k_1$ (sec.⁻¹)</th>
<th>Mean $10^4.k_1$ (sec.⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>79</td>
<td>1.61</td>
<td>1.00</td>
<td>2.80</td>
<td></td>
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<tr>
<td>80</td>
<td>1.60</td>
<td>1.00</td>
<td>2.79</td>
<td>2.80</td>
</tr>
</tbody>
</table>
### TABLE 10

Values of $k_1$ in aqueous polymeric quaternary ammonium hydroxide solutions, at $25.00 \pm 0.02^\circ$C. No added salt.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$10^2[\text{NTAA}]$ (M)</th>
<th>$10^2[\text{OH}^-]$ (N)</th>
<th>$10^4k_1$ (sec.$^{-1}$)</th>
<th>Mean $10^4k_1$ (sec.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>1.60</td>
<td>0.500</td>
<td>1.75</td>
<td>1.74</td>
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<td>76</td>
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</tr>
<tr>
<td>48</td>
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<td>0.750</td>
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<td></td>
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<tr>
<td>49</td>
<td>1.59</td>
<td>0.750</td>
<td>2.61</td>
<td>2.63</td>
</tr>
<tr>
<td>50</td>
<td>1.59</td>
<td>0.750</td>
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<tr>
<td>37</td>
<td>1.61</td>
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<td>1.61</td>
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<td>3.52</td>
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<td>96</td>
<td>1.61</td>
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<td></td>
</tr>
<tr>
<td>128</td>
<td>1.60</td>
<td>1.00</td>
<td>3.52</td>
<td></td>
</tr>
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<td>0.751</td>
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<td>3.52</td>
<td></td>
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<tr>
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<td>6.87</td>
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<td>2.00</td>
<td>6.88</td>
<td></td>
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<tr>
<td>132</td>
<td>1.60</td>
<td>2.00</td>
<td>6.85</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 11

Values of $k_1$ in aqueous sodium hydroxide solutions ($[\text{OH}^-] = 1.00 \times 10^{-2}\text{N}$), at 25.00 ± 0.02°C, in the presence of added sodium chloride.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$10^2[\text{NTAA}]$ (M)</th>
<th>$10^2[\text{NaCl}]$ (M)</th>
<th>$10^4k_1$ (sec.$^{-1}$)</th>
<th>Mean $10^4k_1$ (sec.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>2.03*</td>
</tr>
<tr>
<td>101</td>
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<td>5.00</td>
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<td>1.96</td>
</tr>
<tr>
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<td>5.00</td>
<td>1.96</td>
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</tr>
<tr>
<td>81</td>
<td>1.60</td>
<td>10.0</td>
<td>1.91</td>
<td>1.92</td>
</tr>
<tr>
<td>82</td>
<td>1.60</td>
<td>10.0</td>
<td>1.93</td>
<td></td>
</tr>
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<td>103</td>
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<td>15.0</td>
<td>1.83</td>
<td>1.84</td>
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<tr>
<td>104</td>
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<td>15.0</td>
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</tr>
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<td>94</td>
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<td>20.0</td>
<td>1.84</td>
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<td>95</td>
<td>1.60</td>
<td>20.0</td>
<td>1.80</td>
<td></td>
</tr>
</tbody>
</table>

* from Table 7.
### TABLE 12

Values of $k_1$ in aqueous polymeric quaternary ammonium hydroxide solutions ($[OH^-] = 1.00 \times 10^{-2}$M), at $25.00 \pm 0.02^\circ$C, in the presence of added salts.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$10^2$[NTAA] (M)</th>
<th>Added Salt</th>
<th>$10^2$[Added Salt] (M)</th>
<th>$10^4.k_1$ (sec.$^{-1}$)</th>
<th>Mean $10^4.k_1$ (sec.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NaCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>1.60</td>
<td>0.200</td>
<td>3.06</td>
<td>3.05</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1.59</td>
<td>0.200</td>
<td>3.00</td>
<td>3.04</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>1.60</td>
<td>0.500</td>
<td>2.60</td>
<td>2.60</td>
<td></td>
</tr>
<tr>
<td>62</td>
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<td>1.00</td>
<td>2.30</td>
<td>2.30</td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>1.60</td>
<td>1.00</td>
<td>2.60</td>
<td>2.60</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>1.61</td>
<td>3.00</td>
<td>2.06</td>
<td>2.05</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>1.60</td>
<td>3.00</td>
<td>2.04</td>
<td>2.04</td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>1.60</td>
<td>6.00</td>
<td>1.94</td>
<td>1.93</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>1.60</td>
<td>6.00</td>
<td>1.92</td>
<td>1.92</td>
<td></td>
</tr>
<tr>
<td>68</td>
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<td>10.0</td>
<td>1.86</td>
<td>1.86</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>1.60</td>
<td>10.0</td>
<td>1.86</td>
<td>1.86</td>
<td></td>
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<tr>
<td>70</td>
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<td>1.79</td>
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<td>1.79</td>
<td>1.79</td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>1.60</td>
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<td>2.42</td>
<td>2.42</td>
<td></td>
</tr>
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<td>2.43</td>
<td>2.43</td>
<td></td>
</tr>
<tr>
<td>75</td>
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<td>1.00</td>
<td>2.08</td>
<td>2.08</td>
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<tr>
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<td>1.60</td>
<td>1.00</td>
<td>2.08</td>
<td>2.08</td>
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<td>77</td>
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<td>3.00</td>
<td>1.96</td>
<td>1.96</td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>1.60</td>
<td>3.00</td>
<td>1.98</td>
<td>1.98</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>1.60</td>
<td>5.00</td>
<td>1.95</td>
<td>1.95</td>
<td></td>
</tr>
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<td>80</td>
<td>1.60</td>
<td>5.00</td>
<td>1.95</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>81</td>
<td>1.60</td>
<td>P - Cl</td>
<td>0.500</td>
<td>2.99</td>
<td></td>
</tr>
<tr>
<td>82</td>
<td>1.60</td>
<td>P - Cl</td>
<td>0.500</td>
<td>2.99</td>
<td></td>
</tr>
<tr>
<td>83</td>
<td>1.60</td>
<td>P - Cl</td>
<td>1.00</td>
<td>2.99</td>
<td></td>
</tr>
<tr>
<td>84</td>
<td>1.60</td>
<td>P - Cl</td>
<td>1.00</td>
<td>2.99</td>
<td></td>
</tr>
</tbody>
</table>

* from Table 10.
### TABLE 13

Values of $k_1$ in mixtures of 1,4-dioxan and water at 25.00 ± 0.02°C. [OH⁻] = 1.00 x 10⁻² N. No added salt.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$10^2[\text{NTAA}]$ (M)</th>
<th>Alkali</th>
<th>Wt. % of 1,4-dioxan</th>
<th>D</th>
<th>$10^4.k_1$ (sec⁻¹)</th>
<th>Mean $10^4.k_1$ (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>89</td>
<td>1.61</td>
<td>NaOH</td>
<td>0</td>
<td>78.5</td>
<td>-</td>
<td>2.03*</td>
</tr>
<tr>
<td>90</td>
<td>1.60</td>
<td>NaOH</td>
<td>10.25</td>
<td>69.4</td>
<td>2.09</td>
<td>2.10</td>
</tr>
<tr>
<td>91</td>
<td>1.60</td>
<td>NaOH</td>
<td>20.35</td>
<td>60.4</td>
<td>2.12</td>
<td>2.12</td>
</tr>
<tr>
<td>92</td>
<td>1.60</td>
<td>NaOH</td>
<td>20.35</td>
<td>60.4</td>
<td>2.12</td>
<td>2.12</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>P - OH</td>
<td>0</td>
<td>78.5</td>
<td>-</td>
<td>3.52**</td>
</tr>
<tr>
<td>85</td>
<td>1.61</td>
<td>P - OH</td>
<td>10.25</td>
<td>69.4</td>
<td>3.09</td>
<td>3.08</td>
</tr>
<tr>
<td>86</td>
<td>1.61</td>
<td>P - OH</td>
<td>10.25</td>
<td>69.4</td>
<td>3.07</td>
<td>3.07</td>
</tr>
<tr>
<td>87</td>
<td>1.60</td>
<td>P - OH</td>
<td>20.35</td>
<td>60.4</td>
<td>2.82</td>
<td>2.79</td>
</tr>
<tr>
<td>88</td>
<td>1.60</td>
<td>P - OH</td>
<td>20.35</td>
<td>60.4</td>
<td>2.76</td>
<td>2.79</td>
</tr>
<tr>
<td>97</td>
<td>1.60</td>
<td>P - OH</td>
<td>30.33</td>
<td>51.6</td>
<td>2.60</td>
<td>2.58</td>
</tr>
<tr>
<td>98</td>
<td>1.60</td>
<td>P - OH</td>
<td>30.33</td>
<td>51.6</td>
<td>2.56</td>
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</tr>
</tbody>
</table>

### TABLE 14

Values derived from Table 13.

<table>
<thead>
<tr>
<th>Alkali</th>
<th>D</th>
<th>$10^2.D^{-1}$</th>
<th>Mean $10^4.k_1$ (sec⁻¹)</th>
<th>$4 + \log_{10}k_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>78.5</td>
<td>1.274</td>
<td>2.03</td>
<td>0.3073</td>
</tr>
<tr>
<td>NaOH</td>
<td>69.4</td>
<td>1.441</td>
<td>2.10</td>
<td>0.3219</td>
</tr>
<tr>
<td>NaOH</td>
<td>60.4</td>
<td>1.656</td>
<td>2.12</td>
<td>0.3263</td>
</tr>
<tr>
<td>P - OH</td>
<td>78.5</td>
<td>1.274</td>
<td>3.52</td>
<td>0.5467</td>
</tr>
<tr>
<td>P - OH</td>
<td>69.4</td>
<td>1.441</td>
<td>3.08</td>
<td>0.4884</td>
</tr>
<tr>
<td>P - OH</td>
<td>60.4</td>
<td>1.656</td>
<td>2.79</td>
<td>0.4452</td>
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<tr>
<td>P - OH</td>
<td>51.6</td>
<td>1.938</td>
<td>2.58</td>
<td>0.4115</td>
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</tbody>
</table>

* from Table 7.  ** from Table 10.
TABLE 15

Values of $k_1$ in aqueous sodium hydroxide solutions ($[OH^-] = 1.00 \times 10^{-2} N$), at different temperatures. No added salt.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$10^2$[NTAA] (M)</th>
<th>Temperature (°C)</th>
<th>$10^3 T^{-1}$ (deg.K$^{-1}$)</th>
<th>$10^4 k_1$ (sec.$^{-1}$)</th>
<th>Mean $10^4 k_1$ (sec.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>25.00±0.02</td>
<td>3.356</td>
<td>-</td>
<td>2.03*</td>
</tr>
<tr>
<td>111</td>
<td>1.60</td>
<td>30.02±0.02</td>
<td>3.300</td>
<td>3.28</td>
<td>3.25</td>
</tr>
<tr>
<td>112</td>
<td>1.60</td>
<td>30.02±0.02</td>
<td>3.300</td>
<td>3.22</td>
<td>3.24</td>
</tr>
<tr>
<td>113</td>
<td>1.60</td>
<td>30.02±0.02</td>
<td>3.300</td>
<td>3.24</td>
<td>3.24</td>
</tr>
<tr>
<td>118</td>
<td>1.60</td>
<td>35.03±0.02</td>
<td>3.247</td>
<td>5.10</td>
<td>5.09</td>
</tr>
<tr>
<td>119</td>
<td>1.60</td>
<td>35.03±0.02</td>
<td>3.247</td>
<td>5.07</td>
<td>5.09</td>
</tr>
<tr>
<td>120</td>
<td>1.60</td>
<td>35.03±0.02</td>
<td>3.247</td>
<td>5.09</td>
<td>5.09</td>
</tr>
<tr>
<td>124</td>
<td>1.60</td>
<td>40.10±0.02</td>
<td>3.194</td>
<td>7.95</td>
<td>8.00</td>
</tr>
<tr>
<td>125</td>
<td>1.60</td>
<td>40.10±0.02</td>
<td>3.194</td>
<td>8.02</td>
<td>8.00</td>
</tr>
<tr>
<td>126</td>
<td>1.60</td>
<td>40.10±0.02</td>
<td>3.194</td>
<td>8.04</td>
<td>8.04</td>
</tr>
</tbody>
</table>

TABLE 16

Mean values of the second-order catalytic rate constant, $k_2 (= k_1/[OH^-])$, derived from Table 15.

<table>
<thead>
<tr>
<th>$10^3 T^{-1}$ (deg.K$^{-1}$)</th>
<th>$10^2 k_2$ (sec.$^{-1}$)</th>
<th>$2 + \log_{10} k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.356</td>
<td>2.03</td>
<td>0.3073</td>
</tr>
<tr>
<td>3.300</td>
<td>3.25</td>
<td>0.5114</td>
</tr>
<tr>
<td>3.247</td>
<td>5.09</td>
<td>0.7063</td>
</tr>
<tr>
<td>3.194</td>
<td>8.00</td>
<td>0.9033</td>
</tr>
</tbody>
</table>

* from Table 7.
Values of $k_1$ in aqueous polymeric quaternary ammonium hydroxide solutions ([OH$^-$] = 1.00 x 10$^{-2}$ N), at different temperatures. No added salt.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$10^2$[NTAA] (M)</th>
<th>Temperature (°C)</th>
<th>$10^3$.T$^{-1}$ (deg.K$^{-1}$)</th>
<th>$10^4$.k$^{-1}$ (sec.$^{-1}$)</th>
<th>Mean $10^4$.k$^{-1}$ (sec.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25.00±0.02</td>
<td>3.356</td>
<td>-</td>
<td>3.52$^*$</td>
</tr>
<tr>
<td>109</td>
<td>1.60</td>
<td>30.02±0.02</td>
<td>3.300</td>
<td>5.74</td>
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</tr>
<tr>
<td>110</td>
<td>1.60</td>
<td>30.02±0.02</td>
<td>3.300</td>
<td>5.78</td>
<td>5.76</td>
</tr>
<tr>
<td>114</td>
<td>1.60</td>
<td>35.03±0.02</td>
<td>3.247</td>
<td>9.24</td>
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</tr>
<tr>
<td>115</td>
<td>1.60</td>
<td>35.03±0.02</td>
<td>3.247</td>
<td>9.21</td>
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<td>117</td>
<td>1.60</td>
<td>40.10±0.02</td>
<td>3.194</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>121</td>
<td>1.60</td>
<td>40.10±0.02</td>
<td>3.194</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>122</td>
<td>1.60</td>
<td>40.10±0.02</td>
<td>3.194</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>123</td>
<td>1.60</td>
<td>40.10±0.02</td>
<td>3.194</td>
<td>15.0</td>
<td></td>
</tr>
</tbody>
</table>

Mean values of the second-order catalytic rate constant, $k_2$ (= $k_1$/[OH$^-$]), derived from Table 17.

<table>
<thead>
<tr>
<th>$10^3$.T$^{-1}$ (deg.K$^{-1}$)</th>
<th>$10^2$.k$^{-1}$ (1.mole$^{-1}$.sec.$^{-1}$)</th>
<th>$2 + \log_{10} k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.356</td>
<td>3.52</td>
<td>0.5467</td>
</tr>
<tr>
<td>3.300</td>
<td>5.76</td>
<td>0.7602</td>
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<td>3.247</td>
<td>9.23</td>
<td>0.9651</td>
</tr>
<tr>
<td>3.194</td>
<td>15.0</td>
<td>1.1764</td>
</tr>
</tbody>
</table>

* from Table 10.
The Precision of the Values of $k_1$

The standard deviation, $\sigma$, was calculated for the values of $10^4 k_1$ at 25.00° obtained with $1.00 \times 10^{-2} \text{N aqueous sodium hydroxide solution}$ and $1.00 \times 10^{-2} \text{N aqueous polymeric quaternary ammonium hydroxide solution}$ respectively (see pp. 106 and 108 respectively). $\sigma$ was calculated from the equation [78]

$$\sigma = \sqrt{\frac{\sum(r^2)}{N - 1}},$$

where $r$, the residual, is the difference between the observed value of $10^4 k_1$ and its mean value, and $N$ is the number of determinations.

The results are given in Table 19.

**TABLE 19**

<table>
<thead>
<tr>
<th>Alkali</th>
<th>N</th>
<th>Mean $10^4 k_1$ (sec.)</th>
<th>$\sigma$ (sec.)</th>
<th>Standard Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>6</td>
<td>2.034</td>
<td>0.019</td>
<td>0.93</td>
</tr>
<tr>
<td>P - OH</td>
<td>7</td>
<td>3.521</td>
<td>0.017</td>
<td>0.49</td>
</tr>
</tbody>
</table>

The standard deviation of the determinations is therefore in the region of 0.5 to 1.0%.
The variations of $k_1$ with $[OH^-]$ for sodium hydroxide (Table 7) and for the polymeric quaternary ammonium hydroxide (Table 10) are presented graphically in Fig. 5.

Similarly, the dependence of $k_1$ on added-salt concentration (Tables 11 and 12) is also given graphically in Fig. 6.

The data from Table 14 are given in Fig. 7 and Fig. 8 as graphs of $k_1$ against $D$ and $\log_{10}k_1$ against $D^{-1}$ respectively.

**Derivation of the Activation Parameters**

The activation parameters were derived from the data in Table 16 and Table 18 by means of Arrhenius plots [79] of $\log_{10}k_2$ against $T^{-1}$; see Fig. 9. The Arrhenius activation energy, $E_a$, for each reaction was evaluated from the gradient of the appropriate straight line by the relationship

$$E_a = -R \times 2.303 \times \text{gradient},$$

where $R$ is the universal gas-constant, 1.986 cal.deg.$^{-1}$ mole.$^{-1}$ [80]. The pre-exponential Arrhenius $A$ factor was then obtained by substitution of the appropriate value of $E_a$ in the equation

$$\log_{10}A = \log_{10}k_2 + \frac{E_a}{2.303RT},$$

$\log_{10}k_2$ and $T^{-1}$ being obtained from the ordinate and abscissa, respectively, of any convenient point on the Arrhenius plot (actually, at $10^3 \cdot T^{-1} = 3.356$).
Fig. 6 Salt effects, at 25.00°C. Hydroxide concentration: 1.00x10^-2 N.
Fig. 7 The dependence of $k_1$ upon the macroscopic dielectric constant ($D$) of the solvent, at 25.0°C.
\[ y = \log_{10} k_1 \]

- Sodium hydroxide
- Polymeric quaternary ammonium hydroxide

**Fig. 8**
Fig. 9 Arrhenius plot.

- Sodium hydroxide
- Polymeric quaternary ammonium hydroxide
The enthalpy of activation at 298°C, $\Delta H_{298}^\text{a}$, was obtained from the relationship

$$\Delta H_{298}^\text{a} = E_a - 298R,$$

while the entropy of activation at 298°C, $\Delta S_{298}^\text{a}$, was evaluated from the equation

$$\Delta S_{298}^\text{a} = 2.303R \left( \log_{10} A - 13.227 \right).$$

The free energy of activation at 298°C, $\Delta F_{298}^\text{a}$, was then obtained from the equation

$$\Delta F_{298}^\text{a} = \Delta H_{298}^\text{a} - 298 \cdot \Delta S_{298}^\text{a}.$$

The derivations of these expressions are given in Appendix 5.

Table 20 gives the values obtained for the activation parameters.

**TABLE 20**

Activation Parameters at 298°C

Key. NaOH : sodium hydroxide, P - OH : polymeric quaternary ammonium hydroxide

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$10^{-4} E_a$ (cal.mole$^{-1}$)</th>
<th>$10^{-10} A$ (1.mole$^{-1}$sec$^{-1}$)</th>
<th>$10^{-4} \Delta H_{298}^\text{a}$ (cal.mole$^{-1}$)</th>
<th>$\Delta S_{298}^\text{a}$ (cal.deg$^{-1}$mole$^{-1}$)</th>
<th>$10^{-4} \Delta F_{298}^\text{a}$ (cal.mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>1.69</td>
<td>4.85</td>
<td>1.63</td>
<td>-11.6</td>
<td>1.97</td>
</tr>
<tr>
<td>P-OH</td>
<td>1.79</td>
<td>48.1</td>
<td>1.73</td>
<td>-7.07</td>
<td>1.94</td>
</tr>
</tbody>
</table>
Measurement of the Mean Molal Activity Coefficients of Hydroxyl Ions in Aqueous Polymeric Quaternary Ammonium Hydroxide Solutions

Preparation of Solutions

An aliquot (2.60 ml.) of 0.09618N polymeric hydroxide was added, from a calibrated 5 ml. graduated pipette, to a tared 25.00 ml. graduated flask, and its weight determined. The alkali was then diluted to 25.00 ml. with carbon dioxide-free water saturated with nitrogen, and the weight of the solution ascertained. The molality, m, of the hydroxyl ion would then be calculated, and was found to be 0.01006 m and 0.01003 m respectively for duplicate preparations.

In a similar way, polymeric quaternary ammonium hydroxide solutions were made with molalities of 0.005028 m and 0.005027 m respectively.

Sodium hydroxide solutions were prepared in a corresponding manner.

pH Measurements

An E.I.L. Model 23/A pH meter was employed, with a GHS 23 general purpose glass electrode and a calomel half-cell, containing a saturated aqueous potassium chloride solution. The liquid junction between the test solution and this saturated potassium chloride solution was established by means of a porous
The hydroxonium-ion activity, $a_H^+$, was assumed to be given by the approximate relationship

$$\text{pH} = -\log_{10} a_H^+.$$  

Now $a_H^+$ is related to the activity of the hydroxyl ion, $a_{OH^-}$, by the equation
\[ a_{OH} = K_w a_H^{-1} \]

where \( K_w \) is the thermodynamic ion product constant of water at 25.00°, which is equal to \( 1.008 \times 10^{-14} \) [82]. Hence

\[
\log_{10} a_{OH} = \text{pH} - 13.9965.
\]

The values of \( a_{OH} \) were then used to obtain the mean molal activity coefficients, \( \gamma_+ \), of the hydroxyl ions from the equation

\[
\gamma_+ = \frac{a_{OH}}{m}.
\]

The results are given in Table 21.

**TABLE 21**

Approximate Mean Molal Activity Coefficients of Hydroxyl Ions (\( \gamma_+ \)) at 25.0°C in Aqueous Alkali Solutions


<table>
<thead>
<tr>
<th>Alkali</th>
<th>(10^2m)</th>
<th>pH</th>
<th>(10^2a_{OH})</th>
<th>(\gamma_+)</th>
<th>Mean (\gamma_+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>1.006</td>
<td>11.94</td>
<td>0.878</td>
<td>0.87</td>
<td>0.87</td>
</tr>
<tr>
<td>NaOH</td>
<td>1.003</td>
<td>11.94</td>
<td>0.878</td>
<td>0.88</td>
<td>0.88</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.5018</td>
<td>11.65</td>
<td>0.450</td>
<td>0.90</td>
<td>0.89</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.5017</td>
<td>11.65</td>
<td>0.440</td>
<td>0.88</td>
<td>0.88</td>
</tr>
<tr>
<td>P-OH</td>
<td>1.006</td>
<td>11.71</td>
<td>0.517</td>
<td>0.51</td>
<td>0.51</td>
</tr>
<tr>
<td>P-OH</td>
<td>1.006</td>
<td>11.70</td>
<td>0.505</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>P-OH</td>
<td>0.5028</td>
<td>11.50</td>
<td>0.278</td>
<td>0.55</td>
<td>0.55</td>
</tr>
<tr>
<td>P-OH</td>
<td>0.5027</td>
<td>11.50</td>
<td>0.278</td>
<td>0.55</td>
<td>0.55</td>
</tr>
</tbody>
</table>
Analysis of Products from the Hydroxyl Ion-Catalysed Decomposition of Nitrosotriacetonamine in Aqueous Alkali

The following abbreviated terms will be used to distinguish between two 2,4-dinitrophenylhydrazine reagent solutions which were employed for the preparation of derivatives:

Aqueous DNPH: a 0.4% solution of 2,4-dinitrophenylhydrazine in 2N aqueous hydrochloric acid.

Methanolic DNPH: a 1.9% solution of 2,4-dinitrophenylhydrazine in methanolic sulphuric acid.

The latter reagent was prepared by the addition of concentrated sulphuric acid (8 ml.) to 2,4-dinitrophenylhydrazine (4 g.) followed, after the mixture had been warmed to obtain a clear solution, by methanol, with cooling, until the total volume was 200 ml. Finally, distilled water (10 ml.) was added to the solution.

Gas-liquid Chromatography

A W.G. Pye Argon chromatograph was used in conjunction with a column (2501/2/10 DNP), of 4 mm. internal diameter, packed with Celite on which was adsorbed a dinonyl phthalate stationary phase. The length of the column was 121 cm.

The following operating conditions were employed:
Infra-red Absorption Spectra

These were obtained with a Perkin-Elmer "Infracord" spectrophotometer, the samples being held by capillary action as films between two sodium chloride discs.

Ultra-violet Absorption Spectra

The wavelengths at which solutions of 2,4-dinitrophenylhydrazones in chloroform gave their maximum absorptions were measured by the use of a Perkin-Elmer Model 137 UV spectrophotometer with 1 cm. silica cells.

Conversions 1, 2 and 3

The products obtained from the decomposition of nitroso-triacetonamine in the presence of aqueous sodium hydroxide, and in the presence of polymeric quaternary ammonium hydroxide solution, at the same hydroxyl-ion concentration as that used in the majority of kinetic runs, viz. 0.01 N, were investigated.

Three decompositions were carried out; these were designated Conversions 1, 2 and 3 respectively. Conversions 1
and 2 were effected in the presence of aqueous sodium hydroxide and polymeric quaternary ammonium hydroxide solutions respectively, while Conversion 3 was a repetition of Conversion 1 on a larger scale.

Conversion 1. Nitrosotriacetonamine (2.23 g.) was mixed with 0.01N aqueous sodium hydroxide solution (40 ml.) in a flask which had been purged with nitrogen, and the mixture was left, with occasional swirling, in a thermostat at 25.00° for 24 hours under an atmosphere of nitrogen. The nitrosotriacetonamine, being only slightly soluble in water, remained as a separate phase and formed a froth with the nitrogen which was evolved. After about 1 hour the aqueous phase developed a cloudiness. Meanwhile, the nitrosotriacetonamine was slowly replaced by a supernatant cloudy liquid layer.

The mixture was extracted with distilled diethyl ether (50, 30, 20 ml.), AR sodium chloride (1 g.) being dissolved in the aqueous solution to give a sharp separation of the two phases. Although the ether layer was not washed with water, a small sample of it gave a neutral reaction with water and phenolphthalein, showing that no alkali was present. The ether solution (100 ml.) was dried over sodium sulphate.

Conversion 2. Nitrosotriacetonamine (2.03 g.) was decomposed in the presence of 0.01N aqueous polymeric quaternary ammonium hydroxide solution (40 ml.) under conditions identical
to those used for Conversion 1. The product was also extracted and dried in exactly the same way.

Conversion 3. Nitrosotriacetonamine (5.14 g.) was mixed with 0.01N aqueous sodium hydroxide solution (100 ml.) and the mixture treated in the same way as was that of Conversion 1. After AR sodium chloride (2 g.) had been dissolved in the aqueous solution the product was extracted with distilled diethyl ether (100, 100, 50 ml.) and the ethereal solution dried over sodium sulphate.

Preparation of Authentic Samples

Acetone was distilled; b.p. 56°, \( n_D^{25} \) 1.3558.

Mesityl oxide was fractionally distilled thrice under dry nitrogen to give a colourless liquid; b.p. 128°, \( n_D^{25} \) 1.4412.

The 2,4-dinitrophenylhydrazone was prepared (see p. 140); m.p. 200°, literature value [83]: 198-199°.

Phorone was prepared by the method of Clibbens and Francis [2]. Nitrosotriacetonamine (6.0 g.) was dissolved in 0.025N ethanolic potassium ethoxide solution (8 ml.) under an atmosphere of nitrogen in a loosely-stoppered flask and the solution left for 5 days. Carbon dioxide was then passed through the solution for 5 minutes and the potassium carbonate which had separated was filtered off. Absolute ethanol (2 ml.) was used to wash the precipitate. The combined filtrate and
washings were chilled in a Dewar flask of solid carbon dioxide for thirty minutes and the phorone which had crystallised was quickly separated from the mother liquor by filtration under suction and washed with similarly chilled absolute ethanol (20 ml.). The phorone was then hastily transferred to a Petri dish and dried for 1 hour at 20 mm. to yield a mass of pale yellow, large needles (0.45 g.). The volume of the combined mother liquor and washings was reduced to 6 ml. by evaporation on a steam bath, and the chilling process repeated. By these means a further quantity of phorone (0.43 g.), was obtained. The combined product (0.88 g.) had m.p. 27.5°, literature value \([84]\): 27.54°, and the smell resembled that of geraniums, as reported by Baeyer \([85]\). The phorone was stored in a well-stoppered bottle, since it tends to vaporise \([84]\). 

The 2,4-dinitrophenylhydrazone was prepared (for the method, see p.141); m.p. 114.5°, literature value \([86]\)115-116°.

Gas-liquid Chromatographic Analysis of the Products

The dried ethereal solutions derived from Conversions 1 and 2 were analysed by gas-liquid chromatography, the sample size being 7.35 μl. in both cases. The chromatograms are given in Fig.10 and Fig.11 respectively. The very early large peak in either chromatogram is that of diethyl ether. These chromatograms revealed the presence in both solutions of the same three major components, which were designated A, B and C in the order
Fig. 10 Gas-liquid chromatogram of an ethereal solution of the products from Conversion 1.
Fig. 11 Gas-liquid chromatogram of an ethereal solution of the products from Conversion 2.
of their retention times (5.31, 28.1 and 51.6 minutes respectively). For the sake of brevity, the corresponding peaks will also be referred to as A, B and C. A fourth very small peak, again common to both solutions, was also present, having a retention time of 3.90 minutes. The only outstanding difference between the chromatograms lay in the fact that peak B in the one derived from Conversion 2 was smaller in area than peak B in the other one by a factor of about 7 (see Table 22).

A and C were identified as mesityl oxide and phorone respectively by comparison of the retention times with those for 1% ethereal solutions of the authentic compounds (5.31 and 51.6 minutes respectively). It was further noted that the minor peak, of retention time 3.90 minutes, occurred in the chromatogram of authentic mesityl oxide as well as in those of the reaction products. This peak is possibly due to the isomer, isomesityl oxide, described by Stross, Monger and Finch [87].

Comparison of the relative areas of peaks A and C with those obtained from mixtures of known composition, prepared from the authentic components, indicated that in the products from both Conversions 1 and 2 the proportion of phorone to mesityl oxide was approximately 0.7 : 1 by weight (see Table 22). Since the peaks were approximately triangular in shape, the area of each peak was obtained from the product of the peak height and the width half-way up the peak.
TABLE 22
Areas under the Chromatogram Peaks

<table>
<thead>
<tr>
<th>Conversion</th>
<th>Peak Area (cm.²)</th>
<th>Area under C</th>
<th>Area under B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>1.51</td>
<td>0.735</td>
<td>1.80</td>
</tr>
<tr>
<td>2</td>
<td>1.55</td>
<td>0.105</td>
<td>1.92</td>
</tr>
<tr>
<td>Proportion of Phorone to Mesityl Oxide, w/w.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.15</td>
<td>1.34</td>
<td>-</td>
<td>3.09</td>
</tr>
<tr>
<td>0.548</td>
<td>1.51</td>
<td>-</td>
<td>1.41</td>
</tr>
</tbody>
</table>

A 0.25% ethereal solution of nitrosotriacetanilide (sample size 7.35 μl.) produced no peak when it was added to the column.

Identification of a Water-soluble Product

To each of the aqueous solutions which remained after the ether extractions of the mixtures from Conversions 1 and 2 had been carried out, aqueous DNPH reagent (100 ml.) was added.

The solution from Conversion 1 yielded a yellow precipitate
which coagulated readily. After the mixture had been left for 2 hours, the precipitate was collected by filtration, washed thoroughly with water and dried to give a yellow powder (0.393 g.). The addition of more aqueous DNPH to the filtrate produced no further precipitation. Recrystallisation of the derivative from methanol to constant melting point gave golden yellow prisms and needles, m.p. 125-125.5°.

A sample of acetone 2,4-dinitrophenylhydrazone was prepared in the same way from authentic acetone (see p.128), and had m.p. 125-125.5°. The mixed melting point with the above derivative was also 125-125.5°, whence it was concluded that the derivative was acetone 2,4-dinitrophenylhydrazone and that acetone was a product from Conversion 1.

The aqueous solution from Conversion 2 also gave a yellow precipitate, but because of the presence of the poly-cation the solid remained too finely dispersed for filtration to be possible. After 10 days the precipitate had settled sufficiently for the supernatant liquid to be decanted from the solid. The addition of more aqueous DNPH to the decanted liquid gave no further precipitation. The wet pad of solid was then crystallised from methanol and the mother liquor evaporated to dryness, the combined weight of crystals and residue being 0.366 g. Recrystallisation of the crystals from methanol to constant melting point gave golden yellow needles, m.p. 125.5°.
The mixed melting point with authentic acetone 2,4-dinitrophenylhydrazone was 125.5° also. Acetone was therefore a product from Conversion 2.

**Fractional Distillation of the Products**

Known volumes of the ethereal solutions obtained from Conversions 1, 2 and 3 were distilled separately on a water bath at 60–65° to remove as much of the ether as possible. The weight of the residual yellow liquid was then determined in each case. The results are given in Table 23.

**TABLE 23**

<table>
<thead>
<tr>
<th>Conversion</th>
<th>Volume of Ether Soln. (ml.)</th>
<th>Corresponding Weight of Nitrosotriacetanilide (g.)</th>
<th>Weight of Residual Liquid (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70</td>
<td>1.56</td>
<td>1.42</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>1.42</td>
<td>1.06</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>5.14</td>
<td>3.63</td>
</tr>
</tbody>
</table>

Each liquid sample was fractionally distilled under reduced pressure in the presence of nitrogen. These distillations were carried out slowly in a small bulb of 4 ml. capacity with a well-lagged Vigreux column, 5 cm. long and of
5 mm. internal diameter, the distillates being collected in the side arm at the top of the column. A fine stream of nitrogen was drawn through the liquids during the distillations.

The details of the fractions obtained from Conversions 1, 2 and 3 are given in Tables 24, 25 & 26 respectively.

**TABLE 24**

Fractional distillation of products from Conversion 1

Weight of crude liquid: 1.42 g.

Pressure: 20 mm.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>B.p. (°)</th>
<th>Weight (g.)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/1</td>
<td>32</td>
<td>0.111</td>
<td>colourless</td>
</tr>
<tr>
<td>1/2</td>
<td>82-86</td>
<td>0.035</td>
<td>pale yellow</td>
</tr>
<tr>
<td>1/3</td>
<td>86-92</td>
<td>0.060</td>
<td>pale yellow</td>
</tr>
<tr>
<td>1/4</td>
<td>92-98</td>
<td>0.140</td>
<td>pale yellow</td>
</tr>
<tr>
<td>1/5</td>
<td>98-102</td>
<td>0.068</td>
<td>very pale yellow</td>
</tr>
<tr>
<td>1/Residue</td>
<td>-</td>
<td>0.056</td>
<td>light brown</td>
</tr>
</tbody>
</table>

|          |          | 0.470       |                   |
TABLE 25

Fractional distillation of products from Conversion 2.

Weight of crude liquid : 1.06 g.

Pressure : 20 mm.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>B.P. (°)</th>
<th>Weight (g.)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/1</td>
<td>32</td>
<td>0.099</td>
<td>colourless</td>
</tr>
<tr>
<td>2/2</td>
<td>80-88</td>
<td>0.095</td>
<td>pale yellow</td>
</tr>
<tr>
<td>2/3</td>
<td>88-94</td>
<td>0.271</td>
<td>pale yellow</td>
</tr>
<tr>
<td>2/Residue</td>
<td>-</td>
<td>0.010</td>
<td>light brown</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.475</td>
<td></td>
</tr>
</tbody>
</table>

Redistillation of fraction 2/3

<table>
<thead>
<tr>
<th>Fraction</th>
<th>B.P. (°)</th>
<th>Weight (g.)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/3A</td>
<td>88-92</td>
<td>0.059</td>
<td>pale yellow</td>
</tr>
<tr>
<td>2/3B</td>
<td>92-94</td>
<td>0.018</td>
<td>pale yellow</td>
</tr>
<tr>
<td>2/3/Residue</td>
<td>-</td>
<td>0.029</td>
<td>very pale yellow</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.106</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 26

Fractional distillation of products from Conversion 3.

Weight of crude liquid : 3.63 g.
Pressure : 20 mm.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>B.p. (°)</th>
<th>Weight (g.)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/1</td>
<td>32</td>
<td>0.418</td>
<td>colourless</td>
</tr>
<tr>
<td>3/2</td>
<td>84-90</td>
<td>0.417</td>
<td>pale yellow</td>
</tr>
<tr>
<td>3/3</td>
<td>90-98</td>
<td>0.407</td>
<td>pale yellow</td>
</tr>
<tr>
<td>3/4</td>
<td>98-100</td>
<td>0.291</td>
<td>pale yellow</td>
</tr>
<tr>
<td>3/5</td>
<td>100-102</td>
<td>0.447</td>
<td>very pale yellow</td>
</tr>
<tr>
<td>3/Residue</td>
<td>-</td>
<td>0.140</td>
<td>light brown</td>
</tr>
</tbody>
</table>

Redistillation of fraction 3/2

| 3/2A     | 78       | 0.071       | very pale yellow |
| 3/2/Residue | -    | -           | pale yellow     |
The discrepancy between the total weight of distillate and the weight of the crude liquid in all three instances is attributed to the presence in the crude liquid of diethyl ether and acetone.

Fractions 1/1 and 2/1 both had $n_D^{25} 1.4430$. Fractions 1/5 and 2/3/Residue possessed a sweet smell similar to that from the skins of well-ripened oranges. Fraction 3/5 ($n_D^{25} 1.4655$) also gave this smell. Fraction 3/2A ($n_D^{25} 1.4650$) had an odour which, although similar to, was less powerful than that of phorone. All the other intermediate fractions possessed the characteristic smell of phorone.

Gas-liquid Chromatographic Analysis of the Fractions

Sample size: 0.025 µl.

The analysis showed that both fractions 1/1 and 2/1 were pure mesityl oxide. Fraction 1/2 was estimated to contain approximately equal amounts of phorone and compound B, while fractions 1/3 and 1/4 were progressively richer in phorone. Fraction 2/2 gave a pronounced phorone peak, while the area of peak B was relatively small. Peak B was also small in the chromatogram of the original product mixture in this case. Fractions 2/3A and 2/3B gave the phorone peak only.

The chromatogram of fraction 3/2A showed that this
fraction was rich in compound B, the area of peak B being approximately five times as great as that of the phorone peak; no other peaks were present.

Fraction 3/5 gave a small phorone peak and a new small peak D with a retention time of 92.8 minutes. This peak had approximately the same height as the phorone peak and was unsymmetrical, the following edge tending to "tail off". Furthermore, the base line of the chromatogram began to deviate from a straight line almost as soon as the sample was added to the column. This deviation took the form of a long low "hump" with its highest point at a retention time of about 40 minutes. The base line returned to its original linearity after peak D had developed. It is thought that such behaviour was caused by the decomposition of the compound D on the column.

The Preparation of 2,4-Dinitrophenylhydrazones

To fractions 1/1 and 2/1 (0.1 g. each) was added methanolic DNPH (7 ml. each). Small red prisms separated almost immediately. After 2 hours the solids were isolated and recrystallised from 96% ethanol to constant melting points. Mixed melting points with the 2,4-dinitrophenylhydrazone of mesityl oxide, which had been prepared in the same way from authentic mesityl oxide, were also determined. The values were:
authentic derivative; m.p. 200°.
derivative from fraction 1/1; m.p. 200°.
mixed m.p. 199-200°.
derivative from fraction 2/1; m.p. 199-200°.
mixed m.p. 199-200°.

These results confirm that mesityl oxide was a product of both Conversions 1 and 2.

To fractions 1/4 and 2/3A (0.05 g. each) was added methanolic DNPH (7 ml. each). After 1 hour the red solutions were each scratched with a glass rod, which produced rapid separation of thin red crystals. The mixtures were set aside for 2 hours before the solids were isolated and recrystallised, as thin red needles, to constant melting points from methanol. The melting points and the mixed melting points with the 2,4-dinitrophenylhydrazone which had been prepared in the same way from authentic phorone were:

authentic derivative; m.p. 114.5°.
derivative from fraction 1/4; m.p. 114.5°.
mixed m.p. 114.5-115°.
derivative from fraction 2/3A; m.p. 114.5°.
mixed m.p. 114.5-115°.

The formation of phorone in both Conversions 1 and 2 was therefore confirmed.
To fraction 3/2A (0.03 g.) was added methanolic DNPH (3 ml.). After 1 hour the red solution was scratched with a glass rod, whereupon orange-red crystals rapidly formed. After a further 2 hours the derivative was isolated by filtration and recrystallised from methanol as small orange-red prisms, m.p. 104.5°, N found 17.9, C_{15}H_{18}N_{4}O_{4} requires 17.6%. The m.p. quoted above was 0.5° higher than that of the crystals from the previous crystallisation but there was not a sufficient quantity of the derivative for further purification to be effected.

The main ultra-violet absorption band of this derivative, as a solution in chloroform (0.002 g. dl.⁻¹), had a maximum absorption at 37400 Å.

A mixed melting point of this derivative with the 2,4-dinitrophenylhydrazone of authentic phorone was 84-88°. Consequently it was concluded that the derivative was the 2,4-dinitrophenylhydrazone of B and not the impure phorone derivative.

To fractions 2/3/Residue (0.03 g.) and 3/5 (0.19 g.) was added methanolic DNPH (5 ml. and 15 ml. respectively). Needles separated over a period of 20 hours from both solutions. Each derivative was isolated by filtration, washed with methanol and recrystallised from 96% ethanol to yield light-orange, thin needles of constant m.p. 168.5°; N found 16.8, 16.7
and 16.9, 16.95 respectively, calculated for $C_{15}H_{20}N_4O_5$ : 16.7%.
The two derivatives were shown to be identical when their mixture also gave m.p. 168.5°.

The main ultra-violet absorption hand of this derivative, as a solution in chloroform (0.001 g. dl. $^{-1}$), had a maximum at 3650A.

The melting point of the derivative corresponds reasonably well with that reported by Connolly [83] and Craven and Ward [84] for the common 2,4-dinitrophenylhydrazone obtained from semiphorone, triacetone dialcohol and 2,2,6,6-tetramethyl-tetrahydro-4-pyrene. These authors quote melting points of 171-172.5° and 169.5-170°, respectively.

The orange-like odours of fractions 1/5, 2/3/Residue and 3/5 indicate that semiphorone (2,6-dimethyl-6-hydroxy-2-hepten-4-one) is the major component in all three, since Connolly [83] observed that this compound had such a smell. The 2,4-dinitrophenylhydrazones obtained from these late fractions are therefore probably derived from semiphorone.

The 2,4-dinitrophenylhydrazone of nitrosotriacetonamine was prepared in order to find how it compared with the derivatives isolated from the products.

To nitrosotriacetonamine, m.p. 70-70.5°(0.50 g.) dissolved in methanol (1 ml.) was added a 10% excess of methanolic DNPH (33 ml.). After 5 minutes crystals began to
separate from the orange solution. The mixture was set aside for 2 hours before the derivative was isolated by filtration, washed with methanol (20 ml.) and air-dried. The resulting pale yellow solid (0.76 g.) consisted of small prisms, m.p. 185-187°. Recrystallisation from n-butanol, to constant melting point, yielded lemon-yellow crystals as small prisms, m.p. 188.5°. N found 22.7, 22.7, C15H20N6O5 requires N 23.1%.

None of the derivatives obtained from the products of the decompositions corresponded to this compound.

The Infra-red Absorption Spectra of the Fractions

The spectrum of fraction 3/2A is given in Fig. 12. The absorption peak at 1690 cm.⁻¹ is indicative of the presence of a ketonic carbonyl group in conjugation with a \( \text{C} = \text{C} \) group, and the peak at 1630 cm.⁻¹ corresponds to that of a \( \text{C} = \text{C} \) group. The presence of a \( R_1R_2C = CH_2 \) grouping is suggested by the absorption peaks at 3080 cm.⁻¹ and 895 cm.⁻¹ and by the shoulder at 1640 cm.⁻¹. The spectrum resembles almost exactly that obtained in carbon tetrachloride and cyclohexane by Craven and Ward [84] for the phorone isomer, which these authors showed to be 2,6-dimethyl-1,5-heptadien-4-one. The few regions where the spectra differ slightly can be attributed to the presence of phorone, which is known to be present from the gas-liquid chromatograms, and to semiphorone. The infra-red absorption spectrum of phorone is given in Fig. 13. From this
Fig. 12 Infrared absorption spectrum of fraction 3/2A.
evidence, it was concluded that compound B was 2,6-dimethyl-
1,5-heptadien-4-one.

Fraction 3/5 gave an absorption spectrum, see Fig. 14, with a sharp absorption at 3500 cm.\(^{-1}\) indicating the presence of the hydroxyl group, in intermolecular dimeric association. The conjugated ketonic carbonyl absorption is also present at 1690 cm.\(^{-1}\) with the \(\text{C} = \text{O}\) peak at 1620 cm.\(^{-1}\). A peak at 1160 cm.\(^{-1}\) and a shoulder at 1360 cm.\(^{-1}\) suggest that a tertiary alcohol group is present. On the other hand, however, peaks at 1050 cm.\(^{-1}\) and 1320 cm.\(^{-1}\) could be due to a primary alcohol group, while those at 1110 cm.\(^{-1}\) and 1320 cm.\(^{-1}\) could be attributed to a secondary alcohol group. In spite of this, the spectrum does support the conclusion that semiphorone, and not triacetone dialcohol or 2,2,6,6-tetramethyltetrahydro-4-pyrone, was a product (compound D) from the decompositions.

The Action of Aqueous Alkali on Fraction 3/5

Fraction 3/5 (0.20 g.), consisting mainly of semiphorone, was dissolved in 0.01N aqueous sodium hydroxide solution (20ml.) under an atmosphere of nitrogen, and the solution left for 24 hours at room temperature (approximately 24\(^{\circ}\)).

The solution was then extracted with distilled diethyl ether (10.5, 5 ml.) after AR sodium chloride (0.5 g.) had been added to assist the separation of the two layers. The ether extract was dried over sodium sulphate for 24 hours and then
Fig. 14. Infra-red absorption spectrum of fraction 3/5.
analysed by gas-liquid chromatography. The sample size was 4.90 µl.

A solution of fraction 3/5 (0.007 g.) in distilled diethyl ether (0.7 ml.) was also analysed in the same way. In neither case was peak D detected, while in both cases peak C (phorone) was very small and of the same area. The outstanding difference between the two chromatograms was that the extract from the alkali treatment gave a pronounced peak A (mesityl oxide) while the solution of un-treated fraction 3/5 did not give this peak.

To the aqueous phase, remaining after the ether extraction of the mixture, was added aqueous DNPH (40 ml.). After 2 hours, the yellow precipitate (0.082 g.) which had formed was isolated by filtration and recrystallised to constant melting point from methanol to give golden yellow needles, m.p. 125.5°. The mixed melting point with the 2,4-dinitrophenylhydrazone of authentic acetone was also 125.5°.

**The Stability of Phorone in Aqueous Alkali**

Phorone (0.1 g.) was added to 0.03N aqueous sodium hydroxide (20 ml.) and the mixture warmed slightly to melt the phorone. After it had been left at room temperature for 24 hours the mixture was extracted with distilled
diethyl ether (2 x 20 ml.) and the extract washed with water (3 x 50 ml.).

The gas-liquid chromatogram of the sodium sulphate-dried extract (sample size 7.35 µl.) was identical with that of a 1% solution of phorone in ether; the phorone peak only was present in both cases.
DISCUSSION
The Preparation of Triacetonamine by the Reaction of Acetone and Ammonia

The reaction between acetone and ammonia produces several amines, including diacetonamine(I) and triacetonamine(II).

Heintz [88] showed that triacetonamine was obtained when the reaction mixture was heated, but that diacetonamine was the main product when the reaction was carried out at room temperature. Since acetone dissolves only small proportions of ammonia the preparations were slow, and the passage of ammonia was a lengthy process. However, Everest [89] was able to achieve a rapid exothermic up-take of ammonia by the inclusion of anhydrous calcium chloride in the reaction mixture. The mixture could then be set aside while the conversion to diacetonamine proceeded, the labile calcium chloride-ammonia complex presumably acting as an ammonia reservoir. Ammines of calcium chloride are known with up to eight ammonia groups per calcium atom [90]. The separate lower layer which developed in the reaction mixture was believed to be a concentrated aqueous calcium
chloride solution formed by the water eliminated in the course of the reaction [89].

The triacetonamine preparation used in this investigation (see p. 44) was developed by Francis [53]. In this method anhydrous calcium chloride was again employed, and the reaction mixture was subsequently heated to effect the condensation to triacetonamine. In agreement with the observation of Francis [53], a white solid re-formed during the heating stage of the present preparation. The solid was not calcium chloride since it was insoluble in water, but it did contain calcium.

Triacetonamine can be obtained in good yields when diacetonamine is heated with acetone for prolonged periods [91]. It is also obtained from phorone and ammonia when the reaction mixture is heated, while triacetonediamine is formed in the cold [92]. The analogous reaction occurs with mesityl oxide, when the ammonia adds to the double bond to give diacetonamine [93].

Two possible courses for the condensation of acetone and ammonia have been proposed [94]. In the first, the acetone condenses to mesityl oxide and thence to phorone under the influence of the ammonia, which then adds to these unsaturated products to yield the amines. In the second, the ammonia and the acetone give initially the unstable acetone-ammonia adduct, further condensations of which yield the amines.
Addition Polymers

Certain unsaturated organic compounds possess the ability to undergo conversion into high molecular weight polymers by means of successive addition reactions at the ends of growing polymeric chains. The most widely investigated group of these addition polymers is that derived from vinyl compounds, \( \text{CH}_2 = \text{CHX} \), in which the presence of suitable substituent groups, \( X \), has the effect of facilitating polymerisation. Examples of readily-polymerisable vinyl monomers are: styrene \( (X = -\text{C}_6\text{H}_5) \), vinyl acetate \( (X = -\text{O}_2\text{C} \cdot \text{CH}_3) \) and acrylic acid \( (X = -\text{CO}_2\text{H}) \).

The macromolecular nature of these polymeric substances was not widely accepted until about 1930. Before this time the main body of opinion favoured the view that the high observed molecular weights were due to the existence of aggregates of relatively small individual molecular units held together with intermolecular forces. Thus, Stobbe and Posnjak [95] sought to account for the observed high molecular weight of polystyrene by assigning to it a structure in which relatively small cyclic molecules, formed by addition reactions of styrene, were associated into larger aggregates by intermolecular forces. Staudinger [96], however, in 1920 maintained that polymers such as polystyrene were in fact truly macro-
molecular, each macromolecule being composed of a large sequence of covalently bound repeating units.

An important obstacle to the acceptance of this macromolecular structure for polymers was the absence of any evidence for the presence of end groups, which were necessary to meet the valency requirements at each end of a polymer chain. To circumvent this problem it was assumed that the large sizes of the macromolecules greatly reduced the reactivity of the terminal free radicals, so that no end groups were required. Only when Flory [97] deduced the mechanism of addition polymerisation was it fully realised that the macromolecules were terminated in normal chemical structures with their valency requirements fully satisfied.

Mechanism

The mechanism of addition polymerisation suggested by Staudinger [96] is that of a radical chain reaction, and Flory [97], from a consideration of the kinetics of addition polymerisation, demonstrated that the mechanism consists of the initiation, propagation and termination stages typical of chain reactions. Thus, as the name implies, radical chain polymerisation is initiated by free radicals and is propagated by the generation of chain-molecules bearing free radical end-groups. The initiating free radicals are normally produced in the
reaction mixture by the thermal or photochemical decomposition of a small proportion of an initiator, which is commonly a peroxide, hydroperoxide, azo-compound or diazo-compound. Initiating free radicals can also sometimes be formed by the thermal or photochemical homolytic decomposition of the monomer itself. Styrene, for example, is known to undergo thermally initiated polymerisation.

The polystyrene used in the present investigation was prepared by radical chain polymerisation at 80.5°C in xylene solution with benzoyl peroxide as initiator. The following three mechanistic stages will therefore be considered with particular reference to this system.

**Initiation.** Benzoyl peroxide is considered to generate benzoate and phenyl free radicals in solution at elevated temperatures [98] through homolytic fission:

\[
(C_6H_5COO)_2 \rightarrow 2C_6H_5CO_2^* \rightarrow 2C_6H_5^* + 2CO_2
\]

When one of these primary free radicals encounters a monomer molecule it adds to the double bond, forming a different radical [99], which is the incipient polymer chain, e.g.

\[
C_6H_5CO_2^* + CH_2 = CH \rightarrow C_6H_5CO_2 - CH_2 - CH^* \quad \text{with} \quad C_6H_5
\]
The efficiency of an initiator represents the proportion of the primary free radicals which initiate the growth of polymer chains. For most vinyl radical addition polymerisations, this value lies between 0.6 and 1.

**Propagation.** The chain radical produced in the initiation stage adds to another monomer molecule, and the propagation cycle continues, resulting in the growth of the chain radical:

$$\text{C}_6\text{H}_5\cdot\text{CO}_2\left\{\begin{array}{c} \text{CH}_2 - \text{CH} \\ \text{C}_6\text{H}_5 \end{array}\right\}_n \text{CH}_2 - \text{CH}^{\cdot} + \text{CH}_2 = \text{CH} \rightarrow$$

$$\text{C}_6\text{H}_5\cdot\text{CO}_2\left\{\begin{array}{c} \text{CH}_2 - \text{CH} \\ \text{C}_6\text{H}_5 \end{array}\right\}_{n+1} \text{CH}_2 - \text{CH}^{\cdot} \text{C}_6\text{H}_5$$

**Termination.** The propagation of a chain does not continue unhindered, owing to the strong tendency of free radicals to form covalent bonds. Eventually, therefore, the propagation cycle is halted, normally by one of two mechanisms: combination or disproportionation. Combination proceeds by the pairing of the unpaired electrons on the growing ends of two chain radicals to produce one polymer chain:
Disproportionation also involves the interaction of two growing chains, but in this case a hydrogen atom is transferred from one chain to the other, leaving two separate unreactive chains, one of which contains a terminal double bond:

\[
\text{CH}_2 - \text{CH}^* + \text{CH} - \text{CH}_2 \rightarrow \text{CH}_2 - \text{CH} \quad \text{CH} - \text{CH}_2
\]

Polystyrene chains appear to be terminated predominantly by combination [100].

Polymerisation according to this reaction scheme produces linear polymers since the unpaired electron is always at the propagating end of the chain radical.

Flory [97] realised that the free radicals could transfer their activity to other molecules in the system, e.g. solvent molecules, by the exchange of atoms, and that the resulting free radicals could in turn often themselves initiate polymerisation. Growing polymer chains can therefore be terminated by such a chain transfer, involving the molecule YZ:

\[
\text{CH}_2 - \text{CH}^* + \text{YZ} \rightarrow \text{CH}_2 - \text{CH} - \text{Y} + \text{Z}^*.
\]
The reactivity, however, would not necessarily be lost, since the free radical $Z^*$ could initiate the formation of a new polymer chain. When chain transfer involves a monomer molecule, the deactivated polymer may be left with an unsaturated end group, or alternatively the free radical produced from the monomer may contain a double bond which, when the radical initiates chain formation, survives at the end of the polymer chain. If these unsaturated end groups are subsequently attacked by a growing chain radical and incorporated in its chain, a branched structure then results. Transfer of the unpaired electron from a growing chain to some part of another polymer chain will also result in the development of a branch on the latter. Branching, however, does not usually occur very extensively in vinyl polymerisation.

The formation of covalent bonds from unpaired electrons situated on different chain radicals produces a cross-linked structure. With vinyl polymerisations, in which the monomers contain only one double bond, this is a very infrequent reaction.

Chain transfer agents, or regulators, are sometimes used to prevent the molecular weights of polymers becoming too large. Thus, the molecular weight of polystyrene is depressed by the presence of small quantities of carbon tetrachloride. The molecules of this substance deactivate growing
polystyrene chains by the transfer to them of chlorine atoms, while themselves being converted into active trichloromethyl radicals, which can then initiate new polymer chains.

Since the propagation and termination stages involve reactive free radicals, they occur very quickly, so that the time for a fully-developed polymer chain to form is short (usually a few seconds, or less). Thus, at any stage of a chain radical polymerisation the concentration of growing chains is very low. Consequently, as the conversion of monomer to polymer progresses, the average degree of polymerisation of the product changes little.

Molecular Weight Distribution

A polymer obtained by free radical addition polymerisation is hetero-disperse, being composed of macromolecules with a range of different molecular weights. The observed molecular weight is therefore an average value, the nature of which depends upon the method used to obtain it (see p.165). Careful fractionation is necessary if polymer with a narrow distribution of molecular weight is required.

Arrangement of Structural Units

Potentially, the addition of a free radical, \( R^* \), to a vinyl monomer can occur at either the \( \alpha \)- or the \( \beta \)-carbon atom:
Three types of structural arrangement in the polymer chain are therefore possible, viz.

\[
\text{head-to-head} \quad \text{tail-to-tail} \quad \text{head-to-tail}
\]

Consideration of the stabilities of the possible chain radicals indicates that the head-to-tail structure is energetically favoured, due to the resonance stabilisation which occurs in the transition state when the unpaired electron is formally situated on the \( \alpha \)-carbon atom of the product radical. This effect is expected to be very marked in the case of styrene, since \( X \) is then the phenyl group, which would permit extensive delocalisation of the unpaired electron on the \( \alpha \)-carbon atom to occur. Head-to-tail addition is also thought to be favoured on steric grounds, since it should be easier for \( R^* \) to add to the unsubstituted \( \beta \)-carbon atom of the vinyl group rather than to the substituted \( \alpha \)-carbon atom. The virtually
complete head-to-tail arrangement of structural units in poly-
styrene has been demonstrated by Staudinger and Steinhofer [101]
who found no evidence for the existence of phenyl groups on
adjacent carbon atoms of the polystyrene chain.

The structural unit, \(-\text{CH}_2\text{CH}-\), of vinyl polymers
possesses an asymmetric carbon atom, so that each structural
unit can contain either a d- or an l-configuration. Polymers
prepared by radical chain polymerisation nearly always contain
a random distribution of these d- and l-configurations along
their chains. This atactic nature accounts for the almost
complete absence of crystallinity from these polymers.
The Molecular Weights of Polymers

Number-Average and Weight-Average Molecular Weights

An unfractionated polymer is normally heterodisperse, containing a broad distribution of macromolecular species with different molecular weights.

The number-average molecular weight, $\bar{M}_n$, of a polymer, is given by

$$\bar{M}_n = \frac{\sum c_i}{\sum \frac{c_i}{M_i}},$$

where $c_i$ is the weight of the $i$th species per unit volume of solution, and $M_i$ is the molecular weight of this species. If the number of moles of the $i$th species per unit volume of solution is $N_i$, this equation may also be expressed as

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad \ldots \quad (1)$$

An alternative mean value, the weight-average molecular weight, $\bar{M}_w$, is defined by

$$\bar{M}_w = \frac{\sum c_i M_i}{\sum c_i}$$

This expression is similar to that for $\bar{M}_n$, given in equation (1),
except that the concentration terms are on a weight basis instead of a molar basis.

The number average, $\bar{M}_n$, accentuates the contributions of the lower molecular weight species, while the weight average, $\bar{M}_w$, places greater emphasis on the heavier species. Consequently, $\bar{M}_w$ is always larger than $\bar{M}_n$, except of course when the polymer is composed of one species only. The ratio $\bar{M}_w/\bar{M}_n$ indicates the heterodispersity of the polymer.

**Molecular-Weight Determinations**

The molecular weights of polymers may be determined by the use of the following methods:

- end-group analysis,
- measurements of colligative properties,
- light-scattering measurements,
- ultracentrifugation measurements,
- viscosity measurements.

**End-Group Analysis.** This method involves the determination of the number of end groups in a known weight of the polymer. The number-average molecular weight of the polymer can then be evaluated, provided that the distribution of the end groups in the polymer is known.

**Methods based on Colligative Properties.** Molecular-weight determinations involving colligative properties are based
on thermodynamic considerations applicable to ideal solutions. In all cases therefore the measurements are carried out in dilute solutions, and the data extrapolated to zero concentration in order to derive $\bar{M}_n$.

The most convenient method is the measurement of the osmotic pressure, $\pi$, of the solution. In dilute solutions, when polymer-solvent interactions are not excessive, the graph of $\frac{\pi}{c}$ against $c$, where $c$ is the weight concentration of the polymer, gives a straight line, which, on extrapolation to $c = 0$, yields an intercept from which $\bar{M}_n$ can be obtained.

**Light Scattering.** The intensity of light scattered by macromolecules in solution is a function of their polarizability, size and weight concentration. $\bar{M}_w$ is usually derived from the intercept obtained by the extrapolation of a turbidity-concentration variable to both zero concentration and zero scattering angle.

**Ultracentrifugation.** Ultracentrifugation techniques for the determination of the molecular weights of polymers are based upon the measurement of the tendency for macromolecules in solution to move to the outside of a cell in a rapidly revolving rotor. The average molecular weights obtained by such methods are usually more complicated than either $\bar{M}_n$ or $\bar{M}_w$. 
Viscosity Measurements. Solutions of linear polymers possess high viscosities, which are manifestations of the relatively large volumes occupied by the randomly coiled linear chains. An indication of the molecular weight of a polymer can therefore be obtained by means of viscosity measurements.

The relative increase in the viscosity of a solvent due to the presence of a polymer, at a concentration $c$, is represented by the specific viscosity, $\eta_{sp}$. This quantity is defined as

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0},$$

where $\eta$ and $\eta_0$ are the viscosities of the polymer solution and the solvent, respectively. The ratio $\frac{\eta}{\eta_0}$ is termed the relative viscosity, $\eta_r$. Hence

$$\eta_{sp} = \eta_r - 1 \quad \ldots \ (2)$$

A measure of the ability of a polymer to increase the viscosity of the solvent is then given by $\frac{\eta_{sp}}{c}$, the reduced viscosity. To obtain a value of $\frac{\eta_{sp}}{c}$ which corresponds to the individual contributions of macromolecules, it is necessary to determine the limiting value at infinite dilution. This quantity, the intrinsic viscosity $[\eta]$, is defined by

$$[\eta] = \lim_{c \to 0} \left( \frac{\eta_{sp}}{c} \right) \quad \ldots \ (3)$$
It is generally found that the graph of \( \frac{\eta_{SD}}{c} \) against \( c \) for dilute polymer solutions is a straight line which can be extrapolated to \( c = 0 \) to obtain \([\eta]\). An alternative definition for \([\eta]\), which can be applied to those systems encountered in the present investigation, has been given by Kraemer [63]:

\[
[\eta] = \lim_{c \to 0} \ln \frac{\eta_r}{c} \quad \ldots \quad (4)
\]

This latter definition has the advantage that \( \ln \frac{\eta_r}{c} \) varies linearly with \( c \) less rapidly than does \( \frac{\eta_{SD}}{c} \), so that the extrapolation can sometimes be effected more accurately.

The viscosity measurements are carried out at constant temperature in capillary viscometers, and values of \( \eta_r \) are evaluated from the flow times, \( t \) and \( t_o \), for the solution and solvent respectively, by means of the equation

\[
\eta_r = \frac{t}{t_o}
\]

This is an approximate relationship which takes no account of errors introduced by (a) the difference between the densities of the solution and solvent, (b) non-streamline flow of liquid through the capillary tube, and (c) the conversion of part of the driving pressure into the kinetic energy of the liquid. For the approximation to be valid, the solutions must be sufficiently dilute to make the ratio of the densities of solution and solvent nearly unity, and \( t \) and \( t_o \) must exceed...
100 seconds to ensure that the velocities of the liquids in the capillary tube are low. The values of \( \eta_r \) may then be used to evaluate \([\eta]\) either from equation (4) or from equations (2) and (3).

In a number of cases, the linear variation of \( \frac{\eta_{sp}}{c} \) with \( c \) has been found by Huggins [62] to conform to the equation

\[
\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2c
\]

where \( k' \) is a constant, the Huggins constant, for a given polymer-solvent system. In terms of Kraemer's definition of \([\eta]\) (equation (4)), this relationship is

\[
\frac{1}{c} \ln \eta_r = [\eta] - (\frac{1}{2} - k')[\eta]^2c
\]

Therefore, if \( k' \) is known for the system, \([\eta]\) can be obtained from a single value of \( \eta_r \). This technique was used to evaluate \([\eta]\) for polystyrene in the present investigation.

\([\eta]\) is related to the size, and hence to the molecular weight, of the polymeric macromolecule. The dependence of the molecular weight of a polymer on \([\eta]\) often conforms to the relationship [102]

\[
[\eta] = KM_v^\alpha
\]

where \( K \) and \( \alpha \) are constants for a given polymer-solvent system.
For randomly-coiled linear macromolecules, $a$ lies between 0.5 and 1, commonly between 0.6 and 0.8. $\overline{M}_v$, the viscosity-average molecular weight, is defined by

$$\overline{M}_v = \left[ \sum_i w_i M_i^a \right]^{1/a}$$

(5)

where $w_i$ is the weight fraction of the $i$th species.

$\overline{M}_v$ is therefore dependent on the value of $a$.

Viscosity measurements cannot yield absolute values for molecular weights, since $K$ and $a$ must first be ascertained empirically. This calibration of a polymer-solvent system is carried out with fractionated samples of the polymer, for which $\overline{M}_w$ or $\overline{M}_n$ have been determined by one of the above absolute methods. The molecular-weight distributions of these samples must also be known for this purpose. The value of $\overline{M}_v$ for a heterodisperse polymer is generally 10 to 20% less than that of $\overline{M}_w$, and considerably higher than that of $\overline{M}_n$. Consequently it is preferable to use weight-average molecular weights, from light-scattering measurements, for the correlation of $[\eta]$ and $\overline{M}_v$. The advantage of the viscometric method of molecular-weight determination resides in its relative simplicity.

When the value of $\overline{M}_v$ cannot be estimated from one of the absolute values of average molecular weight, the relationship
\[ [\eta] = K \bar{M}_w^\alpha \]
is sometimes used for the calibration. The values of \( K \) and \( \alpha \), for polystyrene in toluene, used in the present investigation were derived in this way by Green [66], who found that this relationship was applicable for a wide range of polystyrene specimens with \( \bar{M}_w \) between 20,000 and 2,000,000, and was only slightly affected by the heterodispersity of the polymers. Thus, the values of \( \bar{M}_v \) calculated in the present investigation conform only approximately to the definition given in equation (5) and can equally well be considered as values of \( \bar{M}_w \). Consequently, it is felt that the observed values can only be expressed justifiably to two significant figures.

The Huggins constant, \( k' \), for polystyrene in toluene, 0.38, which was used to evaluate \( [\eta] \) for the polystyrene specimens in the present investigation, appears to be insensitive to temperature, since this particular value has been reported at both 25° [103] and 30° [64].

McCormick [104] has found that, for molecular weights less than 60,000, the values of \( k' \) for polystyrene in toluene are not constant, but increase as molecular weight decreases. However, the molecular weights of each batch of polystyrene prepared in the present investigation, when re-evaluated by
the use of the appropriately modified Huggins constant, differed from the uncorrected value by only 1%, so that $\bar{M}_v$, expressed to two significant figures, was unchanged.

In the absence of any reported values of $K$ and $\alpha$ for chloromethylated polystyrene, the observed values of $[\eta]$ obtained for the chloromethylated polystyrenes in the present investigation can only be used as comparative indications of the molecular weights of these polymers.
The Chloromethylation of Polystyrene

The introduction of a chloromethyl substituent group into an aromatic nucleus was first carried out by Grassi and Maselli [105], who were able to prepare benzyl chloride by the action of paraformaldehyde and hydrochloric acid on benzene. Chloromethylation has subsequently been achieved with a wide range of aromatic hydrocarbons by the application of three main procedures. In the first, a mixture of formaldehyde (as formalin or paraformaldehyde) and hydrogen chloride (or concentrated hydrochloric acid) is used, while for the second this mixture is replaced by dimethyl (or diethyl) formal and hydrochloric acid. The third method involves the use of chloromethyl methyl ether or sym-dichlorodimethyl ether as the chloromethylating agent.

Certain compounds, including the Friedel-Crafts catalysts, have proved useful in increasing the rates of some of the slower reactions. Zinc chloride is used widely for this purpose [106] and stannic chloride has sometimes proved more effective with the more unreactive compounds [107]. Glacial acetic acid [108] and concentrated sulphuric acid [109], respectively, have also been used, as have mixtures of glacial acetic acid and syrupy phosphoric acid [110]. Sulphuric acid, also aluminium chloride, when employed as catalysts, have
sometimes promoted the formation of diarylmethane derivatives.

The monochloromethylation of benzene, naphthalene and other unsubstituted aromatic compounds can be effected quite readily. Monoalkylbenzenes yield a monosubstituted product which consists mainly of the p-isomer, together with a smaller proportion of the o-isomer. Dichloromethylation occurs with some readily chloromethylated aromatic compounds such as m-xylene [111]. Alkoxy substituents also facilitate the chloromethylation of an aromatic nucleus. Halogeno substituents render the chloromethylation reaction slower than it is for the unsubstituted aromatic compound, and when the nucleus is highly substituted by halogen atoms the chloromethylation does not occur at all. Similarly, the nitro group in a benzene nucleus retards chloromethylation, as also do the chloromethyl and carboxyl groups [112]. Phenols react very readily with the chloromethylating agent and gave polymeric products.

The main side reaction occurring during chloromethylation involves the reaction of the chloromethylated product with an un-chloromethylated aromatic nucleus, to yield the diarylmethane compound, e.g.

\[
\text{phenyl-CH}_2\text{Cl} + \text{H} \overset{\text{reaction}}{\rightarrow} \text{phenyl-CH}_2\text{phenyl} + \text{HCl}
\]
This occurs more readily with the more easily substituted aromatic systems, such as phenols, and sometimes the diaryl-methane by-product preponderates, making the isolation of the chloromethylated product very difficult [113].

As is to be expected from the reactivity of monoalkyl-substituted benzene compounds, the aromatic nuclei of polystyrene macromolecules can be chloromethylated quite readily. If, however, diarylmethane-formation occurs, it constitutes a serious obstacle to the attainment of high degrees of chloromethylation, since the cross-linkages so produced:

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

render the polymer insoluble before the substitution has progressed very far.

Jones [68] was able to obtain soluble products containing moderate proportions of chloromethylated styrene units by the use of anhydrous zinc chloride as catalyst, and a large excess of chloromethyl methyl ether, which also served as a solvent for the polystyrene and its chloromethyl derivative:

\[
\begin{align*}
\text{CH}_2 &\text{CH} &\text{H} + \text{ClCH}_2\text{OCH}_3 &\text{ZnCl} \rightarrow \text{CH}_2 &\text{CH} &\text{CH}_2\text{Cl} &\text{HOCH}_3
\end{align*}
\]
In the presence of this excess of chloromethyl methyl ether, the chloromethylation of an unreacted phenyl group in the polystyrene was favoured relative to the cross-linking step, thus delaying the insolubilisation of the product. However, as the degree of chloromethylation increased, the tendency for cross-linking to occur became more pronounced, so that the product was eventually rendered insoluble, causing the gelation of the mixture. The reaction was stopped before the onset of the gelation by the addition of aqueous 1,4-dioxan [68].

The rate of the chloromethylation reaction in excess chloromethyl methyl ether with zinc chloride as catalyst is of first order with respect to the polystyrene concentration, and is independent of the degree of polymerisation [114]. The gelation occurs more readily for polystyrene with higher degrees of polymerisation [68], and the gel point appears to be characterised by a critical degree of chloromethylation for a given set of conditions [114].

Pepper, Paisley and Young [69] also investigated the chloromethylation of polystyrene in excess of chloromethyl methyl ether, with stannic chloride as catalyst. They found that the polymer usually became insoluble when its chlorine content reached about 22\%. This represents a high degree of chloromethylation, complete mono-substitution corresponding to a chlorine content of 23.2\%. 

In the present method of preparing chloromethylated polystyrene the proportion of zinc chloride used (3 moles per monomole of polystyrene) was larger, and the temperature was lower, than in the method used by Jones [68]. The chlorine content of the product (22.95%) corresponds closely to that for complete monochloromethylation of the polystyrene (23.2%). The readiness with which the product dissolved, and its low intrinsic viscosity, indicate that the degree of cross-linking resulting from the present method was very low.

The effects of substituents in the aromatic nucleus on the rates of chloromethylation in chloromethyl methyl ether [112], see p. 173, are those typically observed when the attacking reagent is electrophilic, and it is to be concluded that the chloromethyl methyl ether generates some electrophilic entity before or during the reaction, particularly when a catalyst is present. This conclusion is further supported by the fact that Freeman [115] found the proportions of o-, m- and p-isomers, obtained when isopropylbenzene was chloromethylated (with concentrated hydrochloric acid and formalin), to be 12%, 3.2% and 84% respectively, as expected for an electrophilic substitution reaction.

By analogy with these results, it is thought that the
chloromethylated polystyrene is almost completely mono-chloromethylated and contains a high proportion of p-chloromethyl groups together with smaller amounts of o- and m-isomers. This is supported by Alger's observation [67] that depolymerisation of chloromethylated polystyrene by dry distillation yielded mainly p-chloromethylstyrene.
The Quaternisation of the Chloromethylated Polystyrene

Chloromethylated polystyrene can be subjected to the Menschutkin reaction with tertiary amines to yield water-soluble polymeric quaternary ammonium chlorides [68,116]:

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

The reaction rate is of second order and is independent of the degree of polymerisation [116]. In common with the general behaviour of the Menschutkin reaction, the rate of the reaction is higher in solvents with higher dielectric constants [116].

Aqueous solutions of the product prepared with trimethylamine have been found to exhibit a variation of viscosity number with concentration, at concentrations of less than 1 g. dl.\(^{-1}\), which is typical for polyelectrolytes [68], thus indicating that, for low concentrations, the poly-cation expands as the solution is diluted (see p. 25).

Some tendency for the quaternisation of the chloromethylated polystyrene to be accompanied by cross-linking has been observed [68,116]; in the present conversion with triethylamine no indication of such a side reaction was found.
The product was a water-soluble, hygroscopic, colourless powder with a chloride-ion content corresponding to a 95.5% conversion of chloromethyl groups into quaternary ammonium groups.
Modern strongly acidic and basic ion-exchange resins are cross-linked polymers bearing strongly dissociated acidic and basic groups respectively. In an aqueous medium these resins become permeated by the water, and the ionised polymer chains attain a state closely resembling that of a free poly-electrolyte in solution, with the important difference that they are constrained to remain in the resin network by the flexible cross-linkages.

The resins are considered to give rise to two regions in an aqueous medium. The first exists within the charged polymeric network and is equivalent to a concentrated solution, approximately 1 to 10N [117], of the constrained poly-ions. The second region is the rest of the aqueous medium, which is accessible to the simple ions in the system, but not to the ionic groups fixed on the resin. The simple ions are, of course, also able to enter the first region. Such a system lends itself readily to treatment by the Donnan membrane theory [118] since the two regions may be considered to be separated by a membrane, permeable to simple ions but through which the polymeric ions are unable to diffuse. 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 in the polymer chains. If a simple electrolyte is present in the second region the counterions can be interchanged by diffusion through the 'membrane'. In addition, the simple ions with a charge of the same sign as that of the fixed charges on the resin (nebenions) can also enter the first region, accompanied by a further, equivalent, amount of the counterions.

If an anion-exchange resin containing the anion X is exposed in an aqueous medium to a sufficiently large excess of electrolyte containing the anion Y, in such a manner that any X diffusing from the resin region is removed (e.g. by a continuous flow down a column), then in general the resin can be converted completely to its Y-form, even though it may have a greater affinity for X. Similarly, if electrolyte solution containing X as the only anion is passed through an excess of resin in its Y-form, it is possible to obtain, as the issuing solution, electrolyte with Y as the only anion.

An ion-exchange resin is generally found to exhibit different affinities towards different counterions. For two univalent counterions X and Y, this behaviour is expressed in terms of a selectivity coefficient \( K_X^Y \) which applies to the system when it is in equilibrium, and is defined by:

\[
K_X^Y = \frac{[Y]}{[X]} \frac{[Y]}{[X]}
\]
where [—] refers to the concentration of the counterions in
the resin region and [ ] to the concentration of the counterions
in the external aqueous region.

In the present investigation it was found possible to
convert benzyltriethylammonium chloride completely into its
hydroxide in aqueous solution by the use of a column of the
strongly basic anion-exchange resin Amberlite IRA-401 in its
hydroxide form, the resin being present in a 13.6-fold excess.
The polymeric quaternary ammonium hydroxide, prepared under the
same conditions from its chloride, still retained chloride ions
to the extent of 1.56% of its hydroxyl-ion content, i.e. there
was a 98.5% conversion of chloride to hydroxide. Jones, using
a similar procedure, obtained a 96% conversion of a polymeric
quaternary ammonium chloride into its hydroxide [68].

Anion-exchange resins of the same type as Amberlite
IRA-401 exhibit a greater affinity for chloride ions than for
hydroxyl ions, the value for $\text{OH}^-$ being about 0.09 [119]. Thus,
the conversion of a chloride solution into a hydroxide solution
by the use of the resin in its hydroxide form is favoured.
This selectivity also accounts for the large proportion of
sodium hydroxide which was required to convert the resin from
its chloride form into its hydroxide form.

Poly-ion macromolecules in solution can be considered
to occupy regions (see p. 20) in which their counterions become
concentrated by the same Donnan-membrane effect as that which operates in the case of the ion-exchange resins. In the presence of each other, therefore, the anion-exchange resin and the polymeric quaternary ammonium cation would compete for anions. While the resin should exert a stronger affinity for anions than would the poly-cation, due to the greater density of charge in the cross-linked network of the former, it is to be expected that a small proportion of the original chloride anions would still remain in the polyelectrolyte solution after treatment which had been adequate to give complete exchange in low molecular weight electrolyte.
The Reaction Products

The existence of products other than phorone from the decomposition of nitrosotriacetonamine in aqueous alkali was mentioned by Clibbens and Francis [2], but they were not identified.

In the present investigation of the products, nitrosotriacetonamine was decomposed in the presence of both 0.01N aqueous sodium hydroxide and 0.01N aqueous polymeric quaternary ammonium hydroxide. The quantities of nitrosotriacetonamine which were used were in large excess of the amount which would dissolve in the aqueous alkali. Consequently a second phase was always present, changing gradually from the solid substrate to the liquid product. It is felt that it is reasonable to assume that, although the mixture was heterogeneous, the reaction actually occurred in the aqueous solution, as was the case in the kinetic runs.

The same five compounds were detected in the products from the decompositions in the presence of both sodium hydroxide and polymeric quaternary ammonium hydroxide solutions respectively. These were acetone, mesityl oxide (I), phorone (II), semiphorone (III) and the phorone isomer, 2,6-dimethyl-1,5-heptadien-4-one (IV).
The acetone, mesityl oxide and phorone were identified unequivocally by mixed melting point determinations of their 2,4-dinitrophenylhydrazones with authentic specimens. The 2,4-dinitrophenylhydrazone from III is also the same as that obtained from both triacetone dialcohol and 2,2,6,6-tetramethyltetrahydro-4-pyrene V [83].

The ultra-violet absorption maximum of the derivative in chloroform occurred at 3650 Å. This agrees with the value obtained for this compound by Craven and Ward [84] who showed that the common 2,4-dinitrophenylhydrazone was that of V. The infra-red absorption spectrum of the original compound, however, showed that the carbonyl group was in conjugation, which would only be so in the case of semiphorone.
Consideration of the boiling points of triacetone dialcohol, V and III given by Connolly [83]; 128°/15 mm., 70°/15 mm. and 101°/15 mm. respectively, showed that the fraction from the present product-analysis (b.p. 100-102°/20 mm.) was more likely to contain semiphorone than these alternative compounds. Furthermore, the pleasant smell of the liquid agreed with that observed by Connolly [83] for semiphorone. The refractive index of the semiphorone fraction (nD 1.4655) was slightly higher, after allowance for the temperature difference, than the value given by Connolly [83] for semiphorone (nD 1.4666), the change in refractive index with temperature being taken as -0.0004 per deg.

The phorone isomer IV has been described only by Craven and Ward [84]. The infra-red absorption spectrum given by these authors corresponded closely with that obtained in the present product-analysis. The few additional small peaks which occurred in the spectrum of the sample from the product-analysis would be readily attributed to phorone, which was known to be present, or to semiphorone. The peak at 3500 cm.⁻¹ was believed to be due to the hydroxyl group of semiphorone. One peak at 1560 cm.⁻¹ in the spectrum given by Craven and Ward [84] was missing from the spectrum of the present sample. However, the same peak was also missing from the spectrum of authentic phorone. The absence of the peak in both spectra in the present
investigation is thought to be due to the fact that the spectra of Craven and Ward [84] were obtained with the samples in solution, while the samples in the present investigation were not in solution.

The boiling point of the fraction containing IV, 78°/20 mm., was in agreement with that, 74°/15 mm., given by Craven and Ward [84]. The refractive index (nD 1.4650), after allowance for the different temperature, was lower than that given by these authors [84]: nD 20 1.4698. The melting point of the 2,4-dinitrophenylhydrazone prepared from the phorone isomer, 104.5°, did not agree with that (73-76°) reported by Craven and Ward [84], but the wavelength of maximum ultraviolet absorption in chloroform, 3740Å, did agree with that (3730Å) quoted by these authors.

No derivative of IV was isolated from the polymeric hydroxide-catalysed conversion, but the presence of IV was inferred from the gas-liquid chromatogram of the products, which contained a peak, B, with a retention time identical to that attributed to IV.

When mixtures of mesityl oxide and phorone, of known compositions, were subjected to gas-liquid chromatography, the ratios of the areas contained under the chromatogram peaks were not linearly related to the proportions of the components in the mixtures. It was possible, however, to conclude that the
mesityl oxide and phorone were present in the ethereal solutions from both the sodium hydroxide-and polymeric quaternary ammonium hydroxide-catalysed conversions in an approximate ratio of 1 : 0.7 by weight. The gas-liquid chromatographic analysis also revealed that the proportion of 2,6-dimethyl-1,5-heptadien-4-one (IV) produced in the presence of aqueous sodium hydroxide was approximately 7 times as great as that produced in the presence of the aqueous polymeric quaternary ammonium hydroxide solution. This estimate was made by relating the area under the peak for IV to that under the phorone peak in each case. Since the phorone and IV are isomers it is felt that this procedure should give reasonably reliable semi-quantitative information. The approximate proportions of the three components detected by the gas-liquid chromatographic analysis are summarised in Table 27.

**TABLE 27**

Approximate Proportions of Components, by weight

<table>
<thead>
<tr>
<th>Conversion</th>
<th>Alkali</th>
<th>Proportion by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mesityl oxide</td>
<td>IV</td>
</tr>
<tr>
<td>1</td>
<td>Sodium Hydroxide</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Polymeric Hydroxide</td>
<td>1</td>
</tr>
</tbody>
</table>
The failure to detect semiphorone, in the chromatograms of both ethereal solutions of the products, appears to be due to the decomposition of this compound on the column.

Semiphorone was found to undergo decomposition in 0.01N aqueous sodium hydroxide solution at room temperature to yield acetone and mesityl oxide, thus accounting for the presence of these compounds in the products from the nitrosotriacetonamine decomposition. This conversion seems to be analogous to the well-known equilibrium between diacetone alcohol and acetone [120]:

\[
\text{HO.C.CH}_2.\text{CO.CH:C} \rightleftharpoons \text{CH}_3 \quad \text{CH}_3
\]

\[
\text{OH}^- \quad (\text{CH}_3)_2\text{CO} + \text{CH}_3.\text{CO.CH:C} \quad \text{CH}_3
\]

and

\[
\text{HO.C.CH}_2.\text{CO.CH}_3 \quad \text{OH}^- \quad 2(\text{CH}_3)_2\text{CO}
\]

Phorone was stable in 0.03N aqueous sodium hydroxide solution at room temperature.
The Reaction Mechanism

The various investigations of the kinetics of the reaction have been described in the Introduction section of this thesis (see p.11). The relevant facts arising from these and the present investigations are:

(a) the reaction is catalysed by hydroxyl ions in dilute alkali (less than about 0.05N),

(b) the reaction rate obeys a first-order relationship closely in dilute aqueous alkali both with respect to nitroso-triacetonamine concentration and hydroxyl-ion concentration,

(c) there is a short induction period to the reaction in dilute alkali,

(d) the reaction behaves as if there were two consecutive steps, one of which is catalysed by hydroxyl ions, while the rate of the other decreases as the hydroxyl-ion concentration increases, and becomes rate-controlling at higher concentrations of alkali (greater than about 0.5N),

(e) there is also an induction period to the reaction in the more concentrated alkali.

A reaction similar to the nitroso-triacetonamine decomposition has been studied by Jones and Kenner[121]. This involved the decomposition of 4-methyl-4-((propynitrosoamino)-2-pentanone (VI) in dilute aqueous alkali.
These authors found that in dilute aqueous alkali VI gave a 100% yield of nitrogen together with three other products: propylene, n-propyl alcohol and isopropyl alcohol. To account for these Jones and Kenner [121] proposed the existence of an aliphatic diazohydroxide and diazonium hydroxide as intermediates. From these unstable compounds a carbonium ion, \([\text{CH}_3\text{CH}_2\text{CH}_2]^+\) was considered to be formed, and this in turn decomposed in three different ways, by a substitution reaction, an elimination reaction and a "Wagner-Meerwein" change, respectively, to yield n-propyl alcohol, propylene and isopropyl alcohol. The following scheme was given by these authors:
It was further pointed out that an increase in hydroxyl-ion concentration would not cause a continuous increase in the rate of formation of the products since, although the initial step would be favoured, the concentration of diazonium ion would be depressed, thus retarding the rate of formation of the products. Since this behaviour corresponded to that of the nitrosotriacetonamine decomposition, Jones and Kenner [121] suggested that an analogous mechanism operated in this case also. The existence of aliphatic diazotates and diazohydroxides has been demonstrated by Hantzsch and Lehmann [122] and also proposed by de Boer and Backer [123] and by Reimlinger and Skattebøl [124].

The electric dipole moment of nitrosotriacetonamine has not been reported. However, the carbonyl group and the N-nitroso group are known to have group electric dipole moments of $-2.76 \text{ D} [125]$ and $-3.6$ to $-3.7 \text{ D} [126]$ respectively. The resultant dipole moment would depend on the conformation of the
cyclic nitrosotriacetonamine molecule, which is unknown, but from a consideration of the possible conformations it appears that one or other of the hydrogen atoms on each of the methylene groups adjacent to the carbonyl group would be in the positive region of the dipole. The first stage of the reaction therefore probably involves a nucleophilic attack on one of these hydrogen atoms by a hydroxyl ion, to give an enolate anion. The following proposed reaction scheme commences with such a nucleophilic attack and is based on the mechanism suggested by Jones and Kenner [121].

\[
\begin{align*}
(A) & \\
& \xrightarrow{k_1} (E^-)
\end{align*}
\]

\[
\text{i.e. } A + \text{OH}^- \xrightarrow{k_1} E^- + \text{H}_2\text{O} \quad \text{... stage 1}
\]

The next stage would then be the formation of the diazotate anion, \( D^- \), by the following elimination reaction:

\[
\begin{align*}
(A) & \xrightarrow{k_1} (E^-) \\
& \xrightarrow{k_{-1}} \text{D}^- + \text{H}_2\text{O}
\end{align*}
\]
The removal of a proton from a carbon atom can often be a slow reaction \[127\] and it is therefore to be expected that the forward step of stage 1 would be a slow, rate controlling reaction. The enolate anion, \(E^-\), is assumed to be very reactive, rearranging quickly into the diazotate anion, \(D^-\), and, in dilute alkali, also reverting rapidly to the substrate, \(A\).

Stage 2 should be assisted by the participation of the two methyl groups in hyperconjugation with the developing double bond in the transition state:
Stages 1 and 2 could alternatively be replaced by a single, irreversible, relatively slow E2 step:

\[ A + OH^- \rightarrow D^- + H_2O \]

The diazotate anion would tend to be in equilibrium with its diazo hydroxide, F:

\[
\begin{array}{c}
\text{HC} \\
\text{Me}_2\text{C} \\
\text{N} \quad \text{N} \\
\text{O}^{-} \\
(D^-)
\end{array}
\quad \overset{k_3}{\Rightarrow} \quad
\begin{array}{c}
\text{HC} \\
\text{Me}_2\text{C} \\
\text{Me}_2\text{C} \\
\text{N} \quad \text{N} \\
\text{O}^{-} \\
(F)
\end{array}
\]

i.e. \( D^- + H_2O \overset{k_3}{\Rightarrow} F + OH^- \) ... stage 3

while the diazo hydroxide (F) could, in turn, tend to be in equilibrium with the diazonium cation (\( G^+ \)):

\[
\begin{array}{c}
\text{HC} \\
\text{Me}_2\text{C} \\
\text{N} \quad \text{N} \\
\text{OH} \\
(F)
\end{array}
\quad \overset{k_4}{\Rightarrow} \quad
\begin{array}{c}
\text{HC} \\
\text{Me}_2\text{C} \\
\text{Me}_2\text{C} \\
\text{N} \quad \text{N} \\
\text{N}_2 \\
(G^+)
\end{array}
\]

\[
\begin{array}{c}
\text{HC} \\
\text{Me}_2\text{C} \\
\text{Me}_2\text{C} \\
\text{N} \quad \text{N} \\
\text{OH} \\
(F)
\end{array}
\quad \overset{k_{-3}}{\Rightarrow} \quad
\begin{array}{c}
\text{HC} \\
\text{Me}_2\text{C} \\
\text{Me}_2\text{C} \\
\text{N} \quad \text{N} \\
\text{N}_2 \\
(G^+)
\end{array}
\]
This cation \((G^+)\) could then change to the carbonium ion \((J^+)\), liberating nitrogen:

\[
\text{Me}_2\text{C} - \text{C} - \text{Me}_2 \xrightarrow{k_5} \text{Me}_2\text{C} - \text{C} - \text{Me}_2 + N_2
\]

i.e. \(G^+ \xrightarrow{k_5} J^+ + N_2 \quad \ldots \text{stage 5}

The subsequent reactions would be the nucleophilic substitution and the elimination reactions, respectively, of this carbonium ion to yield the observed products II, III and IV:

\[
\text{Me}_2\text{C} - \text{C} - \text{Me}_2 + \text{OH}^- \xrightarrow{k_5} \text{Me}_2\text{C} - \text{C} - \text{Me}_2 + \text{OH}
\]

i.e. \(J^+ + \text{OH}^- \xrightarrow{k_5} \text{III} \quad \ldots \text{stage 6}\)
If it is assumed that in dilute aqueous alkali a state is quickly attained in which the intermediates \( \text{D}^- \), \( \text{F} \) and \( \text{G}^+ \), as soon as they are formed, each change to the next one in the reaction sequence, then the stationary-state approximation [128] may be applied to simplify the derivation of the rate equation. This stationary-state approximation requires that the concentrations of \( \text{E}^- \), \( \text{D}^- \), \( \text{F} \) and \( \text{G}^+ \), respectively, should be small and virtually constant so that their net rates of formation may each be equated to zero.

Thus, for stages 1 and 2 of the proposed mechanism,
\[ \frac{d[E^-]}{dt} = k_1[A][OH^-] - k_{-1}[E^-][H_2O] - k_2[E^-] = 0, \]

whence, \[ [E^-] = \frac{k_1[A][OH^-]}{k_{-1}[H_2O] + k_2} \] \hspace{1cm} ... (6)

For stages 2 and 3,
\[ \frac{d[D^-]}{dt} = k_2[E^-] + k_{-3}[F][OH^-] - k_3[D^-][H_2O] = 0, \]

whence, \[ [E^-] = \frac{k_3[D^-][H_2O] - k_{-3}[F][OH^-]}{k_2} \] \hspace{1cm} ... (7)

From equations (6) and (7),
\[ [D^-] = \frac{k_1k_2[A][OH^-] + k_{-1}k_{-3}[F][OH^-][H_2O] + k_2k_{-3}[F][H_2O]}{k_{-1}k_3[H_2O]^2 + k_2k_3[H_2O]} \] \hspace{1cm} ... (8)

For stages 3 and 4,
\[ \frac{d[F]}{dt} = k_3[D^-][H_2O] + k_{-4}[G^+][OH^-] - k_{-3}[F][OH^-] - k_4[F] = 0 \] \hspace{1cm} ... (9)

whence, \[ [D^-] = \frac{k_{-3}[F][OH^-] + k_4[F] - k_{-4}[G^+][OH^-]}{k_3[H_2O]} \] \hspace{1cm} ... (10)

From equations (8) and (10)
\[ [F] = \frac{k_1k_2[A][OH^-] + k_{-1}k_{-4}[G^+][OH^-][H_2O] + k_2k_{-4}[G^+][OH^-]}{k_{-1}k_4[H_2O] + k_2k_4} \] \hspace{1cm} ... (11)
For stages 4 and 5,

\[
\frac{d[G^+]}{dt} = k_4[F] - k_4[G^+][OH^-] - k_5[G^+] = 0 \quad \ldots (12)
\]

whence,

\[
[F] = \frac{k_4[G^+][OH^-] + k_5[G^+]}{k_4} \quad \ldots (13)
\]

From equations (11) and (13)

\[
[G^+] = \frac{k_1 k_2[A][OH^-]}{k_1 k_5[H_2O] + k_2 k_5}
\]

Therefore,

\[
rate = \frac{d[N_2]}{dt} = k_5[G^+] = \frac{k_1 k_2[A][OH^-]}{k_1[H_2O] + k_2}
\]

Thus, the rate calculated from the proposed mechanism by the application of the stationary-state approximation possesses first-order dependence on both \([A]\) and \([OH^-]\). This agrees with the observed behaviour of the reaction in aqueous alkali of less than 0.05 N, as recorded in the literature (see p.12).

The requirements of the stationary-state approximation used above, that the concentration of the intermediates should be low and their net rates of formation zero, are also needed to account for the catalytic behaviour of the hydroxyl ion in dilute aqueous alkali. Thus, for the concentration of hydroxyl ions to remain constant throughout the reaction, the hydroxyl ion used in the slow forward step of stage 1 must be
replaced immediately by the fast reversal of this step or by a rapid, unobstructed conversion of E⁻ to J⁺. Furthermore, stages 6, 7 and 8 must occur quickly in order that the additional hydroxyl ion produced by the forward step of stage 4 may be removed as soon as it is formed.

The observed induction period of the reaction in dilute alkali would correspond to the short time taken for the steady, small concentrations of the intermediates to become established.

With an increase in the hydroxyl-ion concentration, the rate of the forward step of stage 1 would increase, and at the same time the rates of the reverse steps of stages 3 and 4 would also increase. The situation would then arise in which the concentrations of D⁻ and F were built up during the reaction. The development of appreciable proportions of these intermediate compounds during the reaction would cause the observed reaction rate to deviate from its previously observed simple kinetic order and exhibit the properties of a reaction involving consecutive rate-controlling steps. This corresponds qualitatively to the experimental observations recorded in the literature (see p. 15) for hydroxyl-ion concentrations between about 0.05N and 0.5N.

Eventually, in still higher concentrations of hydroxyl ions, it is envisaged that A would be converted quickly to D⁻, while the value of $k_{-3}[OH^-]$ would be sufficiently large relative
to $k_4$ to enable a stationary state to be established again, with the concentrations of $F$ and $G^+$ being small and virtually constant. On the other hand, the concentration of $D^-$ would increase quickly during the reaction and then fall again, at a slower rate, as $D^-$ was converted through $F$ and $G^+$ to $J^+$. Therefore, after the concentration of $D^-$ had attained its maximum value, the observed rate of the reaction would be controlled by the concentration of $D^-$ and not by the concentration of $A$. Application of the stationary-state approximation \[128\] gives, from equation 9:

$$[F] = \frac{k_3[D^-][H_2O] + k_4[G^+][OH^-]}{k_3[OH^-] + k_4} \quad \cdots \quad (14)$$

From equations (13) and (14)

$$[G^+] = \frac{k_3k_4[D^-][H_2O]}{k_3k_4[OH^-]^2 + k_3k_5[OH^-] + k_4k_5}$$

Therefore, rate $= \frac{d[N_2]}{dt} = k_5[G^+]$

$$= \frac{k_3k_4k_5[D^-][H_2O]}{k_3k_4[OH^-]^2 + k_3k_5[OH^-] + k_4k_5}$$

$$= \frac{[D^-]}{k_6[OH^-]^2 + k_7[OH^-] + k_8} \quad \cdots \quad (15)$$
where \( k_6 = \frac{k_{-3}k_{-4}}{k_3k_4k_5[H_2O]} \),

\( k_7 = \frac{k_{-3}}{k_3k_4[H_2O]} \),

\( k_8 = \frac{1}{k_3[H_2O]} \).

Since the concentrations of hydroxyl ions used by Clibbens and Francis [2] and Francis and Geake [3] in their investigations at high alkali concentrations were in large excess over the initial concentrations of the substrate (0.02M), the variation of \([\text{OH}^-]\) as \([D^-]\) changed would not be significant, and the value of \([\text{OH}^-]\) would remain virtually constant throughout a reaction. The rate of the reaction in the more concentrated alkali, as measured by the rate of evolution of nitrogen, is therefore expected to conform to a first-order relationship, given by equation (15), and the first-order rate constant should decrease with increasing hydroxyl-ion concentrations, since \([\text{OH}^-]\) appears in the denominator of equation (15). This is in qualitative agreement with the observations recorded in the literature for hydroxyl-ion concentrations greater than 0.5N (see P. 13).

In fact, the first-order constants, \( k \), obtained by Francis and Geake [3] for aqueous sodium hydroxide solutions between 0.479 and 2.97N at 30° conform well to an equation with
the same form as that to be expected from equation (15), viz:

\[ k = \frac{1}{a[OH^-]^2 + b[OH^-] + c} \quad \text{(min}^{-1}\text{)} \quad \ldots \quad (16) \]

where the values of the coefficients \(a\), \(b\) and \(c\) are selected so that the curve of \(k\) against \([OH^-]\) coincides with the experimental curve. The following respective sets of values for \(a\), \(b\) and \(c\) were found to produce good agreement with the experimental curve: 3, 20, 0; 6, 15, 0; 6, 14, 1 and 5, 14, 2. This agreement is shown graphically, for the latter example, in Fig. 15.

For alkali concentrations in excess of 3N, the values obtained from equation (16) and the above sets of coefficients deviate below the experimental values of Francis and Geake [3], which are virtually constant at these higher alkali concentrations.

The hydroxyl-ion concentrations referred to in the above equations are the stoichiometric values, whereas Francis and Geake [3] used reduced values, on the assumption that the sodium hydroxide was incompletely dissociated.

The induction period reported for the reactions in alkali solutions with hydroxyl-ion concentrations greater than 0.5N [2] would correspond to the time taken for the concentration of \(D^-\) to be built up, and for the stationary state to be established.
Concentration of sodium hydroxide (N) ([OH])

Fig. 15 Data reported by Francis and Geake [3]. The continuous line represents the equation

\[ k_1 = \frac{1}{5[OH]^2 + 14[OH] + 2} \]
Jones and Kenner [12] showed that a form of "Wagner-Meerwein" rearrangement occurred in the decomposition of 4-methyl-4-(propynitrosoamino)-2-pentanone (see p.191) to give isomeric substitution products. Rearrangements of this type have been termed "Demjanov" rearrangements [129]. They involve the migration of β-hydrogen atoms and β-methyl and β-methylene groups to adjacent carbon atoms in a carbonium ion. For example, the preparation of n-propyl alcohol, iso-propyl alcohol and propylene from n-propylamine and nitrous acid [130] has been explained [129] by the following scheme:

\[
\text{CH}_3\cdot\text{CH}_2\cdot\text{NH}_2 + \text{HNO}_2 \rightarrow \text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} \\
\text{CH}_3\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{CH}_3\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{CH}_3\cdot\text{CH}=(\text{OH})\cdot\text{CH}_3 \\
\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2
\]

By analogy with the foregoing, the following three carbonium ions would be expected to occur in the present proposed reaction scheme:

\[
\begin{align*}
\text{Me}_2\text{C} & \quad \text{Me}_2\text{C} & \quad \text{Me}_2\text{C} \\
\text{CH} & \quad \text{CH} & \quad \text{CH} \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{Me}_2\text{C} & \quad \text{Me}_2\text{C} & \quad \text{Me}_2\text{C} \\
\end{align*}
\]

As well as producing the products II and IV by elimination steps, these carbonium ions may give rise to the following isomeric
alcohols:

![Chemical Structures]

(III)

respectively. Of these, III has been identified among the products. The infra-red absorption spectrum of the high-boiling fraction of the products did, however, contain peaks which could be attributed to primary and secondary alcohol groups.

The presence of acetone and mesityl oxide(I) in the products from the nitrosotriacetonamine decomposition has been accounted for by the demonstration that semiphorone is converted into these products in aqueous alkali. This reaction would occur after those steps in which the nitrogen was released, and would consequently not affect the observed reaction kinetics.

A reaction which bears some resemblance to the semiphorone decomposition is the conversion of diacetone alcohol into acetone in aqueous alkali. This is believed [12] to proceed through the intermediate formation of an alkoxide anion. The semiphorone decomposition could therefore be explained by the following mechanism:
The Effect of the Polymeric Quaternary Ammonium Poly-Cation on the Reaction Kinetics of the Nitrosotri-acetonamine Decomposition

Reaction Kinetics in Salt-Free Aqueous Solutions

The first-order rate constants for the nitrosotri-acetonamine decomposition in dilute aqueous polymeric quaternary ammonium hydroxide solutions (up to 0.02N) are higher than the corresponding values in sodium hydroxide solutions. Thus, at 25° and a hydroxide normality of 0.01N, the rate constant obtained with the polymeric hydroxide is $3.52 \times 10^{-4}$ sec.$^{-1}$, compared with $2.03 \times 10^{-4}$ sec.$^{-1}$ for the reaction in the presence of sodium hydroxide.

Results published in the literature (see p.14)[3] show that the rate constant exhibits a very slight dependence on the nature of the cation of the simple low molecular weight alkali used. It was therefore possible that the higher rate constant in the presence of the polymeric hydroxide was caused by some difference between the properties of the quaternary ammonium and sodium cations, respectively, and not by the polymeric nature of the poly-cation. Consequently, the reaction rate in dilute aqueous sodium hydroxide was compared with that in benzyltriethylammonium hydroxide solution, the latter compound being analogous to the structural unit of the polymeric
hydroxide. The first-order rate constant for aqueous 0.1N benzyltriethylammonium hydroxide solution at 25°, 2.08 × 10^{-4} \text{sec.}^{-1}, is slightly higher than the corresponding value in the presence of sodium hydroxide, 2.03 × 10^{-4} \text{sec.}^{-1}. This slight difference may be caused by the deactivation of a small proportion of the hydroxyl ions in sodium hydroxide solution, due to ion-pair formation. Such an effect has been reported [131] for the hydroxyl-ion catalysed decomposition of diacetone alcohol.

In view of the relatively small difference between the rate constants in the presence of the two low molecular weight hydroxides, it is considered that the rate constants obtained with sodium hydroxide as the catalyst can be used to represent the catalytic efficiencies of the hydroxyl ion in solutions of simple low molecular weight hydroxides. It is therefore apparent that the polymeric nature of the poly-cation enhances the catalytic action of the hydroxyl ions.

The value of the first-order rate constant obtained at 25.0° with aqueous sodium hydroxide at a hydroxyl-ion concentration of 0.01N, 2.03 × 10^{-4} \text{sec.}^{-1}, is in agreement with that reported by King and Marion [9], 2.00 × 10^{-4} \text{sec.}^{-1} or 0.0120 \text{min.}^{-1}, at 24.9°.

Graphs of the first-order rate constant, k_1, against
hydroxide normality, for both polymeric hydroxide and sodium hydroxide, are straight lines which pass through the origin (see Fig. 5). Hence, the rate of the reaction is first order with respect to the hydroxyl-ion concentration in both cases, and is not catalysed by water to any measurable extent. The second-order catalytic rate constants, $k_i/\left[\text{OH}^-\right]$, obtained from the gradient of each line, are $3.48 \times 10^{-2}$ and $2.03 \times 10^{-2}$ mole$^{-1}$sec$^{-1}$ for the polymeric hydroxide and sodium hydroxide, respectively. The ratio of these values, 1.72, represents the factor by which the reaction rate is increased due to the polymeric nature of the poly-cation.

Compared with the increases in the rate of glycyl-glycine hydrolysis obtained by the use of strong polymeric acids in place of simple acids (see p. 35) [44], the present observed increase in reaction rate is relatively small. The ratio is, however, of the same order as some of those observed for other reactions in which one of the reactants is uncharged. For example, the inversion of sucrose is slower in poly(vinyl-sulphonic acid) than in hydrochloric acid by a factor of 1.53 [42], and the rate of hydrolysis of ethyl acetate in poly-(styrenesulphonic acid) is between 1.3 and 1.8 times as fast as that in p-toluenesulphonic acid [46].
The Cause of the Polyelectrolyte Effect

If the higher reaction rate obtained in the presence of the polymeric hydroxide is to be explained in terms of Morawetz's approach (see p. 38) [47], the hydroxyl ions and nitrosotriacetonamine molecules, in contrast to their even distributions in sodium hydroxide solution, must be more concentrated within and near the poly-cations due to the high electrostatic potentials in these regions. The increased hydroxyl-ion concentration in these regions is to be expected, since counterions are distributed in this way in polyelectrolyte solutions (see p. 31). The low observed activity coefficients of the hydroxyl counterions also provide an experimental indication of this effect. The enhancement of the nitrosotriacetonamine concentration in and around the poly-cations cannot be accounted for so readily. In Morawetz's treatment [47] the distribution of uncharged molecules is not considered to be disturbed to any detectable extent by the presence of a poly-ion, and this was borne out by the reported insensitivity of the rate of the hydroxyl ion-catalysed hydrolysis of p-nitrophenyl acetate to the presence of poly(acrylate-maleate) poly-anions [48]. Nitrosotriacetonamine, from a consideration of its structure and the group electric dipole moments of the carbonyl and N-nitroso groups, -2.76D [125] and -3.6 to -3.7D [126]
respectively, is a molecule of appreciable polarity. It would therefore be affected by the electrostatic field of the poly-
cation. Furthermore, it has been shown [132] that polar mole-
cules, e.g. phenol and pyridine, can participate in association with poly-ions, e.g. polyacrylate. Consequently, it is thought that the increase of rate in the presence of the polymeric hydroxide is in fact due to a marked increase of the hydroxyl-
ion concentration within and around the poly-cations, together with a less pronounced increase of the nitrosotriacetonamine concentration in these regions.

The high electrostatic potential around the poly-
cations, and the resulting observed low hydroxyl-ion activity coefficient indicate that activity coefficients may attain greater significance in the reaction kinetics of the polymeric hydroxide-catalysed decomposition than in the case of the reaction in low-molecular weight hydroxide solution. If it is assumed that the rate-controlling step of the nitrosotriaceton-
amine decomposition is the reaction of a hydroxyl ion with a nitrosotriacetonamine molecule, A, (see p.194) then the observed first-order rate constant, $k_1$, is given by

$$k_1 = kk^* \frac{\gamma_A \gamma_{OH}}{\gamma_{OH}^*} [OH^-]$$

where $k^*$ is the equilibrium constant for the formation of
the activated complex, \( k \) is the rate constant for the decomposition of the activated complex into products, and \( \gamma_A \), \( \gamma_{OH} \) and \( \gamma_X \) are the activity coefficients of the nitrosotriacetonamine, hydroxyl ion and activated complex, respectively.

In dilute simple low-molecular weight hydroxide solution the activity coefficient term, \( \frac{\gamma_A \gamma_{OH}}{\gamma_X} \), is approximately unity, so that the effect of the activity coefficients is not very marked in this case. In polymeric hydroxide solution, however, under the influence of the high electrostatic potentials established by the poly-cations, the term \( \frac{\gamma_A \gamma_{OH}}{\gamma_X} \) may deviate appreciably from the value which it possesses in dilute low-molecular weight hydroxide solution. Thus, apart from the effect of the increased reactant concentrations in the poly-cation regions, it is possible that this activity coefficient term will also cause the rate constant in the presence of the polymeric hydroxide to differ from that in the presence of sodium hydroxide solution. An increase of the activity coefficient term \( \frac{\gamma_A \gamma_{OH}}{\gamma_X} \) under the influence of the poly-cation would therefore produce a higher rate constant. Measurements obtained in the present investigation (see p. 124) indicate that \( \gamma_{OH} \) in polymeric hydroxide solution is considerably lower than the value in sodium hydroxide solution. However, the lack of information concerning \( \gamma_A \) and \( \gamma_X \) in the presence of poly-ions
prevents further development of this approach.

Kargin, Kabanov and Kargina [46] have suggested that the high concentration of hydronium counterions within the poly-anions in poly(styrenesulphonic acid) solutions can result in a large increase of the hydronium counterion activity co-efficient. However, such an increase is entirely contrary to the generally accepted views on the magnitudes of counterion activity coefficients in the presence of poly-ions (see p. 27).

The linearity of the graph of $k_1$ against $[OH^-]$ for the polymeric hydroxide-catalysed reaction, over a range of hydroxide normality from 0.005 to 0.02N (Fig. 5) indicates that the proportions of hydroxyl ions and nitrosotriacetonamine molecules, respectively, which exist within and near the poly-cations, remain constant over this range of hydroxyl-ion concentration. Presumably therefore, although hydroxyl counterions would have tended to escape from the poly-cation on dilution, the expansion of the poly-cation enabled it to retain its influence on these counterions.

When a mixture of 0.005N polymeric hydroxide and 0.005N sodium hydroxide was used as the catalyst, the hydroxyl ions from the two components appeared to act independently, since the resulting first-order rate constant, $2.80 \times 10^{-4}$ sec$^{-1}$ (see Table 9), was approximately equal to the sum of the rate...
constants in the presence of each separate component, 
\[ 2.74 \times 10^{-4} \text{sec}^{-1} \].

**Salt Effects**

The presence of sodium chloride in low concentrations (less than 0.005 M) produces a sharp decrease in the rate constant of the reaction in 0.01 N polymeric hydroxide solution at 25° (see Fig. 6). Thus, at a sodium chloride concentration of 0.005 M, the first-order rate constant is \[ 2.60 \times 10^{-4} \text{sec}^{-1} \], 0.74 times the value in a solution free of added salt. As the sodium chloride concentration is increased, the decrease in the rate constant becomes progressively more gradual until, at a sodium chloride concentration of about 0.045 M, the rate constant is the same as that in 0.01 N sodium hydroxide solution with the corresponding concentration of added sodium chloride. Further increases in the sodium chloride concentration cause only a gradual decrease in the rate constant, which becomes slightly less than that in 0.01 N sodium hydroxide solution with corresponding concentrations of added sodium chloride (see Fig. 6).

In contrast to this behaviour, the rate constant in the presence of sodium hydroxide solution is only slightly affected by the addition of sodium chloride. The small negative linear salt effect observed in 0.01 N sodium hydroxide at 25°
is in qualitative agreement with that observed by King and Marion [9] at 24.9° (see p. 17), although the gradient in the present work was slightly steeper than that reported by these authors. They give the equation

\[ k_1 = 0.0120 - 0.0049\mu, \text{min.}^{-1}, \]

where \( k_1 \) is the observed first-order rate constant, and \( \mu \) is the ionic strength of the solution. The results from the present investigation fit the equation

\[ k_1 = 2.03 \times 10^{-4} - 1.08 \times 10^{-4}\mu, \text{sec.}^{-1} \]

or

\[ k_1 = 0.0122 - 0.0065\mu, \text{min.}^{-1} \]

The pronounced decrease in the rate constant of the polymeric hydroxide-catalysed reaction produced by the addition of sodium chloride indicates that the non-catalytic chloride counterions displace hydroxyl ions from the regions of high counterion concentration near the poly-cations. The added simple electrolyte also partially screens the electrostatic fields of the poly-cations. As a result of these effects, the hydroxyl ions and nitrosotriacetonamine molecules become more evenly distributed throughout the solution, while at the same time the poly-cation contracts (see p. 21). Eventually, as the concentration of the added salt is increased, the hydroxyl ions and nitrosotriacetonamine molecules attain an even distribution.
At this stage, therefore, the rate constant should adopt the same characteristics as those of the rate constant of the low molecular weight hydroxide-catalysed reaction. This is in fact observed in the present investigation, where, for sodium chloride concentrations in excess of 0.045M, the first-order rate constants in the presence of 0.01N polymeric hydroxide become approximately the same as those in the presence of 0.01N sodium hydroxide solution.

A similar effect has been observed by Morawetz and Shafer [48] for the hydroxyl-ion catalysed hydrolyses of cationic phenyl esters in the presence of polymethacrylate poly-anions: an increase in sodium counterion concentration caused the rate constants to approach that for the reaction in the absence of the poly-anion.

The decrease in the rate constant of the nitrosotriacetonamine decomposition in the presence of 0.01N polymeric hydroxide, produced by the incorporation of 0.01N sodium chloride (3.52 x 10^{-4} to 2.31 x 10^{-4} sec.^{-1}, 25°) is 81.2% of the difference between the rate constants in the presence of salt-free polymeric hydroxide and sodium hydroxide. This relatively sharp diminution indicates that the poly-cation exhibits a considerable degree of selectivity, accommodating the chloride counterions preferentially with respect to the hydroxyl
counterions. The slightly lower rate constants of the polymeric hydroxide-catalysed reaction, compared with those of the sodium hydroxide-catalysed reaction, at sodium chloride concentrations in excess of 0.045M, may be the result of a depletion of the hydroxyl-ion concentration in and around the poly-cations while the nitrosotriacetonamine concentration is still slightly enhanced in these regions. This partial separation of the reactants would then give a rate constant slightly lower than that for the evenly distributed sodium hydroxide system. Sodium sulphate also causes a sharp reduction of the rate constant in polymeric hydroxide solution (see Fig.6). At low sodium sulphate concentrations (less than 0.02M) the decrease in rate constant is greater with sodium sulphate than with sodium chloride of the same equivalent concentration. However, at higher concentrations of sodium sulphate, where the rate constant is less sensitive to changes in salt concentration, the rate is slightly higher than that in the presence of sodium chloride.

The larger reduction in rate constant at low concentrations of sodium sulphate, for a given equivalent concentration of added salt, is in agreement with the theoretical deduction by Wall [39], that counterions with the higher charge are expected to be associated with the poly-ions to a larger
extent than are counterions of a lower charge, for the same equivalent concentration of the counterions. The sulphate counterions, possessing the greater tendency to concentrate near the poly-cation, would displace the hydroxyl ions from these regions more readily than would the chloride counterions, so causing a more pronounced reduction in the rate constant.

The addition of polymeric quaternary ammonium chloride to the polymeric hydroxide solution also causes a decrease in the rate constant, but to a smaller extent than does the addition of an equivalent amount of simple low molecular weight salt.

When polymeric quaternary ammonium chloride is added to a polymeric hydroxide solution, the ratio of poly-cations to counterions remains constant at a value of unity, whereas the addition of an equivalent amount of low-molecular weight salt to the polymeric hydroxide solution causes a reduction in this ratio. Consequently there is, in the former case, a greater proportion of poly-cations in relation to the reactants, and also relatively less screening of the electrostatic fields of the poly-cations. Therefore, in the reaction mixture containing polymeric hydroxide and polymeric quaternary ammonium chloride, the hydroxyl ions and nitrosotriacetonamine molecules are concentrated about the poly-cations to an extent greater than that which exists when the polymeric quaternary ammonium
chloride is replaced by an equivalent quantity of low-molecular weight salt. The increase in rate constant observed when polymeric quaternary ammonium chloride replaces low molecular weight salt can therefore be attributed to this increased localisation of reactants.

The localisation of hydroxyl ions and nitrosotriacetinamine molecules around the poly-cations in a polymeric hydroxide-polymeric quaternary ammonium chloride solution is, however, not so effective in increasing the rate constant of the reaction as the localisation in the corresponding salt-free polymeric hydroxide solution.

The polymeric hydroxide used in the present investigation contained a small proportion of chloride ions (see p. 105). In view of the sensitivity of the rate constant to the presence of small proportions of chloride ions, the rate constant observed with the present polymeric hydroxide, free of added salt, will be slightly less than the true value for the polymeric hydroxide completely free of chloride.

Effect of Macroscopic Dielectric Constant

Little variation of the rate constant in 0.01N sodium hydroxide solution at 25° occurs as the macroscopic dielectric constant, D, is varied from 78.5 to 60.4 by the addition of 1,4-dioxan (see Fig. 7). The results agree with those given by
King and Lionetti (see p.18)\[13\]. On the other hand, a similar
decrease in D from 78.5 to 51.6 in 0.01N polymeric hydroxide
solution produces a steady decrease of the rate constant from
3.52 \times 10^{-4} to 2.58 \times 10^{-4} sec^{-1}. It should be emphasised here
that the macroscopic dielectric constant of the solvent is
thought to be considerably higher than the values which actually
exist within and near poly-ions [133]. The graph of 10^4 k_1
against D for the polymeric hydroxide-catalysed reaction is a
curve, as also is the graph of \log_{10} k_1 against D^{-1} (see Figs.
7 and 8). The latter graph was constructed because the
Laidler-Eyring equation [14] for reactions between ions and
neutral molecules predicts a relationship in which \log_{10} k_1
should increase linearly as D^{-1} increases (see p.18). This re-
lationship obviously does not hold in the present case.

The decrease of the rate constant with decreasing
dielectric constant in the presence of polymeric hydroxide
solution was contrary to expectation, since the decrease of
dielectric constant was expected to result in a stronger electro-
static attraction of the reactants by the poly-cation, thus
producing a higher rate constant. A possible explanation for
the observed behaviour is that, as the dielectric con-
stant is lowered, ion-pair formation between the charged groups
of the poly-cation and the hydroxyl counterions occurs, with
the result that the effective hydroxyl-ion concentration decreases, causing a corresponding decrease in the rate constant.

**Activation Parameters**

The activation parameters obtained for the sodium hydroxide-catalysed reaction at 25°C ($\Delta F^\neq = 1.97 \times 10^4$ cal.mole$^{-1}$, $\Delta S^\neq = -11.6$ cal.deg.$^{-1}$mole$^{-1}$) are similar to those reported by King and Lionetti [13] ($\Delta F^\neq = 1.976 \times 10^4$ cal.mole$^{-1}$, $\Delta S^\neq = -12.4$ cal.deg.$^{-1}$mole$^{-1}$). The polymeric hydroxide-catalysed reaction has an enthalpy of activation (see Table 20) higher than that of the sodium hydroxide-catalysed reaction by 1000 cal.mole$^{-1}$. Thus, the enthalpy of activation favours the sodium hydroxide-catalysed reaction. However, the entropy of activation of the polymeric hydroxide-catalysed reaction (see Table 20) is sufficiently higher than that of the sodium hydroxide-catalysed reaction to overcome this effect, so that the higher rate constant obtains in the presence of the polymeric hydroxide. The higher entropy of activation of the polymeric hydroxide-catalysed reaction indicates that the increase in the order of the system, which occurs when the nitrosotriacetonamine and hydroxyl ion combine to form the activated complex, is smaller in the presence of the poly-cation than in the presence of low molecular weight electrolyte. The difference between the free energies of activation, 300 cal.mole$^{-1}$, for the reactions
in the presence of sodium hydroxide and polymeric hydroxide, respectively, reflects the difference between the respective rate constants.

Similar results have been reported for reactions catalysed by ion-exchange resins and their respective low molecular weight analogues. For example, the enthalpies and entropies of activation for the hydrolyses of dipeptides by an acidic cation-exchange resin were both higher than the corresponding values for the reactions catalysed by hydrochloric acid [49].

The results can be interpreted more clearly in terms of the collision theory of reaction kinetics [134]. The activation energies obtained from the Arrhenius plots show that the reaction catalysed by sodium hydroxide has an activation energy 1000 cal.mole\(^{-1}\) less than that of the polymeric hydroxide-catalysed reaction. However, the larger pre-exponential term, \(A\), for the latter reaction (see Table 20) outweighs the activation energy effect, and causes this reaction to possess the higher rate constant. The collision theory interprets \(A\) as being a frequency factor. This represents the number of collisions, leading to reaction, which occur at unit concentration of reactants in unit time. On this basis, therefore, the frequency factor of the polymeric hydroxide-catalysed reaction, \(48.1 \times 10^{-10}\text{ mole}^{-1}\text{sec}^{-1}\), is 9.9 times that for the sodium
hydroxide-catalysed reaction, $4.85 \times 10^{10} \text{ mole}^{-1} \text{sec}^{-1}$. This is consistent with the concept of the existence of regions in and around the poly-cations where both the reactant concentrations are increased, causing the average number of reactant collisions in unit volume of the solution in unit time to be higher than that for an evenly distributed low molecular weight system.

The same behaviour has also been observed by Kargin, Kabanov and Kargina [46] for the hydrolysis of ethyl acetate in poly(styrenesulphonic acid). In this case, the activation energies for the reactions in the presence of the polymeric acid and its low molecular weight analogue, respectively, were the same. The higher rate constant observed in the presence of the polymeric acid was therefore due to the higher frequency factor of the reaction in the presence of this polymeric acid.
The Mean Hydroxyl-Ion Activity Coefficient in Aqueous Polymeric Quaternary Ammonium Hydroxide Solution

The pH, pH(S), of the 0.01M sodium hydroxide solution, S, used to standardise the pH meter, is given by the formal definition

$$\text{pH}(S) = -\log_{10} a_{H}(S)$$

where $a_{H}(S)$ is the mean activity of the hydronium ion in S. The value of pH(S) for this standard reference solution at 25°, 11.94, was derived by Bates, Pinching and Smith [81] using a cell without liquid junction. After it had been standardised with this solution, the pH meter then automatically yielded the pH, pH(X), of a test solution, X, according to the relationship

$$\text{pH}(X) = \text{pH}(S) + \frac{(E_{X} - E_{S})F}{RT\ln 10}$$

where $E_{X}$ and $E_{S}$ are the e.m.f. values of the cell when it contains X and S respectively, F is one faraday, R is the universal gas constant, and T is the absolute temperature (298°K).

If it is assumed that the difference $(E_{X} - E_{S})$ is due solely to a difference in the mean hydronium ion activities in X and S respectively, then pH(X) provides an expression for the mean hydronium ion activity, $a_{H}(X)$, in X:
\[ \text{pH}(X) = -\log_{10} a_{H}(X) \]

In dilute solutions of simple low molecular weight electrolyte, this assumption is accepted as justifiable when \( \text{pH}(X) \) and \( \text{pH}(S) \) are in the same part of the pH scale, since the extraneous potentials would then cancel out. However, when solution X contains polyelectrolyte it is not certain if this assumption is still valid. For example, it is not known if the presence of the poly-cation in the polymeric hydroxide solution modifies the response of the glass electrode, or if the liquid-junction potential when the cell contains polyelectrolyte is different from that when the standard reference solution is present.

Subject to these uncertainties, the present results show that the mean hydroxyl-ion activity coefficients of aqueous polymeric hydroxide solutions are less than those of the corresponding sodium hydroxide solutions. In this respect, the present results resemble those reported by Lapanje, Haebig, Davis and Rice [22] for the activity coefficients of chloride ions in solutions of poly(ethyleneimine hydrochloride), which were also measured by means of a cell containing a liquid junction.

The observed low activity coefficients of the hydroxyl counterions in the polymeric hydroxide solutions conform to the general pattern of behaviour of polyelectrolytes (see p.26), and indicate that the hydroxyl counterions are affected appreciably by the electrostatic fields of the poly-cations.
PART II

The Acid-Catalysed Isomerisation of Cinchonine

into Cinchotoxine
INTRODUCTION
The Isomerisation of Cinchonine(I) into Cinchotoxine(II)

This reaction occurs when an aqueous solution of a cinchonine salt is heated in the presence of a weak-acid catalyst, such as acetic acid [135].

The reaction is reported to be irreversible [136,137], and of first order with respect to the concentrations of both the univalent protonated cinchonine cation and the undissociated form of the weak acid, respectively [138], the observed first-order constant, $k_1$, conforming approximately to the relationship

$$k_1 = k_o + Ac$$

where $k_o$ and $A$ are constants, and $c$ is the concentration of undissociated acid [138]. In addition, the rate constant of the isomerisation increases when the strength of the acid catalyst decreases [139], e.g. propionic acid is more effective than acetic acid [140], while hydronium ions from strong acids,
such as hydrochloric acid, inhibit the conversion [137, 140]. The concentrations of cinchonine used in these reported investigations were about 0.1m, while those of the acids ranged from 0.15 to 17.24m [140]. In most cases, the reactions were carried out at about 100°C.

Both gravimetric and polarimetric methods have been reported [141] for the evaluation of the rate constants. In the former technique, the progress of the reaction was followed by the measurement of the weight of unreacted cinchonine, which was precipitated from an aliquot of the reaction mixture by the addition of ammonium nitrate and ammonia solution. The polarimetric method, which appears to be more accurate, was applicable because the optical rotatory power of a solution containing a cinchonine salt and a cinchotoxine salt was a linear function of its composition.

In the present investigation, the polymeric weak acid, poly(methacrylic acid), and acetic acid, respectively, were used as catalysts.
All melting points determined in this investigation have been corrected.
The Reaction Kinetics

A severe limitation to the present investigation was caused by the low solubility, in all the suitable solvents tested, of the cinchonine polymethacrylate salt formed from cinchonine and poly(methacrylic acid), even at temperatures as high as 100°. Water by itself is a very poor solvent, and the most suitable one was found to be a mixture of 1,4-dioxan and water (3 : 1v/v). Even so, it was not possible to obtain cinchonine polymethacrylate solutions in excess of 0.05M.

Attempts were made to follow the progress of the reaction by a polarimetric method. The reaction was carried out at 84.9 ± 0.1°, i.e. just below the boiling point of the water-1,4-dioxan azeotrope, in a 1 decimetre polarimeter tube designed to withstand the strains imposed by the high temperature. The temperature was maintained by the passage of water, from a thermostat, through a jacket surrounding the polarimeter tube. The polarimeter reading, $r_t$, at time t, for light from a sodium lamp (wavelengths of doublet: 5890 and 5896Å) was then obtained by means of a Lippich polarimeter, readable to 0.01°. As the reaction progressed, so the positive angle of rotation decreased towards the smaller positive value corresponding to the cinchotoxine salt.

Owing to the small concentrations of cinchonine
polymethacrylate which could be attained, the complete reaction corresponded to a change of only 2° in the polarimeter readings. Furthermore, the reaction mixture darkened steadily, with the result that the accuracy of the readings progressively deteriorated. In addition, the reaction was also slow (half-life: ca. 24 hours) so that it was impracticable to take an infinity reading. It was therefore impossible to evaluate the first-order constant, $k_1$, for the reaction by the use of the infinity reading, while the alternative Guggenheim method [77] was rendered very inaccurate due to the limitations imposed by the darkening.

In order to obtain a value for $k_1$, an artificial infinity reading, $r_\infty$, was obtained from a cinchotoxine-poly(methacrylic acid) solution exactly equivalent to the reaction mixture. Since the first-order rate constant is given by

$$k_1 t = 2.303 \log_{10}\left(\frac{r_1 - r_\infty}{r_t - r_\infty}\right),$$

where $r_1$ is the polarimeter reading at an arbitrary zero time, then $k_1$ can be obtained from the gradient of the straight-line graph of $\log_{10} (r_t - r_\infty)$ against $t$. If the gradient is $G$, $k_1$ is given by the relationship

$$k_1 = -2.303 G.$$

Owing to the darkening of the reaction mixture, it was possible
to observe only about the first 15% of the reaction. The values of \( k_1 \) obtained in the presence of poly(methacrylic acid) and acetic acid, respectively, are given in Table 28.

**TABLE 28**

First-Order Rate Constants, \( k_1 \), for the Isomerisation of Cinchonine, at 84.9 ± 0.1°.

\( \text{c}_0 = \text{initial cinchonine concentration} \)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( 10^2[\text{Catalyst}] ) ( (\text{N}) )</th>
<th>( 10^2\cdot \text{c}_0 ) ( (\text{M}) )</th>
<th>( 10^6\cdot k_1 ) ( \text{(sec.}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(methacrylic acid)</td>
<td>30.7</td>
<td>2.60</td>
<td>6.7</td>
</tr>
<tr>
<td>Poly(methacrylic acid)</td>
<td>30.3</td>
<td>5.02</td>
<td>6.7</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>30.7</td>
<td>2.60</td>
<td>1.6</td>
</tr>
</tbody>
</table>
The Preparation of Cinchotoxine Derivatives

The preparations of a number of functional derivatives of cinchotoxine were attempted, to ascertain if any of them would be suitable for the possible identification of cinchotoxine in the reaction products of the kinetic runs.

Cinchotoxine was prepared from cinchonine (m.p. 258.5 - 259.5°, \([\alpha]^{25}_D + 225°, 99\% \text{ ethanol } c = 0.5\)) by the method of von Miller and Rohde [142]. The product was a pale yellow crystalline solid, m.p. 52-53° with sintering commencing at 46°, \([\alpha]^{25}_D + 46°, 96\% \text{ ethanol } c = 1\). Recorded values are: m.p. 58 - 59° [142] and 49 - 50° [143], \([\alpha]^{14}_D + 57.6°, \text{ absolute ethanol } c = 1\) [143] and \([\alpha]^{15}_D + 48°, 95\% \text{ ethanol } c = 1\) [144].

The preparations of the functional derivatives are described below.

N-p-Toluenesulphonylcinchotoxine

To a solution of cinchotoxine (1.00 g., 0.0034 moles) in pyridine (1.0 ml.) was added, dropwise with shaking, a solution of p-toluenesulphonyl chloride (0.65 g., 0.0034 moles) in pyridine (3.0 ml.). After it had been set aside for two hours, the mixture was heated in a bath of boiling water for one hour, the flask being fitted with a reflux condenser and calcium chloride guard tube. The solution was then left overnight.
at room temperature. Addition of 2N hydrochloric acid (30 ml.) resulted in the separation of a pale yellow soft solid mass. This was withdrawn from the liquid and left under water for one day. The resulting hard pale yellow solid (1.19 g., 78% yield) contained no chloride. It was recrystallised from aqueous ethanol (with animal charcoal) to give N-p-toluenesulphonyl-cinchotoxine as small colourless prisms, m.p. 125.5-126.5°, N found 6.7, C_{26}H_{28}N_{2}O_{3}S requires 6.25%.

**N-Picrylcinchotoxine**

To a solution of cinchotoxine (1.00 g., 0.0034 moles) in 96% ethanol (1.0 ml.) a solution of picryl chloride (0.84 g., 0.0034 moles) in 96% ethanol (40 ml.) was added dropwise, with stirring. A red coloration, produced immediately the solutions were mixed, gave way to yellow, finely divided crystals. The mixture was then heated, under reflux, in a bath of boiling water for 1½ hours. The crude solid (0.92 g., 54% yield) consisted of small, bright yellow prisms, m.p. 181-182°, and contained no chloride. It was recrystallised from dry n-butanol to yield N-picrylcinchotoxine as small, bright yellow prisms, m.p. 184°, N found 13.9, C_{25}H_{23}N_{5}O_{7} requires 13.85%.

**N-(1-naphthylaminocarbonyl)-cinchotoxine**

To dry cinchotoxine (1.00 g., 0.0034 moles), which had
been liquified at 60°, was added 1-isocyanatonaphthalene (0.58 g., 0.0034 moles). The viscous mixture, contained in a stoppered flask, was warmed on a steam bath for 5 minutes, and swirled until the reactants were completely mixed. After two hours at room temperature the mixture had become a hard, glassy, yellow mass. This was dissolved in boiling dry benzene, and the hot solution diluted with sufficient n-hexane to cause the separation of a pale yellow crystalline solid when the solution was allowed to cool slowly. The crude product (1.18 g., yield 75%) was recrystallised from a mixture of benzene and n-hexane to yield N-(1-naphthylaminocarbonyl)-cinchotoxine as small colourless prisms, m.p. 125-126°, N found 9.35, C_{30}H_{29}N_{3}O_{2} requires 9.05%.

N-benzenesulphonylcinchotoxine

This derivative has already been reported by Rohde and Antonaz, m.p. 108-109° [145]. It was prepared in the present investigation from cinchotoxine (1.00 g., 0.0034 moles) and benzenesulphonyl chloride (0.66 g., 0.0038 moles) in the presence of excess 2.5N aqueous sodium hydroxide solution. Recrystallisation from dry n-butanol gave N-benzenesulphonylcinchotoxine as small colourless prisms, m.p. 105-106°, N found 6.8, calculated for C_{25}H_{26}N_{2}O_{3}S 6.45%. 
Attempts to Prepare other Derivatives

No solid derivatives were obtained with benzoyl chloride, formic acid, or 4-phenylsemicarbazide. The reaction of cinchotoxine with benzaldehyde, semicarbazide, phenylhydrazine, p-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine yielded crude solid products, none of which could be recrystallised. This was due, in the last instance, to the insolubility of the product, and in the other cases to the separation of persistent oils when recrystallisations were attempted.
DISCUSSION
The Reaction Mechanism

The reaction mechanism has not been established fully. Rabe and Schuler [136] consider that the reaction proceeds through the loss of a proton from the carbon atom of the secondary alcohol group of the cation formed by the protonation of the nitrogen atom in the quinuclidine group, i.e.

The product in this scheme is the enolic form of cinchotoxine.
The reliability of the results is limited by the experi-
mental difficulties which were encountered. There is, however,
a definite indication that poly(methacrylic acid) is more
effective than acetic acid as a catalyst for the reaction in
aqueous 1,4-dioxan solution.

This effect may simply be in accord with the trend ob-
served by Rabe [146], and Biddle and Brauer [140] for low mole-
cular weight catalysts, whereby the rate constant increases as
the dissociation constant of the acid catalyst decreases. The
apparent dissociation constant, $K'_a$, of poly(methacrylic acid)
in aqueous solution decreases as the degree of ionisation in-
creases [147], reflecting the increasing difficulty with which
protons leave the carboxyl groups as the proportion of anionic
carboxylate groups on the polymer chain increases. Poly(meth-
acrylic acid) in aqueous solution at $25^\circ$, with a degree of ioni-
sation of 0.08, has a $pK'_a$ of 6.16 [147], i.e. $K'_a = 6.9 \times 10^{-7}$,
while acetic acid has a dissociation constant, $K_a$, of $1.77 \times 10^{-5}$
in aqueous solution at $25^\circ$ [148]. Therefore, on these grounds
alone, the rate constant in the presence of poly(methacrylic
acid) could be expected to exceed that in the presence of acetic
acid under the same conditions. It is consequently not possible
to deduce if any enhancement in rate constant is caused by a
concentration of reactant in the regions occupied by the
partially-ionised poly(methacrylic acid) macromolecules.
APPENDIX 1

Standardisation of Benzoyl Peroxide

Titrations with 0.01050N sodium thiosulphate (at 23°)

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank titre (ml.)</td>
<td>0.70</td>
<td>0.72</td>
<td>0.71</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>0.71 ml.</td>
<td></td>
</tr>
<tr>
<td>Wt. of benzoyl peroxide (g.)</td>
<td>0.0510</td>
<td>0.0567</td>
<td>0.0532</td>
</tr>
<tr>
<td>Titre (ml.)</td>
<td>39.12</td>
<td>44.07</td>
<td>41.42</td>
</tr>
<tr>
<td>Correction (ml.)</td>
<td>-0.71</td>
<td>-0.71</td>
<td>-0.71</td>
</tr>
<tr>
<td>Corrected titre (ml.)</td>
<td>38.41</td>
<td>43.36</td>
<td>40.71</td>
</tr>
</tbody>
</table>

Calculations.

\[
242.23 \text{ g. Ph.CO.00.CO.Ph} \equiv 2 \text{ g. electrons} \\
\equiv \frac{2 \times 1000}{0.01050} \text{ ml. of 0.01050N.}
\]

Let \( \frac{242.23 \times 0.01050}{2} = a \).

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoyl peroxide content (%)</td>
<td>96.01</td>
<td>97.50</td>
<td>97.57</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>97.0%</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX 2

The Determination of Chloride Ion in the Polymeric Quaternary Ammonium Chloride, Batch Q-3, and Calculation of the Percentage Quaternisation

Silver nitrate solution : 0.09939N (at 20°).
Polymeric chloride dissolved in chloride-free distilled water (50 ml.).
5% aqueous AR potassium chromate solution (1.00 ml.) added from a pipette.
Blank titrations carried out with AR calcium carbonate (0.5 g.) and distilled water (60 ml.).

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of polymeric chloride (g.)</td>
<td>0.3540</td>
<td>0.3315</td>
<td>0.3056</td>
</tr>
<tr>
<td>Titre (ml.)</td>
<td>13.72</td>
<td>12.91</td>
<td>11.90</td>
</tr>
<tr>
<td>Correction (ml.)</td>
<td>-0.10</td>
<td>-0.10</td>
<td>-0.10</td>
</tr>
<tr>
<td>Corrected titre (ml.)</td>
<td>13.62</td>
<td>12.81</td>
<td>11.80</td>
</tr>
</tbody>
</table>

35.457 g. Cl⁻ = \( \frac{1000}{0.09939} \) ml. of 0.09939N.

Let 0.09939 x 3.5457 = b.
For completely mono-chloromethylated polystyrene, the g. molecular weight of the structural unit, \( \text{CH}_2\text{CH}\.\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{Cl} \), is 152.628.

The g.molecular weight of a quaternised unit, \( \text{CH}_2\text{CH}\.\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{N(C}_2\text{H}_5)_3\cdot\text{Cl} \), is 253.822.

The g.ionic weight of the chloride ion is 35.457.

Let the ionic chloride content of the quaternised polymer be \( p \)%, by weight.

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

If 100 chloromethyl groups were present before the quaternisation, then \( x \) quaternary groups were produced, leaving \( (100 - x) \) residual chloromethyl groups.

Therefore \( \frac{35.457 \times x}{253.822 \times x + 152.628(100-x)} = \frac{p}{100} \),
Whence \( x = \frac{15262.8 \ p}{3545.7 - 101.194 \ p} \)

Hence, for batch Q - 3, where \( p = 13.59 \),

\( x = 95.5 \).

Thus, 95.5% of the chloromethyl groups were quaternised when batch Q - 3 was prepared.
APPENDIX 3

The Evaluation of the Rate Constants for the Nitrosotriacetonamine Decomposition, by the Guggenheim Method

Symbols:

\[ \Delta \] : constant time interval (min.).

\[ C_0 \] : initial concentration of nitrosotriacetonamine (mole \( l^{-1} \)).

\[ d \] : density of mercury (g \( cm^{-3} \)) in the Fortin barometer.

\[ g \] : acceleration due to gravity (cm \( sec^{-2} \)).

\[ k \] : observed first-order rate constant (min \( ^{-1} \)).

\[ k_1 \] : observed first-order rate constant (sec \( ^{-1} \)).

\[ m \] : number of moles of nitrogen liberated, per litre of solution, after time \( t \).

\[ n \] : number of moles of nitrogen liberated, per litre of solution, after time \( t + \Delta \).

\[ p \] : vapour pressure of the solvent (cm. mercury).

\[ P_i \] : atmospheric pressure (cm. mercury) at the start of the reaction.

\[ P_t \] : atmospheric pressure (cm. mercury) at time \( t \).

\[ P_t + \Delta \] : atmospheric pressure (cm. mercury) at time \( t + \Delta \).

\[ r_i \] : burette reading (ml.) at the start of the reaction.

\[ r_t \] : burette reading (ml.) at time \( t \).

\[ r_t + \Delta \] : burette reading (ml.) at time \( t + \Delta \).

\[ R \] : universal gas-constant (erg \( deg^{-1} mole^{-1} \)).
For the first-order reaction:

\[ \frac{dm}{dt} = k(C_0 - m), \]

whence \( m = C_0[1 - \exp(-kt)] \)

and \( n = C_0[1 - \exp(-kt)\exp(-k\Delta)], \)

\[ \therefore \ln(n - m) = K_1 - kt \]

\[ \ldots (17) \]

where \( K_1 = \ln C_0 [1 - \exp(-k\Delta)] \) = a constant.

Nitrogen acts as an ideal gas under the conditions used. Therefore:

Quantity of nitrogen present at the start of the reaction = \( \frac{(V + r_i)(P_i - p)dg}{RT} \) moles.

Quantity of nitrogen present after time \( t = \)

\( \frac{(V + r_t)(P_t - p)dg}{RT} \) moles.

Hence,
\[ m = \frac{1000 \, \text{d} \left[ (V + r_t)(P_t - p) - (V + r_i)(P_i - p) \right]}{vRT}, \]
\[ n = \frac{1000 \, \text{d} \left[ (V + r_t + \Delta)(P_t + \Delta - p) - (V + r_i)(P_i - p) \right]}{vRT}. \]

Therefore,
\[ \ln(n - m) = \ln \frac{1000 \, \text{d} \left[ (V + r_t + \Delta)(P_t + \Delta - p) - (V + r_t)(P_t - p) \right]}{vRT} \]
\[ \ldots \text{(18)} \]

From equations (17) and (18)
\[ \ln \left[ (V + r_t + \Delta)(P_t + \Delta - p) - (V + r_t)(P_t - p) \right] = K_2 - kt \]
\[ \ldots \text{(19)} \]

where \( K_2 = K_1 - \ln \frac{1000 \, \text{d} \left[ (V + r_t + \Delta)(P_t + \Delta - p) - (V + r_t)(P_t - p) \right]}{vRT} = \text{a constant}. \]

For all the runs conducted, the variation of \( P_t \) while a reaction was in progress did not exceed 0.2\%. At \( T = 298^\circ \) \( p \) was about 3.1\% of \( P_t \) and at \( T = 313^\circ \) \( p \) was about 7.2\% of \( P_t \). Therefore, for all the runs, \( (P_t - p) \) can be treated as a constant, \( P \).

Equation (19) then becomes
\[ \ln(r_t + \Delta - r_t) = K_3 - kt \]
where \( K_3 = K_2 - \ln P = \text{a constant}. \)

If the gradient of the straight line, obtained by plotting \( \log_{10}(r_t + \Delta - r_t) \) against \( t \), is \( S \text{ min}^{-1} \), then
\[ S = - \frac{k}{2.303}. \]
\[ \therefore \quad k = -2.303 \times S. \]
and \( k_1 = \frac{2.303 \times S}{60}. \)
APPENDIX 4

**Typical Kinetic Run with Polymeric Quaternary Ammonium Hydroxide (H - 5) as Catalyst**

<table>
<thead>
<tr>
<th>Run no.</th>
<th>128</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of nitrosotriacetonamine</td>
<td>0.2061 g.</td>
</tr>
<tr>
<td>Nitrosotriacetonamine concentration</td>
<td>1.60 x 10^{-2}M</td>
</tr>
<tr>
<td>Hydroxyl-ion concentration</td>
<td>1.00 x 10^{-2}N</td>
</tr>
<tr>
<td>Solvent</td>
<td>nitrogen-saturated water</td>
</tr>
<tr>
<td>Temperature</td>
<td>25.00 ± 0.02°C.</td>
</tr>
<tr>
<td>Δ</td>
<td>50 min.</td>
</tr>
</tbody>
</table>

The atmospheric pressure increased from 749.50 to 749.75 mm. mercury during the run.
The graph of \( \log_{10}(r_{t+50} - r_t) \) against \( t \) (see Fig. 16) gave:

\[
\text{gradient} = - \frac{0.458}{50} \text{ min.}^{-1}
\]

\[
\therefore \quad k_1 = \frac{2.303 \times 0.458}{60 \times 50} \text{ sec.}^{-1}
\]

\[
= 3.52 \times 10^{-4} \text{ sec.}^{-1}
\]
APPENDIX 5

Derivation of the Expressions for the Activation Parameters

Symbols:

A : pre-exponential Arrhenius A factor (l.mole\(^{-1}\)sec\(^{-1}\)).

\(E_a\) : Arrhenius activation energy (cal.mole\(^{-1}\)).

h : Planck's constant (erg.sec.).

k : Boltzmann's constant (erg.deg\(^{-1}\)).

\(k_2\) : observed second-order catalytic rate constant (l.mole\(^{-1}\)sec\(^{-1}\)).

R : universal gas-constant (cal.deg\(^{-1}\)mole\(^{-1}\)).

T : absolute temperature (deg.K).

\(K^*\) : equilibrium constant for the formation of the activated complex.

\(\Delta F^*\) : free energy of activation (cal.mole\(^{-1}\)).

\(\Delta H^*\) : enthalpy of activation (cal.mole\(^{-1}\)).

\(\Delta S^*\) : entropy of activation (cal.deg\(^{-1}\)mole\(^{-1}\)).

\(\Delta F^*, \Delta H^*\) and \(\Delta S^*\) apply to a standard state of 1 mole l.\(^{-1}\).
In the transition-state theory [149], $\Delta F^\neq$, $\Delta H^\neq$ and $\Delta S^\neq$ are defined, respectively, by

\[
\Delta F^\neq = -RT \ln K^\neq
\]

\[
\Delta H^\neq = RT^2 \frac{d \ln K^\neq}{dT}
\]

and

\[
T \Delta S^\neq = \Delta H^\neq - \Delta F^\neq
\]

while $k_2$ is given by

\[
k_2 = \frac{kT}{h} \exp(-\Delta F^\neq/RT),
\]

or

\[
k_2 = \frac{kT}{h} K^\neq
\]

From equations (21) and (22),

\[
k_2 = \frac{kT}{h} \exp(-\Delta H^\neq/RT) \cdot \exp(\Delta S^\neq/R)
\]

From equation (23),

\[
\frac{d \ln k_2}{dT} = \frac{1}{T} + \frac{d \ln K^\neq}{dT}
\]

From equations (20) and (25),

\[
\Delta H^\neq = RT^2 \left( \frac{\frac{d \ln k_2}{dT}}{T} - \frac{1}{T} \right)
\]

The Arrhenius equation [79],

\[
k_2 = A \exp(-E_a/RT),
\]

gives

\[
\ln k_2 = \ln A - \frac{E_a}{RT}
\]
and \[ \frac{\text{dln}k_2}{\text{dT}} = \frac{E_a}{RT^2} \] \[ \ldots \quad (28) \]

Therefore, from equations (26) and (28),

\[ \Delta H^\neq = E_a - RT \] \[ \ldots \quad (29) \]

Therefore, at 298°K, \[ \Delta H^\neq_{298} = E_a - 298R \]

Equations (24) and (29) give

\[ k_2 = \frac{e^{kT}}{h} \exp\left(\frac{\Delta S^\neq}{R}\right) \exp\left(-\frac{E_a}{RT}\right) \] \[ \ldots \quad (30) \]

Hence, from equations (27) and (30),

\[ A = \frac{e^{kT}}{h} \exp(\Delta S^\neq/R) \]

Therefore

\[ \Delta S^\neq = R(\ln A - \ln \frac{e^{kT}}{h}) \]

At 298°K, \[ \log_{10} \frac{e^{kT}}{h} = 13.227 \ [80] \]

\[ \therefore \Delta S^\neq_{298} = 2.303R(\log_{10}A - 13.227) \]

From equation (21),

\[ \Delta F^\neq_{298} = \Delta H^\neq_{298} - 298 \Delta S^\neq_{298} \]
Summary

Part I

Chloromethylated polystyrene has been converted with triethylamine into a polymeric quaternary ammonium chloride containing 95.5% of (vinylbenzyltriethylammonium chloride) groups, as estimated from the chloride-ion content. This polyelectrolyte was then converted, in aqueous solution, into the corresponding polymeric quaternary ammonium hydroxide by means of an anion-exchange resin, Amberlite IRA-401, in its hydroxide form. The alternative conversion with moist silver oxide yielded darkly coloured solutions.

Triacetonamine hydrate was prepared from acetone and ammonia. N-nitrosation of the product then yielded nitroso-triacetonamine.

The first-order rate constants of the hydroxyl ion-catalysed decomposition of nitrosotriacetonamine in aqueous solutions of the strongly basic polymeric quaternary ammonium hydroxide at 25.00°C have been obtained by measurement of the rates of nitrogen evolution. These values (Table 10) were compared with those similarly obtained in the presence of sodium hydroxide (Table 7) and benzyltriethylammonium hydroxide (Table 8). At a hydroxyl-ion concentration of 0.01N the rate constant of the reaction in the presence of the polymeric hydroxide (3.52 x 10^{-4} sec.^{-1}) was higher than those for the
sodium hydroxide- and benzyltriethylammonium hydroxide-catalysed reactions (2.03 x 10^{-4} and 2.08 x 10^{-4} sec^{-1}, respectively) by a factor of 1.7.

The first-order constants varied linearly with hydroxyl-ion concentration for both polymeric hydroxide- and sodium hydroxide-catalysed reactions (Fig. 5). Catalytic rate constants, from the gradients of the linear graphs, were 3.48 x 10^{-2} and 2.03 x 10^{-2} l.mole^{-1}sec^{-1} respectively.

The addition of simple salts to the polymeric hydroxide solution (hydroxyl-ion concentration 0.01N) produced a sharp initial decline in the rate constant. At sodium chloride concentrations in excess of 0.045M the rate constants of the reactions catalysed by 0.01N polymeric hydroxide assumed approximately the same values as those of the corresponding sodium hydroxide-catalysed reactions (Tables 11 and 12, Fig. 6). Sodium sulphate at low concentrations (less than 0.04 g.equiv.l^{-1}) was more effective than sodium chloride in reducing the rate constants (Table 12, Fig. 6). In contrast to this behaviour, sodium chloride produced a relatively small, negative linear salt effect in the sodium hydroxide-catalysed reactions. The polymeric quaternary ammonium chloride also caused a reduction of the rate constant of the polymeric hydroxide-catalysed decomposition (Table 12, Fig. 6), but was not so effective as sodium chloride in this respect.
A decrease in the macroscopic dielectric constant of the solvent, effected by the addition of 1,4-dioxan, brought about a marked decrease in the rate constant of the polymeric hydroxide-catalysed reaction (Table 13, Fig.7), but had only a slight influence on the rate constant of the sodium hydroxide-catalysed reaction (Table 13, Fig.7).

The higher rate constant obtaining in the polymeric hydroxide solution was associated with a higher entropy of activation. This parameter outweighed the opposing influence of the enthalpy of activation (Table 20) which favoured the sodium hydroxide-catalysed reaction.

Potentiometric measurements have shown that the mean hydroxyl-ion activity coefficients in dilute aqueous solutions of the polymeric hydroxide, at 25°, are lower than those in the corresponding sodium hydroxide solutions (Table 21).

The following products of the above decomposition were identified: acetone, mesityl oxide, phorone, semiphorone and, probably, 2,6-dimethyl-1,5-heptadiene-4-one. In the course of this investigation, the 2,4-dinitrophenylhydrazone of nitrosotriacetetonamine, m.p. 188.5°, was prepared.

A mechanism has been proposed for the hydroxyl ion-catalysed decomposition of nitrosotriacetetonamine. In this mechanism, the enolate anion from nitrosotriacetetonamine
rearranges into a diazotate anion, which gives a diazohydroxide, and thence a diazonium cation, the latter intermediate yielding nitrogen and a carbonium cation. This carbonium cation gives rise to three primary products: phorone, 2,6-dimethyl-1,5-heptadiene-4-one and semiphorone. The semiphorone then undergoes decomposition into acetone and mesityl oxide in the alkaline medium.

The higher catalytic efficiency of the polymeric hydroxide has been attributed to an increase in the concentrations of both nitrosotriacetonamine molecules and hydroxyl ions in the regions of solution in and around the polymeric cations, under the influence of the electrostatic fields of these poly-cations.

**Part II**

The rate constants of the isomerisation of cinchonine into cinchotoxine have been measured, with acetic acid and poly(methacrylic acid) as the catalysts. This investigation (commenced before the work described above) was discontinued because of the experimental difficulties encountered. The preliminary results showed that poly(methacrylic acid) was approximately four times as effective as acetic acid (Table 28). It was not possible to deduce whether the higher rate constant
of the isomerisation in the presence of poly(methacrylic acid) was due to the polymeric nature of the catalyst, or merely to its lower dissociation constant.

Three new cinchotoxine derivatives have been prepared, namely N-p-toluenesulphonylcinchotoxine, m.p. 125.5 - 126.5°, N-picrylcinchotoxine, m.p. 184°, and N-(1-naphthylaminocarbonyl)-cinchotoxine, m.p. 125-126°.
REFERENCES

[50] Letsinger, R.L. and Savereide, T.J., ibid., 1962, 84, 3122.
[56] Heintz, W., Annalen, 1875, 178, 320.
[57] Idem, ibid., 1877, 187, 233.
[58] Idem, ibid., 1877, 185, 3.
[72] Idem, ibid., p. 251.
[74] Ladenburg, A. and Struve, 0., Berichte, 1877, 10, 43.


[80] Idem, ibid., p.222.


[85] Baeyer, A., Annalen, 1866, 140, 297.


[88] Heintz, W., Annalen, 1874, 174, 133.


[91] Heintz, W., Annalen, 1875, 178, 315.

[92] Idem, ibid., 1880, 203, 336.


[107] Sommelet, M., Compt. rend., 1913, 157, 1443.


[136] Rabe, P. and Schuler, W., Berichte, 1948, 81, 139.


[138] Idem, ibid., 1915, 37, 2088.

[139] Idem, Berichte, 1912, 45, 2832.


[144] Hesse, O., Annalen, 1875, 178, 244.


