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TECHNICAL REPORT

KINETIC STUDY OF ION-SENSITISED TERMINATION OF RADICAL POLYMERISATION

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Abstract

Rates of polymerisation of acrylamide have been measured in aqueous solution in the presence of a number of transitional metal salts. It was shown that some metal salts are able to terminate polymerisation by a reaction which is first order with respect to the salt concerned. Uranyl perchlorate was found to be a more effective chain terminator than ferric perchlorate, which in turn was more effective than vanadyl perchlorate. In addition, uranyl perchlorate is able to initiate polymerisation by a non-photochemical mechanism, the rate being proportional to the uranyl salt concentration.

The effect of the variation in the anion concerned was also investigated and in the case of termination by ferric salts, the chloride and sulphate were both found to be considerably more effective than the perchlorate. Ferric chloride is also able to initiate polymerisation, the rate being independent of the ferric chloride concentration.

In selected cases, the effect of temperature variation was studied and Arrhenius parameters of the appropriate termination reactions have been computed. These are all small and are consistent with an electron transfer mechanism for the termination reaction.

No correlation between rates of termination and the magnitudes of the thermodynamic functions of the metal ions concerned was observed.

Introduction

Salts derived from metals of variable valence such as iron are known to terminate the radical polymerisation of certain vinyl monomers by a reaction which is first order with respect to both the metal salt and the polymer radical concerned.[1] The objects of the present investigation were to determine how far the rate of this termination reaction depends upon:-

(a) the chemical character and properties of the metal ion,

(b) the nature of the associated anion and

(c) the temperature of the reaction.

Acrylamide was the monomer chosen for this study because of its solubility in water and for the same reason, 4-4'-azo-bis-4-cyanopentanoic acid was used to initiate polymerisation. Water seemed to be the most suitable solvent because most of the relevant information on metal salts available refers to aqueous solutions.

Experimental

Kinetic measurements

Rates of polymerisation were measured either by precipitating and weighing the polymer produced (gravimetric method) or by measuring in a suitable dilatometer the contraction in volume during polymerisation. The deaeration procedure employed was the same for both methods.

Known volumes of monomer and initiator solutions of known concentration were placed in separate vessels connected by an inverted U-shaped tube, which in turn was fused to one arm of a T-piece. Of the remaining limbs of the T-piece, one was attached to a vacuum line and the other either connected to a dilatometer or sealed off as required. The dilatometer consisted of a spherical bulb of about 15 ml. capacity sealed to a length of precision 1 mm. bore capillary tubing.

Solutions were deaerated two or three times at pressures of 10^{-4} - 10^{-5} mm. Hg, after which the connexion to the vacuum line was sealed off and the whole deaeration unit transferred to a thermostat operating at $25.00 \pm 0.02^{\circ}C$. When reactants had attained thermostat temperature, they were thoroughly mixed and either transferred to the dilatometer, which was then removed from the deaeration unit, or returned to the thermostat for a

suitable period of time. In the gravimetric method, polyacrylamide was precipitated from solution by the gradual addition of either ethanol or dioxan and was dried to constant weight in vacuo over anhydrous calcium chloride at room temperature. In both methods no observations were made for conversions greater than 10%.

Water used as solvent in kinetic experiments was purified[2] by distillation followed by percolation through Amberlite monobed resin MB-1 and had a specific conductance of less than 10^{-6} mhos at room temperature.

Viscosity measurements

Once precipitated, polyacrylamide produced under our experimental conditions could only be redissolved in water with extreme difficulty. Viscosity measurements were, therefore, made by means of a U-tube viscometer on solutions of polymer prepared by the same procedure as that adopted in kinetic experiments. The polymer concentration was determined by precipitating and weighing the polymer as above and a small correction for the presence of unconverted monomer was applied in the calculation of specific viscosities.

Results and Discussion

Kinetics of polymerisation, metal salts absent

Rates of polymerisation obtained by the two methods employed are compared in Table 1; a shrinkage factor of 0.050 mmoles of acrylamide polymerised for a contraction of 1 mm. in a capillary of 1 mm. diameter[3] was used to evaluate rates quoted for the dilatometric method. Agreement between the two sets of results is generally satisfactory, particularly as reproducible kinetic results were difficult to obtain. Small amounts of impurities, have a pronounced effect upon the rate of polymerisation.

Table 1. Comparison of rates of polymerisation (R_p) obtained by dilatometric and gravimetric methods at 25.00°C.

Monomer concn. (mole/l.)	$10^4 \cdot$ Initiator concn. (mole/l.)	$10^4 \cdot R_p$ (mole/l. min.) gravimetric	dilatometric
0.640	1.64	6.90	7.90
0.528	1.64	6.42	6.30
0.528	0.85	4.80	4.92
0.419	1.64	4.52	4.28

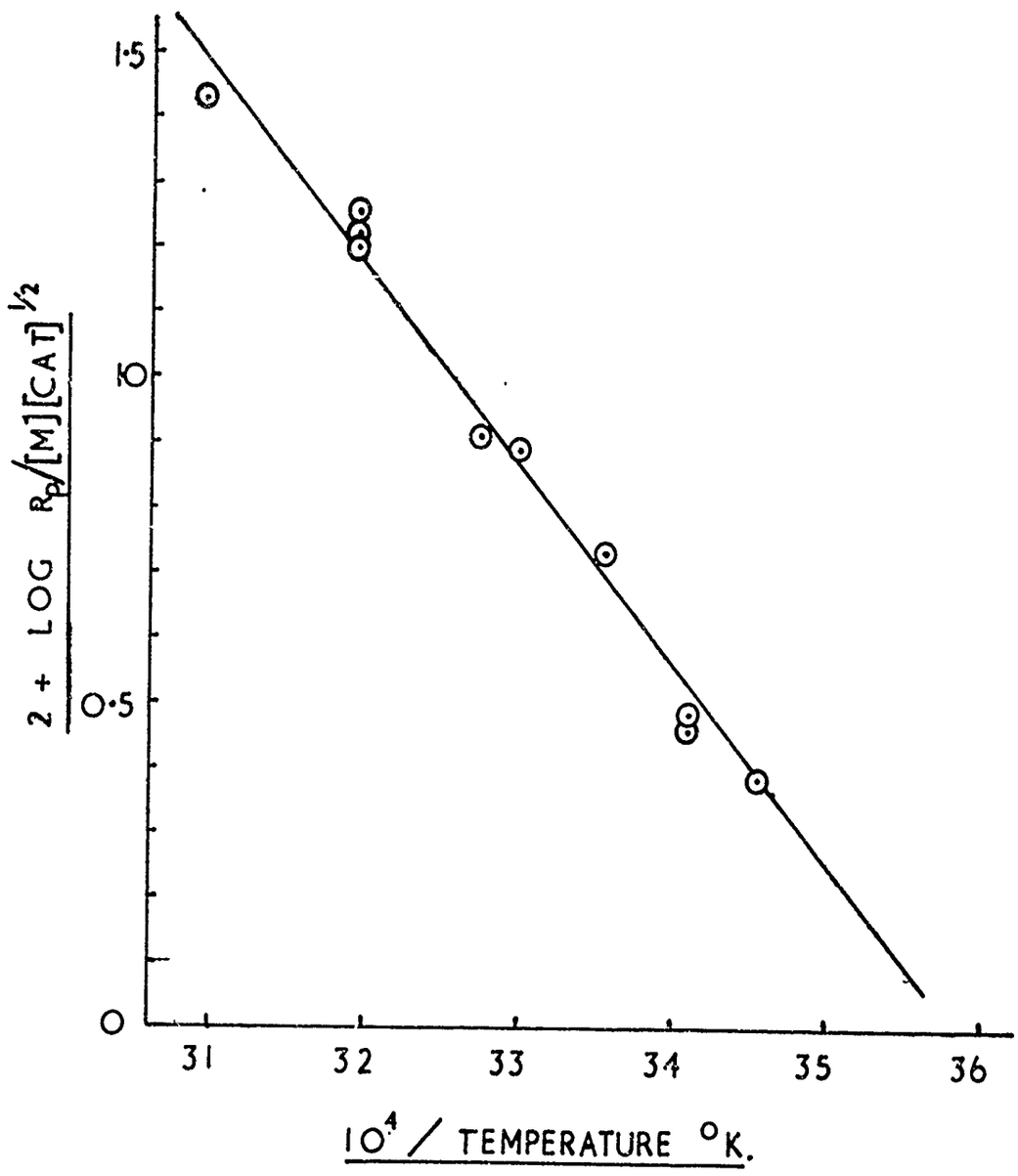
In spite of the variation between individual experiments, analysis by the method of least squares of the kinetic data obtained has shown that under our experimental conditions, the rate of

polymerisation (R_p) is proportional to $[monomer]^{1.04}$ and to $[initiator]^{0.49}$ for conversions of up to 10%. We find the mean value of the ratio $R_p/[m_1][cat]^{\frac{1}{2}}$ to be $(1.70 \pm 0.17) \times 10^{-3}$ $l.^{\frac{1}{2}}/mole^{\frac{1}{2}}.sec.$ at $25^{o}C$.

These kinetic results show that the mechanism of polymerisation follows the usual pattern and that quadratic termination of radical chains predominates. Molecular weight measurements have shown that transfer reactions are also significant,[5] but these do not influence the rate of polymerisation and are therefore not considered further here. The kinetic data obtained may also be used to evaluate the initiation coefficient (k_i), since the propagation and termination rate constants are known[4] to be $(1.80 \pm 0.15) \times 10^{4}$ l./mol. sec and $(1.45 \pm 0.20) \times 10^{7}$ l./mol. sec. respectively at $25^{o}C$. This has been found to be $(1.29 \pm 0.29) \times 10^{-7}$/sec.

The effect of temperature variation on the rate of polymerisation is illustrated in Fig. 1, where log $R_p/[m_1][cat]^{\frac{1}{2}}$ has been plotted against the reciprocal of the absolute temperature. The overall energy of activation of the reaction i.e. $E_p + \frac{1}{2}(E_i - E_t)$ has been found to be 14.4 kcal./mole, so that E_i is 26.0 kcal/mole, since E_p and E_t are known[4] to be 1.38 ± 0.25 and 0 ± 0.5 kcal./mole respectively.

FIG. 1. ARRHENIUS PLOT OF LOG $R_p/[M][CAT]^{1/2}$ AGAINST $1/T\,^{\circ}K$.

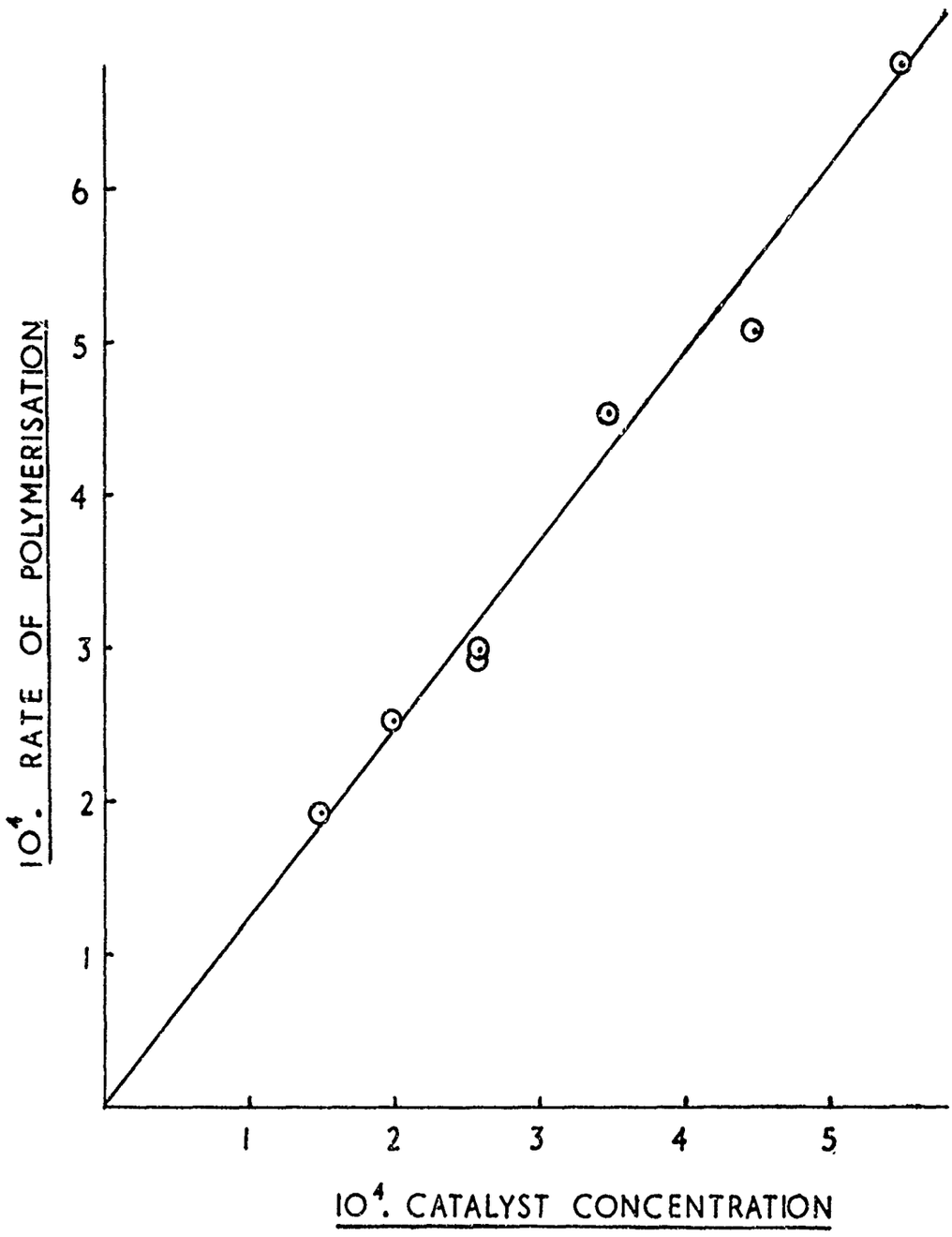


Effect of ferric perchlorate on kinetics of polymerisation.

In order to minimise complications arising from hydrolysis, the pH of aqueous solutions containing ferric salts was kept as low as possible. However, when concentrations of perchloric acid much greater than decimolar were employed, there was a noticeable tendency for solutions containing monomer to polymerise during deaeration. In fact, at 35°C. we have found that in the presence of 0.6M perchloric acid and between 10^{-4} and 10^{-5}M ferric perchlorate but with no other initiator present, a 2M solution of acrylamide in water polymerises at a rate of about 2×10^{-4}moles/l.min., this rate being approximately independent of the concentration of the ferric salt. All solutions used in the kinetic measurements discussed below were therefore approximately decimolar with respect to the appropriate acid. An increase in perchloric acid concentration from 0.1M to 0.3M was found to increase the overall rate of polymerisation by about 50%.

The effect on the rate of polymerisation (R_p) of varying the concentration of initiator with about 10^{-4}M ferric perchlorate present is illustrated in Fig. 2. Analysis of this kinetic data by the method of least squares has shown that R_p is proportional to $[\text{initiator}]^{0.95}$. The relation between the rate of polymerisation and the concentration of ferric salt is rather more complex. Above about 8×10^{-5}M, R_p

FIG. 2. VARIATION OF R_p WITH CATALYST CONCENTRATION



FERRIC PERCHLORATE CONCENTRATION = $9{\cdot}28 \times 10^{-5}$ M.

has been found to be inversely proportional to the concentration of the metal salt, as shown in Fig. 3. Below this value the rate seems to become increasingly less sensitive to changes in the concentration.

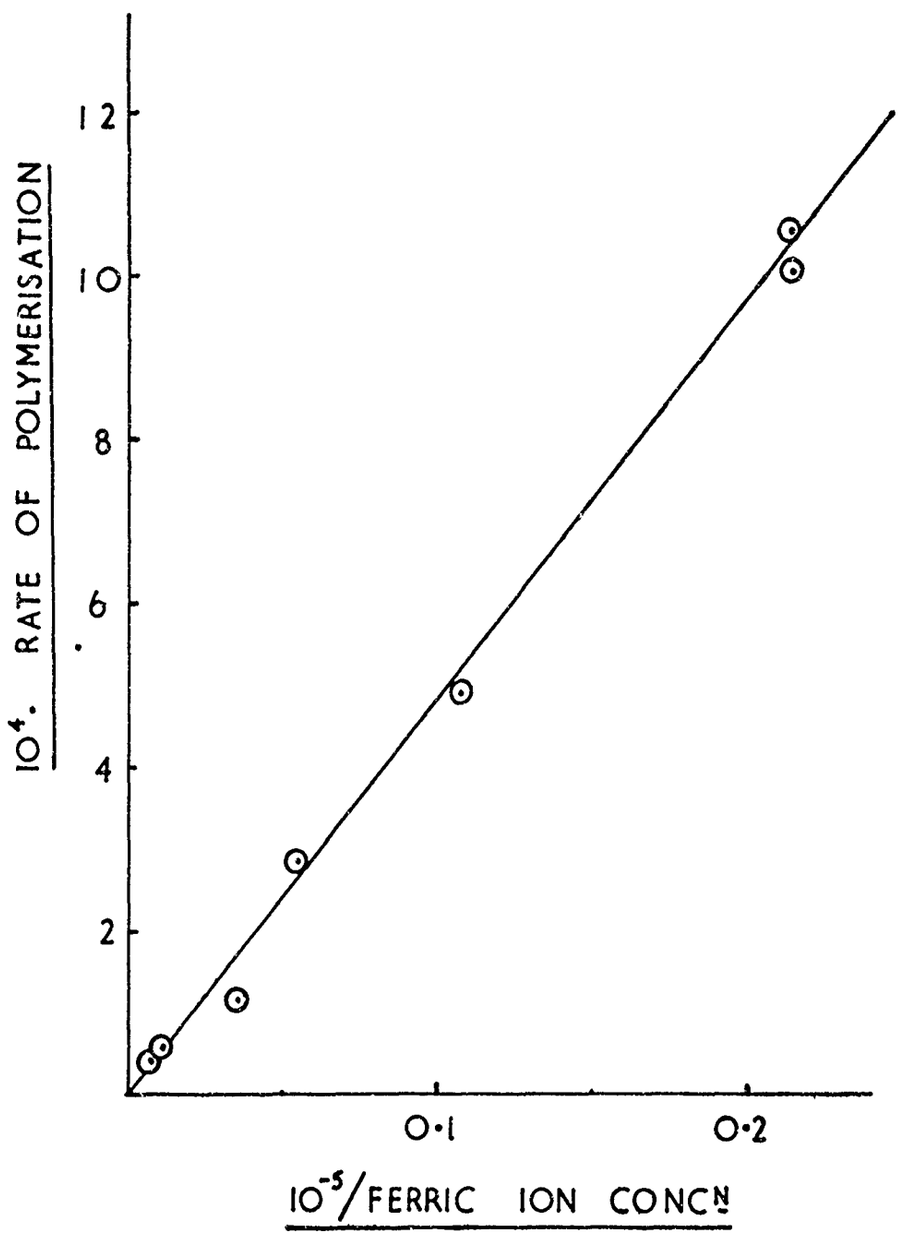
All our kinetic data are consistent with the conclusion reached by other authors[1, 4] that in the presence of a suitable metal salt, radical polymerisation may be terminated by a reaction which is first order with respect to both polymeric radical and metal salt in addition to the normal second order process operative when the salt is absent. Termination of polymerisation by ferric salts has been shown to involve reduction to the ferrous state and we too have shown, by means of o-phenanthroline, that the concentration of ferrous ion increases during the course of the polymerisation. No indication of the incorporation of halogen into the final polymer has been obtained from polymerisations performed in aqueous solution. Termination probably, therefore, proceeds by an electron transfer mechanism.

The inclusion of this additional mode of chain termination into the overall kinetic scheme leads to the following relationship for the rate of initiation:-

$$k_i[\text{cat}] = \frac{k_4[\text{Fe(III)}]R_p}{k_p[m_1]} + k_t \left\{ \frac{R_p}{k_p[m_1]} \right\}^2 \qquad (1)$$

in which k_4 is the specific rate constant for the termination reaction involving the ferric salt, the other symbols having their usual

FIG. 3. VARIATION OF R_p WITH FERRIC PERCHLORATE CONCENTRATION



CATALYST CONCENTRATION = $4{\cdot}00 \times 10^{-4}$ M

significance. Now in the case of the ferric perchlorate terminated polymerisation of acrylamide all the appropriate kinetic constants on the r.h.s. of eqn. (1) are available in the literature[4] so that the present experimental results may be used to confirm initiation coefficients for each of the temperatures studied, from which the Arrhenius parameters for the initiation reaction may be calculated. For most of the concentrations of ferric salt employed, the second term on the r.h.s. of eqn. (1) is sufficiently small to be neglected, in which case the rate of polymerisation becomes proportional to the concentration of the catalyst and inversely proportional to that of the ferric salt.

In aqueous solution ferric salts are known to be subject to a series of complex hydrolytic equilibria. The termination coefficient (k_4) appropriate for a solution having a pH of one is, therefore, a composite quantity, because the termination coefficient for aquated ferric ions is considerably less than those for the partially hydrolysed ionic species present.[4] For this reason, limiting values of the ratio $R_p[Fe(III)]/[m_1][cat]$ tend to increase as the concentration of acid present is increased. However, the high concentration of acid employed ensures that the relative proportions of the various cations present, except the dimer $Fe_2(OH)_2^{4+}$ the concentration of which is very small, do not change when the total concentration of ferric salt is varied.

At 25°C. the composite termination coefficient (k_4) for ferric perchlorate in solutions containing decimolar perchloric acid is known[4] to be 4.1×10^3 l/mol. sec. The initiation coefficients assembled in Table 2 were calculated by means of eqn. (1) using this value of k_4 and those quoted for k_p and k_t in Table 2. The mean value of k_i obtained viz. $(4.62 \pm 0.40) \times 10^{-7}$/sec. is nearly four times larger than that calculated from rates of polymerisation obtained with no ferric salt present. This would seem to indicate that ferric perchlorate has an accelerating effect on the decomposition of A. C. V., 4-4'-azo-bis-4-cyanopentanoic acid, in aqueous solution.

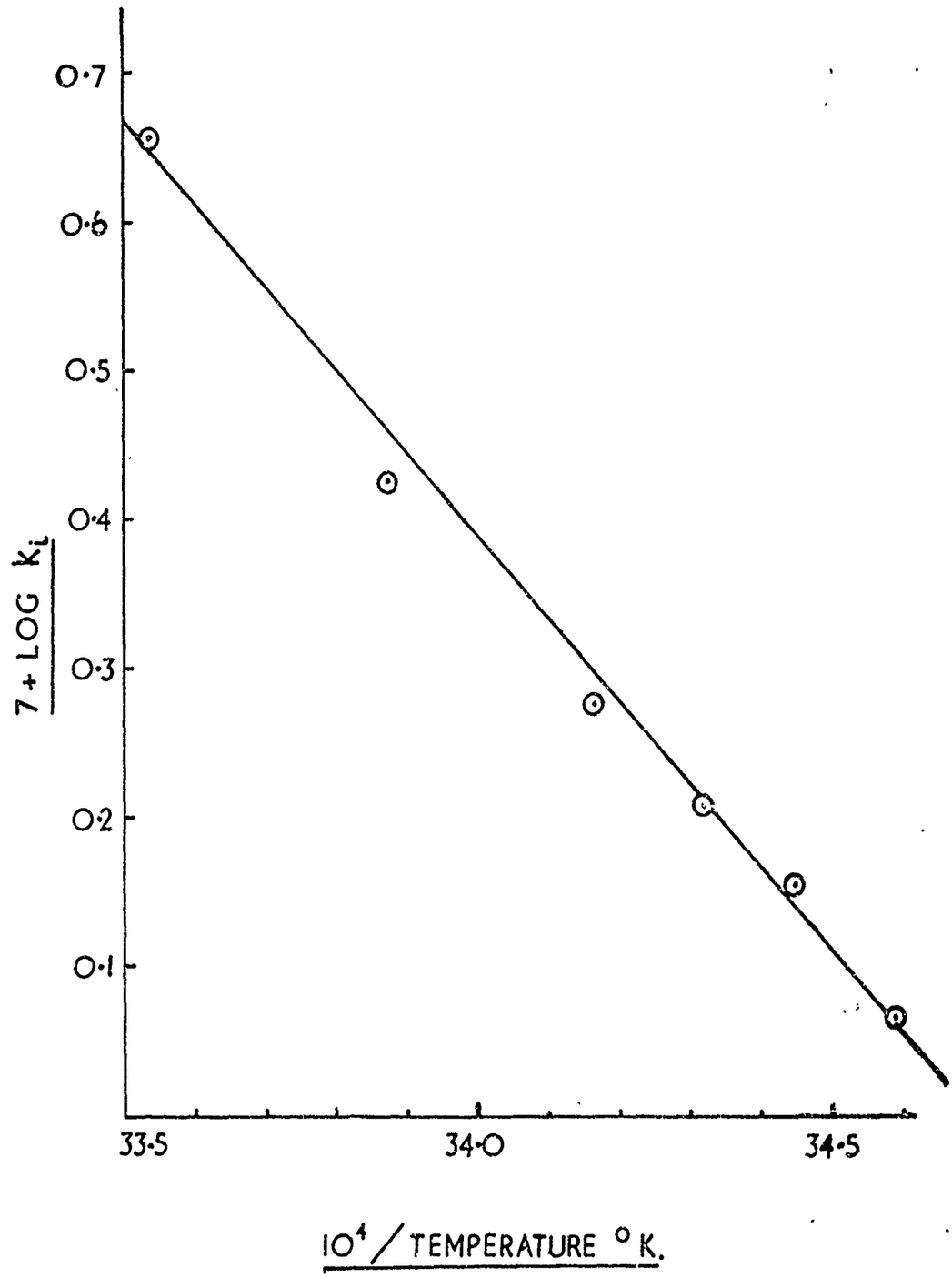
Table 2. Values of initiation coefficient (k_i) at 25°C. calculated from rates of polymerisation (R_p) by means of eqn. (1): monomer concn. $[m_1] = 1.00$M, $k_p = 1.8 \times 10^4$ l/mol. sec., $k_t = 1.45 \times 10^7$ l/mol. sec.[4]

10^4 catalyst concn. (mole/l)	$10^5 Fe(ClO_4)_3$ conc. (mole/l)	$10^4 R_p$ mol/l. min.	$10^7 k_i$/sec.
1.50	9.28	1.92	4.55
2.00	9.28	2.52	4.50
2.60	9.28	2.97	4.09
3.51	9.28	4.53	4.63
4.51	9.28	5.06	4.07
5.51	9.28	7.61	5.00
3.00	11.6	2.64	3.90
4.00	139.2	0.413	5.46
4.01	2.78	19.1	5.17
4.00	18.6	2.85	5.05
4.01	4.64	10.3	4.56

Energies of activation for the termination of polymerisation of acrylamide by aquated ferric ions and by the partially hydrolysed ions $FeOH^{2+}$ have recently been determined[4] and are 2.35 and 0.37 k. cals/mole respectively. In order to calculate the composite termination coefficient (k_4) for the other temperatures employed in this investigation, it is necessary to allow for the effect of change in temperature upon the degree of hydrolysis of the ferric salt as well as for its effect on the termination rate coefficients of the individual ionic species concerned. Equilibrium constants for the hydrolysis of ferric perchlorate in solutions of the ionic strength employed were, therefore, calculated from the relation given by Milburn and Vosburg[6] for 25°C. and then adjusted to the other temperatures concerned by assuming a heat of hydrolysis (ΔH) of 9.9 k. cal/mole.[7] Composite termination coefficients obtained in this way were then substituted in eqn. (1) together with the other temperature adjusted velocity constants concerned and the initiation coefficients evaluated. An Arrhenius plot of the values of k_i so obtained is given in Fig. 4 from which we have found the energy of activation of the initiation reaction to be 26.05 k. cal/mole and the pre-exponential factor 5.64×10^{12}/sec.

The energy of activation for the thermal decomposition of 4-4'-azo-bis-4-cyanopentanoic acid with no monomer present, as calculated from rates of evolution of nitrogen, was found by Lewis

FIG. 4. ARRHENIUS PLOT OF LOG k_i AGAINST 1/TEMPERATURE



and Matheson[8] to be 34.0 k. cal/mole. Cases of the induced decomposition of initiators e. g. benzoyl peroxide,[9] in the presence of vinyl monomers are well known, although rates of decomposition of aliphatic azo-compounds are apparently not very sensitive to changes in environment.[10] However, there is evidence that in dimethylformamide solution, ferric salts are able to catalyse the decarboxylation of the azo-initiator[11] used in the present investigation, so that it may be this, which is responsible for the lower energy of activation obtained here.

Termination of polymerisation by vanadyl perchlorate

Vanadyl perchlorate is also able to terminate the polymerisation of acrylamide by a reaction which is first order with respect to both the vanadyl salt and the polymer radical. An analysis of the kinetic data obtained by the method of least squares has shown that R_p is directly proportional to $[\text{initiator}]^{0.95}$ and inversely proportional to $[VO(ClO_4)_2]^{0.89}$.

These kinetic results are consistent with a mechanism of polymerisation similar to that discussed for the ferric perchlorate terminated reaction. In which case, eqn. (2) will correlate the rate of polymerisation with the specific rate constants of the various steps involved in the overall reaction, and may be used to calculate the velocity coefficient k_4 for the linear termination process

involving the vanadyl salt.

$$k_4[VO(ClO_4)_2] = \frac{k_i[cat]k_p[m_1]}{R_p} - \frac{k_t R_p}{k_p[m_1]} \qquad (2)$$

Now several hydrolysis products of the 4-valent vanadium ion have been recognised, but Rossotti and Rossotti[12] have shown that it exists as either VO^{2+} or $V(OH)_2^{2+}$ in the range of acidity from 3M to 0.002M. It has, therefore, been assumed here that the termination coefficient, k_4, obtained later applies to the vanadyl ion itself as all reactions were carried out in 0.11M perchloric acid media.

It has also been assumed that vanadyl ions have the same effect on the rate of decomposition of the initiator as ferric ions have. The value of k_i of 4.62×10^{-7}/sec. has therefore been substituted together with the other experimentally determined quantities into eqn. (2), when an average value of k_4 of 2.80×10^3 l./mol. sec. was obtained for 25°C.

Rate measurements have also been made at 35° and 40°C in order to determine the energy of activation for the termination process, E_4. At each of these temperatures, the average value of $R_p[VO(ClO_4)_2]/[m_1][cat]$ has been computed and Fig. 5 shows the plot of the log. of this quantity against the reciprocal of the absolute temperature. The slope of this line yields an overall energy of activation i.e. $E_p + E_i - E_4$, of 26.2 k cal/mol. Since E_i = 26.05 k. cal/mol.

FIG. 5. VARIATION OF LOG 'B' WITH TEMPERATURE

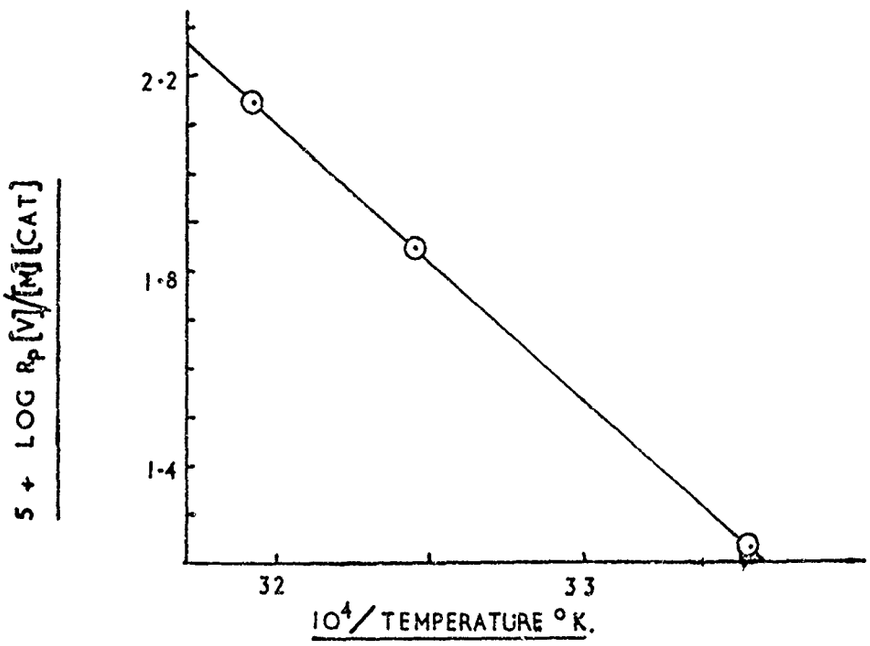
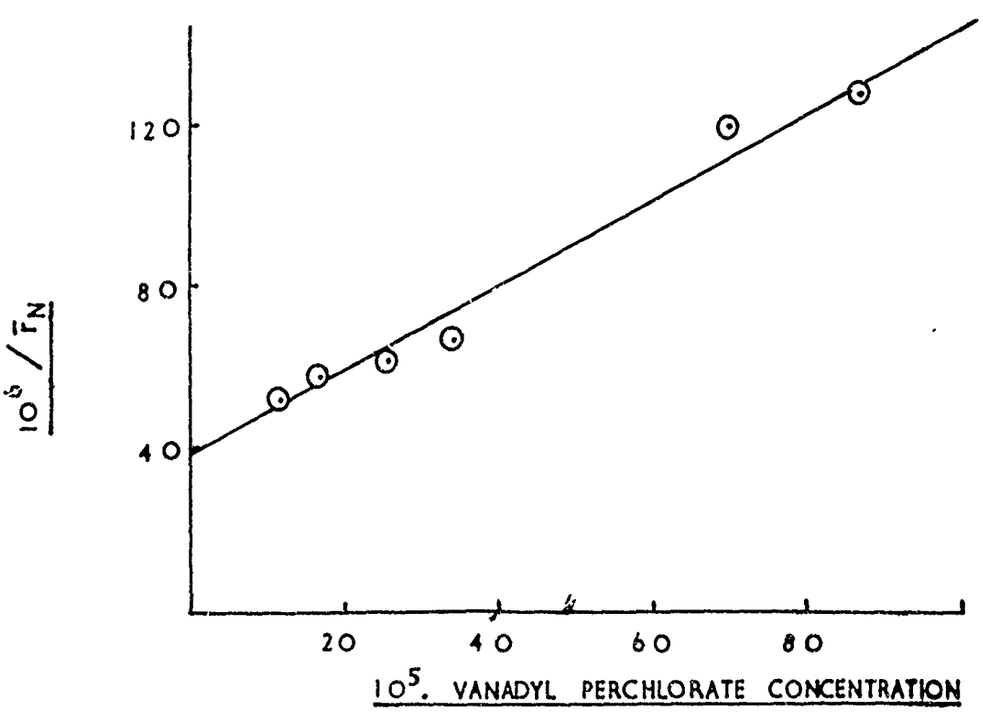


FIG. 6. DEPENDENCE OF MOLECULAR ON VANADYL SALT CONC^{N}



estimated uncertainty of about $\pm$ 1 kcal.

In order to obtain some experimental confirmation for the value of initiation coefficient employed in the calculation of k_4, the molecular weights of polymers produced under kinetic conditions with fixed monomer and catalyst but variable vanadyl perchlorate concentrations, were measured, average degrees of polymerisation ($\bar{r}_v$) being calculated from limiting viscosity numbers [η] by means of Scholtan's relation,[15] which for polymer concentrations expressed in g./dl., is

$$[\eta] = 6.31 \cdot 10^{-5}(71.1\ \bar{r}_v)^{0.80} \qquad (3)$$

These are approximately weight average values, which in turn are twice the number average degrees of polymerisation ($\bar{r}_n$).[5]

The kinetic scheme appropriate to the present system which considers transfer reactions and linear termination of chains, leads to the following relationship in which T is a transfer agent for the number average degree of polymerisation:-

$$\frac{1}{\bar{r}_n} = \frac{\sum (k_f[T])}{k_p[m_1]} + \frac{k_4[VO(ClO_4)_2]}{k_p[m_1]} \qquad (4)$$

Thus, a plot of $1/\bar{r}_n$ (or $2/\bar{r}_v$) against the metal salt concentration, with all other quantities being kept constant, will have a slope of k_4/k_p. Fig. 6 shows this plot for a range of vanadyl perchlorate concentrations from 12 to 86 x 10^{-5}M at 25°C., the value of k_4 calculated from the slope being 1.9 x 10^3 as compared with the kinetic value of 2.80 x 10^3 l./mol. sec. Such agreement,

although not entirely satisfactory, is not unreasonable in view of the assumptions employed in the comparison of kinetic and molecular weight data.

Since vanadyl perchlorate is able to lower both the rate of polymerisation of acrylamide and the molecular weight of the resulting polymer, the problem arises as to the precise mechanism of the termination reaction concerned. The very low energy of activation of this process is consistent with an electron transfer reaction, but there are two possible ways in which this could occur:-

1. reduction of the vanadyl ion by the donation of an electron by the polymer radical;
2. oxidation of the metal ion by a reverse process.

In addition, there is the possibility of some kind of complex-formation between the metal ion and the radical. This would be equivalent to a radical combination reaction except that one of the species involved would be a charged entity. Experiments were, therefore, carried out in an attempt to detect the presence of lower or higher valency vanadium species, which might be present in solutions which had been allowed to polymerise in the presence of vanadyl ions.

The specific valency indicator, cacotheline (prepared here by the nitration of brucine), gives a red colour in the presence of V(III). The indicator was, therefore, added to solutions containing

high concentrations of vanadyl perchlorate and which had been allowed to polymerise for several weeks. This test was carried out both on solutions which had been quenched with air and was also added under anaerobic conditions but in neither case was any trace of the expected red colour noted. The oxidation potential of the V(III) $\longrightarrow$ V(IV) couple is -0.314V which is sufficiently low for reduction to V(III) to occur in this system, so that failure to detect a change of valency may be due to the use of an insufficiently sensitive technique. Experiments have also shown that V(III) itself does not initiate or terminate the polymerisation of acrylamide so the possibility of the removal of V(III) ions produced by such reactions seems to be ruled out.

The solutions of vanadyl perchlorate employed in kinetic experiments contained a trace (less than 1%) of 5-valent vanadium. In order, therefore, to determine whether or not oxidation to the 5-valent state occurred during the course of polymerisation, the spectrum of a deaerated solution containing monomer, initiator and a relatively high vanadyl perchlorate concentration (ca. 10^{-2}M), was mapped in the region 300 to 900 mμ at periodic intervals of time over several days. A very slight increase in transmission at about 750 mμ, i.e. removal of V(IV) and a slight decrease in transmission between 400 and 500 mμ/i.e. production of V(V) was noted. The changes observed were very small and must, therefore, be regarded with some caution.

Similarly, no compelling experimental evidence for the third possibility, namely termination by combination between vanadyl ions and polymer radicals, could be obtained. Samples of polymer produced in the presence of vanadyl perchlorate were analysed, but no vanadium was detected in them.

Effect of Uranyl Perchlorate on the Kinetics of Polymerisation

The oxidation potential of the reaction:-

$$U^{4+}_{aq} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$$

is -0.334 V, so that it is reasonable to suppose that the uranyl ion, UO_2^{2+} is also capable of the oxidative termination of the radical polymerisation of acrylamide.

The use of uranyl salts as photosensitisers of polymerisation is well established and the polymerisation of acrylamide is no exception in this respect. Indeed, solutions of acrylamide containing only traces of uranyl perchlorate polymerised rapidly in the light even when only one deaeration cycle had been carried out. A similar phenomenon was apparent when thorium perchlorate was employed but no detailed kinetics were carried out on this compound. All experiments with uranyl perchlorate were, therefore, performed in the dark in order to eliminate photochemical initiation of polymerisation.

Initially, rates of polymerisation were measured with uranyl perchlorate and perchloric acid present but with no addition of ACV. It was found that even in the dark, polymerisation took place, showing that the uranyl salt is able to bring about initiation of chains by a non-photochemical mechanism. The dependence of the rate of polymerisation on the uranyl salt concentration in the absence of other initiator is shown in Fig. 7 where R_p^o is plotted against [U(VI)]. (R_p^o is used to denote the rate of polymerisation when no ACV is present). A double logarithmic plot of the data illustrated in Fig. 7 has shown that the rate exponent of the uranium salt concentration is about 0.85. It was, therefore, concluded that uranyl perchlorate, or some species derived from it, is capable of initiating chains, the net rate of polymerisation being proportional to the overall uranyl salt concentration.

This rate dependence provides no evidence in itself for the existence of termination by the uranium salt, so that a similar series of experiments were carried out but with a fixed concentration (2.00×10^{-4}M) of ACV present. The rate of polymerisation was increased by the addition of ACV although in all cases the rate was lower than that which would be expected had there been no uranyl perchlorate present. This lowering of the rate is good evidence that at least some termination of chains by a linear mechanism involving the metal salt is taking place.

FIG. 7. VARIATION OF R_p^o WITH

URANYL PERCHLORATE CONCENTRATION

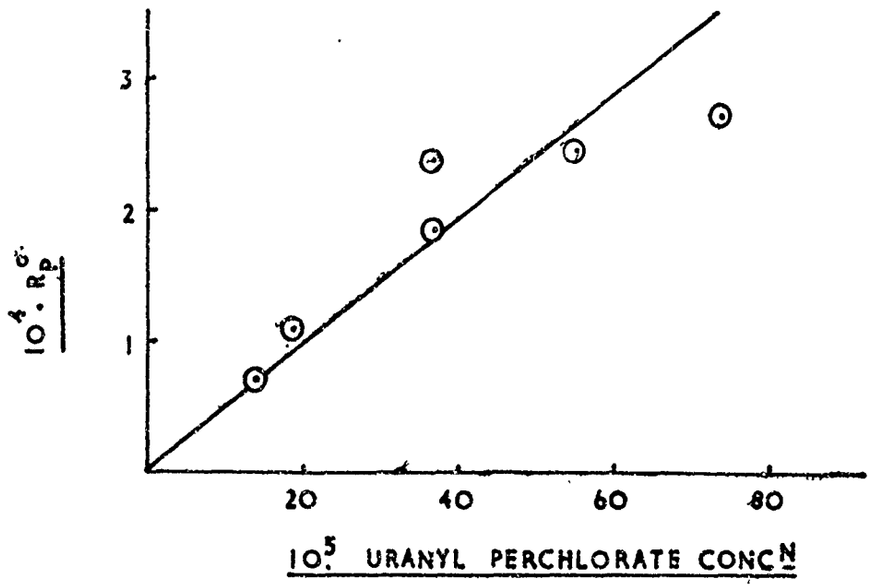
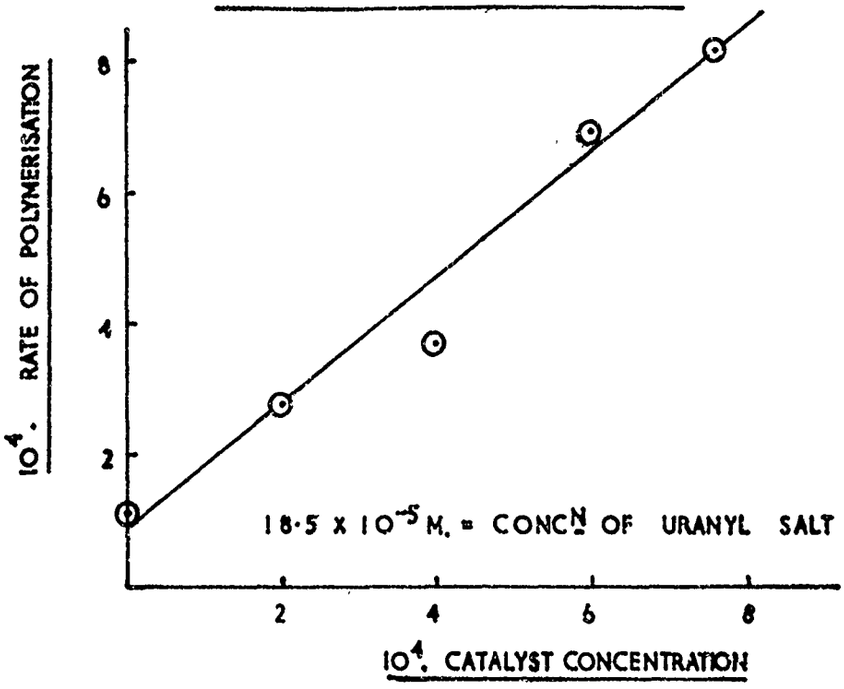


FIG. 14. VARIATION OF R_p WITH

CATALYST CONCENTRATION



Santappa[13] has shown that, in the uranyl perchlorate photosensitised polymerisation of methyl methacrylate and several other monomers, the metal ions do not participate in any termination process. In the case of acrylamide the results obtained here show that linear termination is important when uranyl perchlorate is present. A plot of R_p against [cat], gave a straight line which intercepted the ordinate axis at R_p = 0.75 mole/l. min. when [cat] = O (Fig. 14).

From the observation that $R_p^o \alpha [U(VI)]$ it may be inferred that if mutual chain termination takes place, i.e. $R_p^o \alpha (R_i')^{\frac{1}{2}}$ where R_i' is the rate of initiation by the uranyl salt, then R_i' is proportional to the square of the uranyl salt concentration. On the other hand, if linear chain termination occurs, i.e.

$$R_p^o \alpha \; R_i' \; / \; [U(VI)]$$

then again R_i' is proportional to $[U(VI)]^2$. No distinction between these two possibilities of chain termination can be made on the basis of the observed concentration dependence of R_p^o alone. However, in the presence of ACV as catalyst, chains are terminated linearly by uranyl perchlorate. It is reasonable to suppose, therefore, that the same linear mechanism of termination also operates in the absence of ACV as initiator.

The rate of polymerisation has been shown to be directly proportional to $[m_1]$ for the range of concentrations studied. It

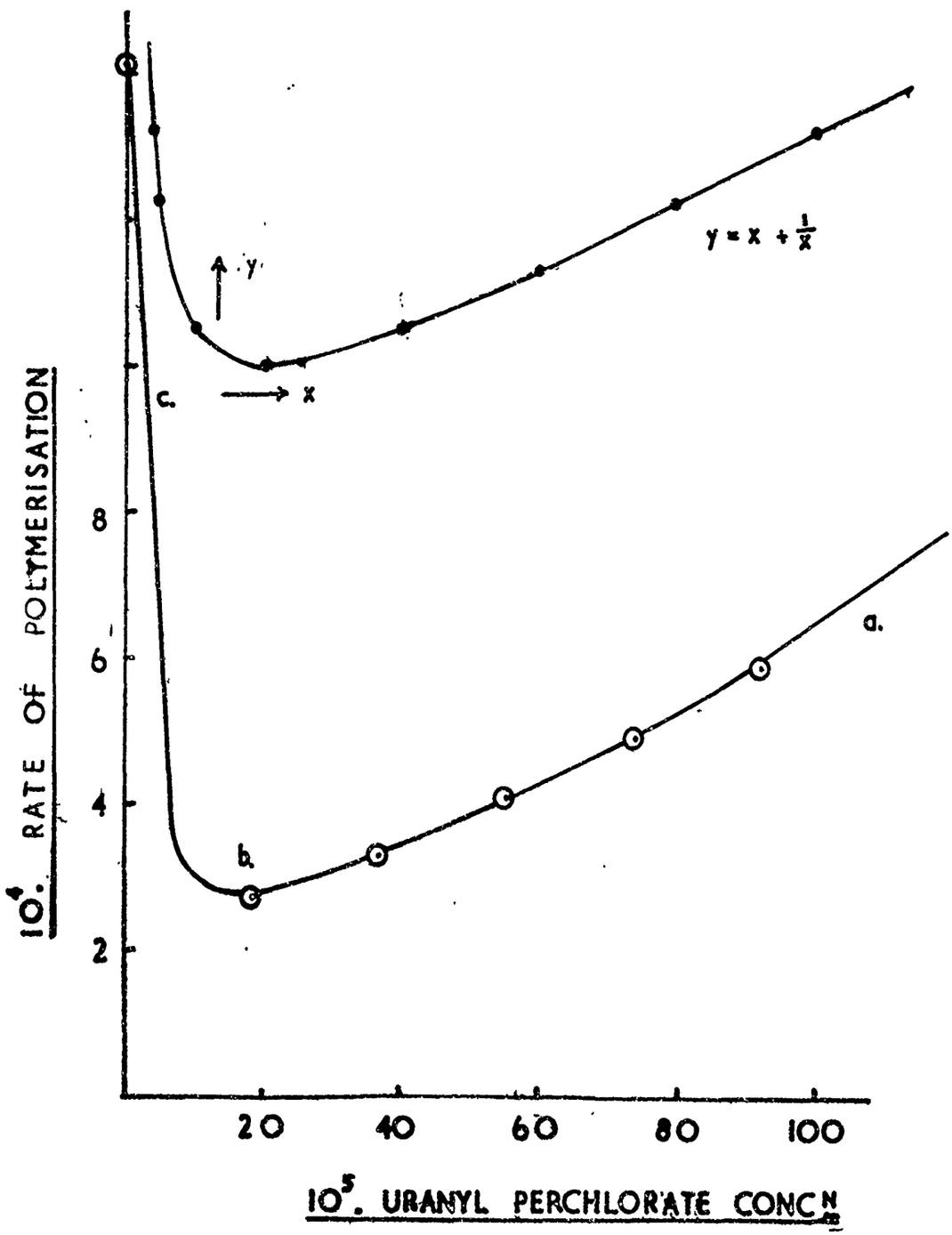
follows, therefore, that in the presence of ACV and uranyl perchlorate the rate of polymerisation of acrylamide is given by:-

$$R_p = k_p[m_1]\,(k_i[cat] + k_i'\,[U(VI)]^2)\ /\ k_4[U(VI)\,] \qquad (5)$$

where k_i' is the velocity coefficient for initiation by uranyl perchlorate, mutual termination of radical chains being neglected. Eqn. (5) also shows that at high concentrations of uranyl perchlorate, the rate of polymerisation in the presence of a low but fixed concentration of ACV should be proportional to the concentration of uranyl salt. However, if the latter is diminished sufficiently, a concentration should be reached such that further reductions in concentration of the uranyl compound cause the rate of polymerisation to increase, rather than to decline still further. Unfortunately, it was not possible to obtain satisfactory rate measurements at very low concentrations of uranyl perchlorate owing to the occurrence of long but irreproducible inhibition periods. Such kinetic results as were obtained in the presence of a fixed concentration of ACV of 2.0×10^{-4}M are given in Fig. 8, the rates of polymerisation obtained being consistently higher, of course, than those summarised in Fig. 7, which refers to a zero concentration of ACV.

The hydrolysis of uranyl perchlorate has been studied quite extensively and several partially hydrolysed species are said to exist. Ahrland and co-workers[14] have stated that, to a good approximation, reactions 1 and 2 below are the most important hydrolytic equilibria.

FIG. 8. VARIATION OF R_p WITH URANYL PERCHLORATE CONCENTRATION



CATALYST CONCENTRATION = $2{\cdot}00 \times 10^{-4}$ M.

$$UO_2^{2+} + H_2O + UO_2^{2+} \rightleftharpoons (UO_2)_2O^{2+} + 2H^+ \quad \ldots\ldots\ldots\ldots 1.$$

$$UO_2(OUO_2)_n^{2+} + H_2O + UO_2 \rightleftharpoons UO_2(OUO_2)_{n+1}^{2+} \quad \ldots\ldots 2.$$

Hietanen and Sillen[16] concluded that the two main reactions are 1 and 3.

$$2UO_2^{2+} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+ \quad \ldots\ldots\ldots\ldots 3.$$

It was stated that the concentrations of these species are very low, the equilibrium constant for reaction 1 being 8.91×10^{-7}. It is possible that the initiating species in solutions of uranyl perchlorate is the dimer or some other aggregate involving two uranyl ions, so that the concentration of the effective species is proportional to the square of the total uranyl salt concentration.

Termination is probably due to the uranyl ion itself and the relevant value of k_4 has been computed by plotting $R_p - R_p^o$, against the reciprocal of the uranyl salt concentration, where R_p^o is the rate of polymerisation observed at the same concentration of uranyl perchlorate but with no added ACV. In the absence of further information, k_i has been assumed to be 4.62×10^{-7}/sec. at 25°C. for the calculation of k_4, which was found to be 8.3×10^3 l./mol. sec. at the same temperature. Now the slope of the straight line obtained by plotting R_p^o against the concentration of uranyl perchlorate (Fig. 7) is equal to $k_p[m_1]k_i'/k_4$, so the rate coefficient for initiation by uranyl perchlorate (k_i') may be evaluated by substituting the appropriate values of k_p and k_4 in this expression. The value of k_i' so obtained

was 3.6×10^{-4}/sec., which is considerably larger than k_i for initiation by ACV. However, k_i' is itself probably a composite quantity and may represent the numerical product of a "true" rate constant and an equilibrium constant.

If the equilibrium constant concerned refers to a process similar to reaction 3 above, then the concentration of the dimer and hence the rate of polymerisation R_p^o would be expected to decline as the concentration of acid is increased. Some kinetic results obtained for the uranyl perchlorate initiated reaction in the presence of different concentrations of perchloric acid are tabulated below, Table 3. It is clear that the rate of polymerisation is dependent upon the pH of the solution, although until the actual species responsible for initiation is identified it is not possible to express this dependence in an explicit form.

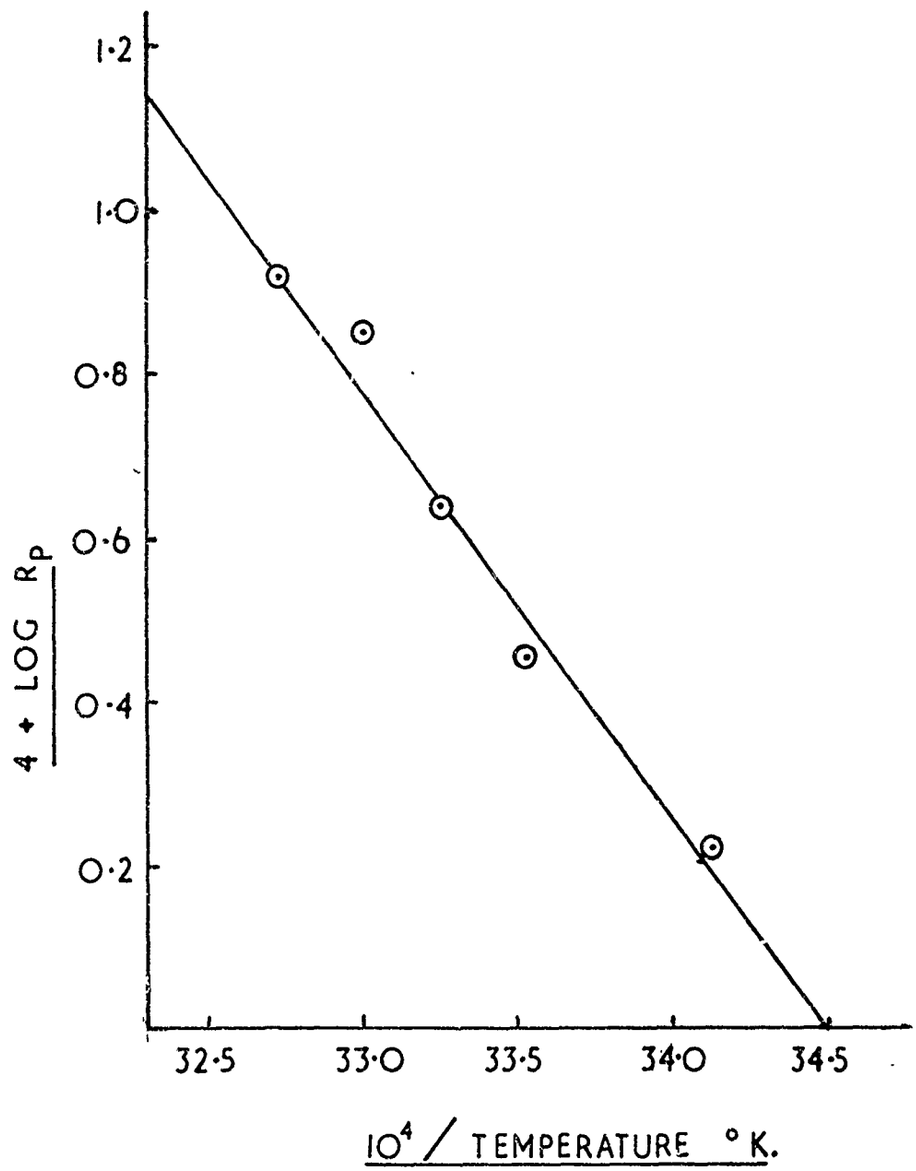
Table 3.

Perchloric acid concentration M	$10^4 . R_p^o$ (mol/l. min)
0.044	4.12
0.11	2.65
0.22	1.64
0.33	1.98

The effect of variation in temperature upon the overall rate of polymerisation is illustrated in Fig. 9, in which log R_p has been

FIG. 9. ARRHENIUS PLOT OF

LOG R_p AGAINST 1/TEMP. °K.



CATALYST CONCENTRATION = $2{\cdot}00 \times 10^{-4}$ M.

plotted against the reciprocal of the absolute temperature. The kinetic data employed in this plot were obtained with fixed concentrations of ACV (2×10^{-4}M), uranyl perchlorate (5.6×10^{-4}M), monomer and perchloric acid, so that on the basis of the mechanism proposed the overall energy of activation (E_A) calculated from the slope of this plot should be related to the energies of activation of the individual steps by the relation:-

$$E_A = E_p - E_4 + RT^2 \; d\log (k_i + 2.8 \; k_i')/dT \qquad (6)$$

The numerical value of E_A found was 24.3 kcal./mole, which indicates that E_4 is small, probably not exceeding 4 kcal./mole.

Comparison of termination coefficients for various metal ions.

The uncertainties involved in formulating the precise mechanism by which individual ions terminate the polymerisation of acrylamide makes the task of comparing rate coefficients and energies of activation exceedingly hazardous. Nevertheless, we have tabulated below (Table 4) various kinetic magnitudes obtained during the present investigation together with other relevant information from the current literature. One point which does emerge is that the oxidation-reduction potential of a metal ion is not a reliable indication of its capacity to terminate the radical polymerisation of acrylamide.

Table 4.

Ion	$10^{-3}.k_4(25^oC)$ 1/mol. sec.	E_4 kcal/mole	Reduction potential[17] volts
Fe^{3+}_{aq}	2.8	2.35	0.77
Cu^{2+}	1.17	5.4	0.15
$FeOH^{2+}$	21.2	0.37	-
$V(OH)_2^{2+}$	2.85	1.2	0.314
$U(OH)_2^{2+}$	8.3	$\not>4$	0.334

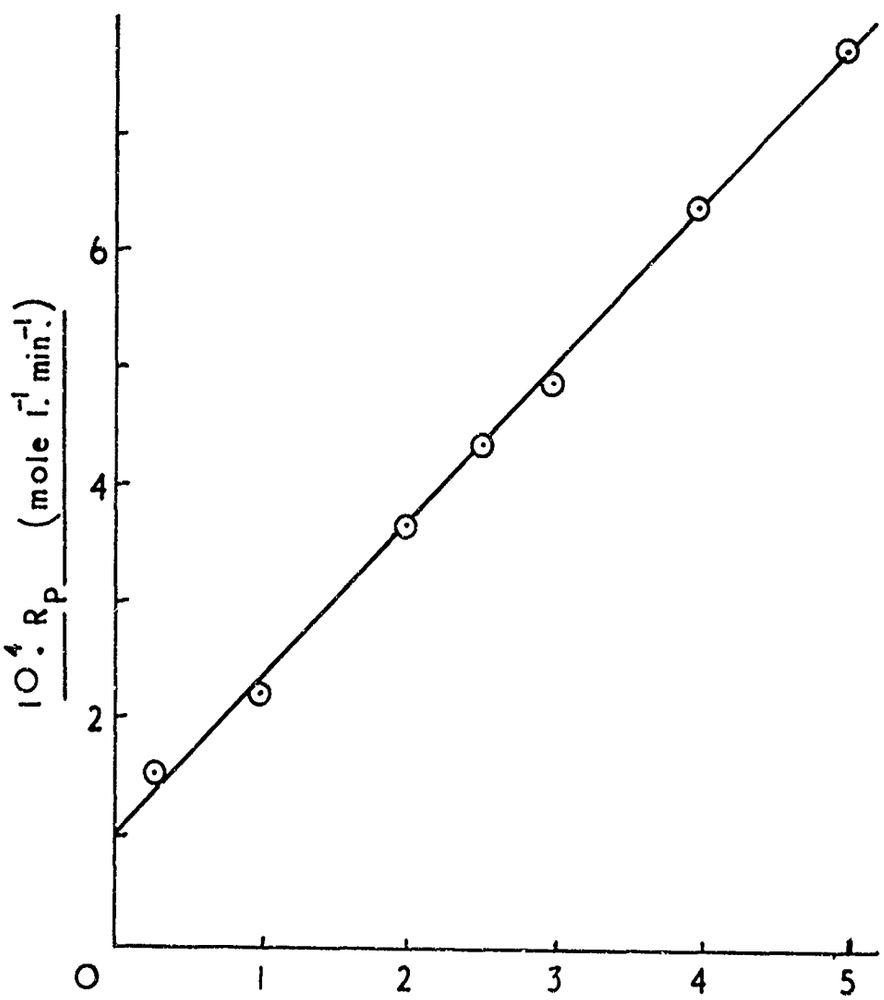
In addition to those metal ions referred to in Table 4, we have also shown that neither chromic nor hexammino-cobaltic ions have any effect on the rate or the mechanism of the termination reaction concerned.

Effect of ferric chloride on rate of polymerisation

A preliminary series of experiments carried out in the presence of decimolar hydrochloric acid alone showed that at this concentration the acid itself has no effect on the rate of polymerisation of acrylamide under our experimental conditions. The mean value of the ratio $R_p/[m_1][cat]^{\frac{1}{2}}$ obtained was $(1.77 \pm 0.43) \times 10^{-3} l.^{\frac{1}{2}}/mol.^{\frac{1}{2}} sec.$ as compared with $(1.70 \pm 0.17) \times 10^{-3}$ obtained in the absence of acid.

Plots showing the variation of rate with initiator concentration and with concentration of ferric chloride are given in Fig. 10 and 11. It is apparent that the best straight line through the experimental points

FIG.10. VARIATION OF RATE OF POLYMERISATION WITH CATALYST CONCENTRATION IN THE PRESENCE OF FERRIC CHLORIDE



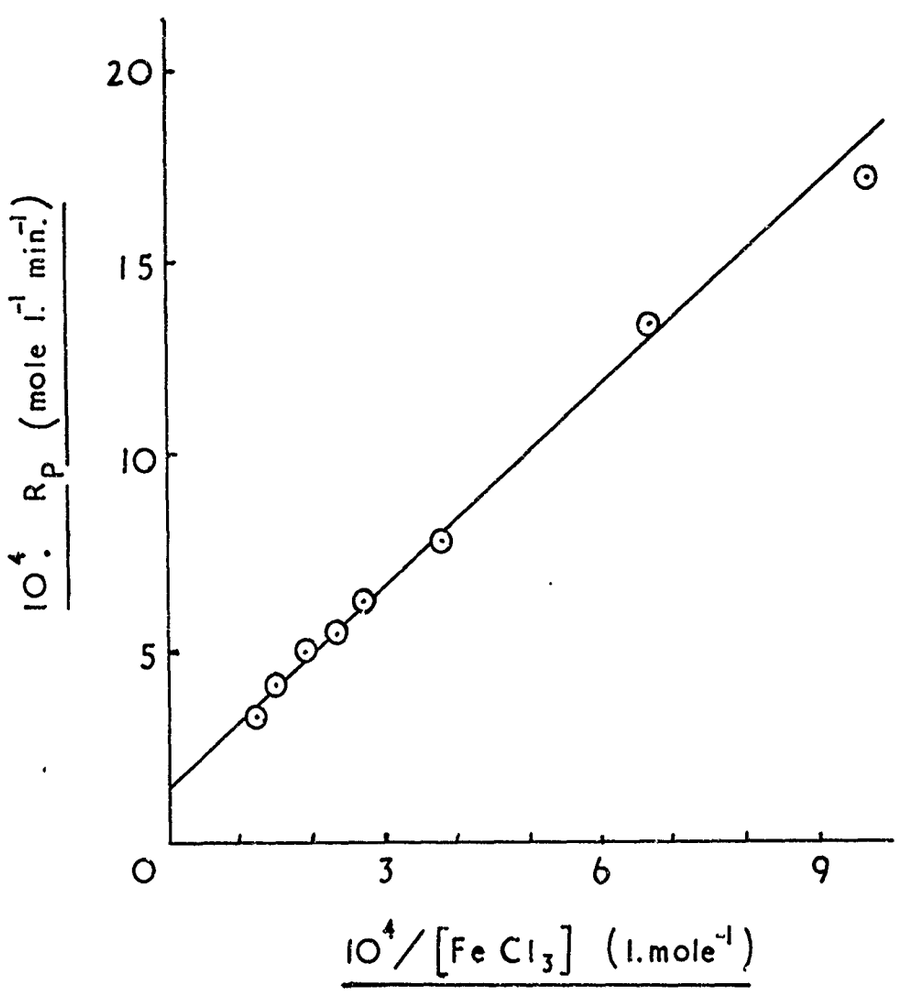
ferric chloride concentration = $2{\cdot}58 \times 10^{-5}$ M

hydrochloric acid concⁿ = 0·122 M

FIG.11. VARIATION OF R_p WITH FERRIC CHLORIDE CONCENTRATION

catalyst concentration = $5{\cdot}0 \times 10^{-4}$ M

hydrochloric acid concⁿ = 0·122 M



gives a positive intercept on the rate axis for both plots, and that this intercept is the same for both series of experiments. These observations suggest that acrylamide might polymerise in the presence of ferric chloride without any A. C. V. being present.

Experiments were, therefore, undertaken to study the effect on the rate of polymerisation of changes in the ferric chloride concentration, with no other initiator present keeping the concentration of chloride ion constant, and also the effect of changing the chloride ion concentration whilst keeping the ferric salt concentration constant. The same concentration of monomer was employed in both cases. The results obtained are summarised in Table 5 and it is evident that the rate of polymerisation is independent of both the concentration of the chloride ion and of ferric chloride.

Table 5

Polymerisation of Acrylamide in the absence of A. C. V.

(a) Variable ferric chloride $[m_1]$ = 1.00 mole/l.

$[Cl^-]$ = 0.122 mole/l.

$10^5[FeCl_3]$mole/l.	$10^4 R_p^o$ mole/l. min.
3.72	0.97
6.00	0.89
7.43	1.25
7.43	1.00
11.15	0.91
11.15	1.15
14 86	0.60

(b) Variable chloride ion concentration m_1 = 1.0 mole/l.

$FeCl_3$ = 7.43×10^{-5}mole/l.

$[Cl^-]$ mole/l.	$10^4 R_p^o$ mole/l. min.
0.073	0.95
0.073	0.92
0.122	1.25
0.122	1.00
0.244	1.02
0.244	0.78
0.366	1.08

If it is assumed that initiation by some species derived from the ferric salt is also possible, then this must be included in any overall kinetic scheme. Initiation, however, cannot involve either aquated ferric ions or the partially hydrolysed species $FeOH^{2+}$ since, in the absence of A. C. V., polymerisation does not occur when either ferric perchlorate or ferric sulphate (see later) are present. The concentration of the entity responsible for initiating polymerisation in this instance would seem to depend on the overall concentration of ferric chloride since no polymerisation occurs if this is absent. In the presence of ferric chloride as the only initiator the rate of initiation, R_i', has therefore been assumed to be:-

$$R_i' = k_i' [FeCl_3] \qquad (7)$$

$$= k_4[FeCl_3][m^*] \text{ under steady conditions,}$$

where $[m^*]$ is the stationary concentration of radicals.

Hence, the rate of polymerisation will be given by:-

$$R_p^o = k_p[m_1] \frac{k_i'}{k_4} \qquad (8)$$

i. e. in the absence of A. C. V., the rate is independent of the ferric chloride concentration.

By including this additional mode of initiation in the overall kinetic scheme operating in the presence of A. C. V. and ferric chloride, the following relation is obtained:-

$$R_p = k_p [m_1] \left(\frac{k_i [cat] + k_i' [FeCl_3]}{k_4 [FeCl_3]} \right)$$

$$= \frac{k_p [m_1] k_i [cat]}{k_4 [FeCl_3]} + \frac{k_p k_i' [m_1]}{k_4} \qquad (9)$$

Consequently, plots of R_p against [cat] and against $[FeCl_3]^{-1}$ will give a positive intercept on the rate axis of $k_p k_i' [m_1]/k_4$ which is R_p^o. For variable initiator, $R_p^o = 1.0 \times 10^{-4}$ mol/l. min. ; for variable ferric chloride in the presence of A. C. V., $R_p^o =$ 1.1×10^{-4} mole/l. min. and in the absence of A. C. V. $R_p^o =$ 1.0×10^{-4} mole/l. min.

The slopes of the graphs for variable initiator and variable ferric salt concentrations will be

$$\frac{k_p [m_1] k_i}{k_4 [FeCl_3]} \quad \text{and} \quad \frac{k_p [m_1] k_i [cat]}{k_4} \quad \text{respectively.}$$

The independence of R_p^o within the limits of experimental error, to changes in chloride ion concentration is more difficult to explain. The ionic species which merit consideration include the aquated ferric ion $Fe6H_2O^{3+}$, an inner sphere complex[19] $FeCl5H_2O^{2+}$ and possibly also an outer sphere complex $Fe6H_2O^{3+}Cl^-$.

Since polymerisation of acrylamide does not occur in the presence of either ferric perchlorate or ferric sulphate alone, the species present in ferric chloride solutions responsible for initiating polymerisation must be one that does not exist in solutions of either of the other ferric salts. It cannot, therefore, be either $Fe6H_2O^{3+}$ or

$FeOH5H_2O^{2+}$ but must presumably be a chloro substituted complex.

R_p^o does not change with changes in chloride ion concentration although the concentration of both $Fe^{3+}aq$ and $FeOH^{2+}aq$, if present, would be expected to change. Neither $Fe^{3+}aq$ or $FeOH^{2+}aq$ are themselves able to initiate polymerisation, although they can terminate it and therefore if present they would make an appropriate contribution to the denominator of the rate expression. In terms of the concentrations of the individual ionic species, the rate of the ferric chloride initiated polymerisation, R_p^o, will therefore be given by

$$\frac{R_p^o}{k_p[m_1]} = \frac{k_i' \beta [FeCl_3]}{k_{40}(1 - \beta)[FeCl_3] + k_{42} \beta [FeCl_3]} \qquad (10)$$

where β is the fraction of ferric chloride as $FeCl_5H_2O^{2+}$, the remainder $(1 - \beta)$ being assumed to be in the form $Fe6H_2O^{3+}$, the terminating coefficients being k_{42} and k_{40} for $FeCl^{2+}aq$ and $Fe^{3+}aq$ respectively.

Eqn. (10) shows that R_p^o is independent of the total ferric chloride concentration, but is dependent on the magnitude of β, which in turn is determined by the total chloride ion concentration. Consequently, eqn. (10) cannot be applicable to our conditions. We, therefore, assume that the concentration of $Fe6H_2O^{3+}$ is negligible and that the other ionic species present is an outer sphere complex $Fe6H_2O^{3+}Cl^-$ which is also capable of initiating polymerisation at an appropriate rate. In addition, a small amount of $FeOH5H_2O^{2+}$ will

also be present, and its concentration will vary from 2% to 0.5% of the total ferric ion concentration. Any change in R_p^o due to a change in the concentration of $FeOH^{2+}$ would probably, therefore, be within experimental error.

If the termination coefficients of the two species are designated as k_{41} and k_{42} for $Fe6H_2O^{3+}Cl^-$ and $FeCl5H_2O^{2+}$ respectively, and their initiating coefficients k_{11} and k_{12} respectively, then ignoring the small concentration of hydrolysis products present, the concentration of the inner sphere complex will be β and that of the outer sphere complex $(1 - \beta)$,

$$\text{i.e.} \quad R_p^o = k_p[m_1] \frac{k_i}{k_4} \frac{[FeCl_3]}{[FeCl_3]}$$

$$\text{or} \quad \frac{R_p^o}{k_p[m_1]} = \frac{k_i'}{k_4} = \frac{k_{11}(1 - \beta) + k_{12}\beta}{k_{41}(1 - \beta) + k_{42}\beta} \qquad (11)$$

Within the limits of experimental error, we may assume that the ratio of the initiation and termination coefficients is the same for both species, i.e. $k_{11}/k_{41} \approx k_{12}/k_{42} = \gamma$.

Hence, $R_p^o/k_p[m_1]$ also equals γ i.e. R_p^o is independent of β and is therefore independent of the total chloride ion concentration.

Since initiation occurs by a reaction involving a species derived from ferric chloride then some ferrous ion may also be produced at a rate equal to $k_i'[FeCl_3]$, in addition to that produced by the termination reaction involving the oxidation of the polymeric radicals.

Consequently, in the presence of A. C. V. as initiator, the total rate of production of ferrous ion will be:-

$2k_i'[FeCl_3] + k_i\,[cat]$ if this assumption is correct.

This was determined by measuring the concentration of ferrous ion produced during the course of the polymerisation reaction by a colorimetric method, in which o-phenanthroline was used as a complexing agent, measurements being made at 505 mμ, where maximum absorption occurs.

Now k_i'/k_i can readily be calculated from the ratio of the intercept to the slope of the straight line obtained by plotting the rate of polymerisation against either the A. C. V. concentration (Fig. 10) or the reciprocal of the ferric chloride concentration (Fig. 11). The mean value of k_i'/k_i obtained in this way was 3. 19, so that the total rate of production of ferrous ions is given by -

$$d[Fe^{II}]/dt = k_i([cat] + 6.38\,[FeCl_3]) \qquad (12)$$

The specific rate constant for initiation of polymerisation by A. C. V can, therefore, be obtained by plotting the rate of production of ferrous ion against ($[cat] + 6.38\,[FeCl_3]$). The value of k_i so obtained was $(2.37 \pm 0.25) \times 10^{-6}$/sec. at 25°C. which is about five times larger than that calculated from rate data obtained with ferric perchlorate present. However, using this value for k_i, we estimate the composite termination coefficient (k_4) and the initiation coefficient (k_i') for ferric chloride to be $(7.41 \pm 0.87) \times 10^4$ l/mol. sec. and $(7\ 55 \pm 1.1) \times 10^{-6}$/sec. respectively.

As pointed out previously, molecular weight measurements may be used to confirm the value of the termination coefficient (k_4) since the number average degree of polymerisation ($\bar{r}_n$) is given by

$$\frac{1}{\bar{r}_n} = \frac{\sum k_f [T]}{k_p[m_1]} + \frac{k_4[FeCl_3]}{k_p[m_1]} \qquad (13)$$

Consequently a plot of the reciprocal of the number average degree of polymerisation against ferric chloride concentration should give a straight line having a slope of $k_4/k_p[m_1]$. From a plot of $(2/\bar{r}_v)$ against ferric chloride concentration the value of the termination coefficient, k_4, obtained was 7.65×10^4 l/mole sec. In view of the inaccuracies involved in such determinations of molecular weights the value of k_4 obtained is in very good agreement with that computed from kinetic measurements, i.e. 7.41×10^4 l/mole sec.

In solutions of ferric chloride in hydrochloric acid several chloro-substituted ferric species have been postulated, but recently Gallagher, King and Woods[19] have shown from spectrophotometric, calorimetric and electromotive force measurements that substitution is limited to the formation of a simple inner sphere chloro-complex $FeCl^{2+}5H_2O$ although they consider that an outer sphere complex $(Fe6H_2O)^{3+}Cl^-$ might also be present. However, in order to account for our observations in connexion with the initiation of polymerisation by ferric chloride, it was necessary to assume that both inner and outer sphere complexes are actually present, and that the composite

termination coefficient (k_4) was given by -

$$k_4 = k_{41} (1 - \beta) + k_{42} . \beta. \qquad (14)$$

where β is the fraction of the salt as the inner sphere complex and k_{41} and k_{42} are the termination coefficients for the outer and inner sphere complexes respectively. In eqn. (14), the effect of hydrolysis products has been neglected, although the necessary correction for these will be applied in due course.

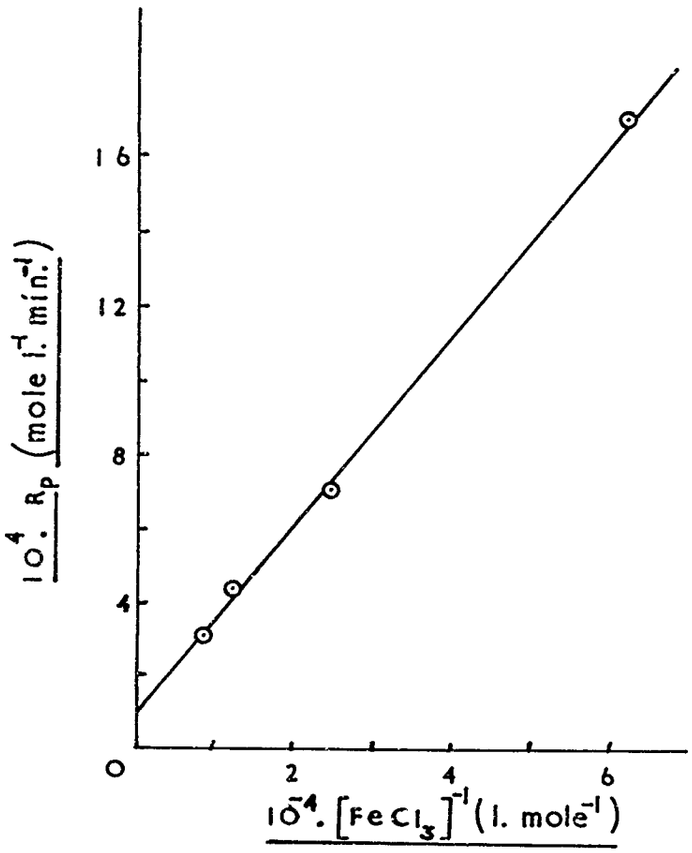
In order to determine the individual constants k_{41} and k_{42}, a number of determinations of the rate of polymerisation of acrylamide with A. C. V. as initiator was carried out in the presence of a range of chloride ion concentrations, added as potassium chloride. Some of the results obtained are shown in Fig. 12 where R_p has been plotted against the reciprocal of ferric chloride concentration for two different total chloride concentrations. Reasonably good linear plots are obtained for each chloride ion concentration studied, showing that the general kinetic scheme is not altered by changing the relative concentrations of the various species existing in solution.

Now the equilibrium constant (K_2) for the formation of the inner sphere complex, which can be calculated from the data of Gallagher, King and Woods is related to β by:-

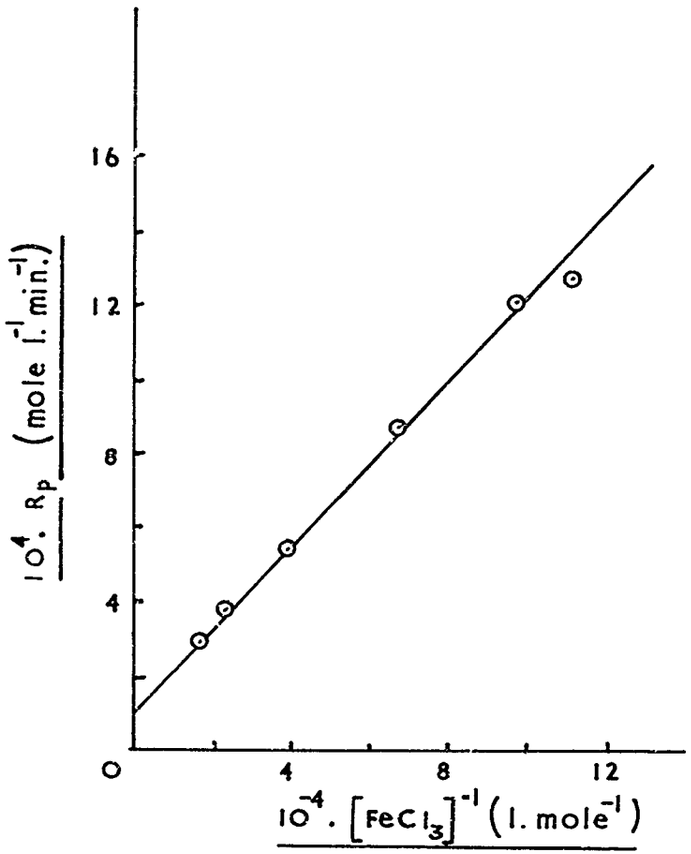
$$K_2 = \beta / (1 - \beta) [Cl]$$

so that the expression for the composite termination coefficient (k_4)

FIG.12. VARIATION OF R_p WITH FERRIC CHLORIDE CONCENTRATION AT DIFFERENT CHLORIDE ION CONCENTRATIONS



$[Cl^-] = 0{\cdot}052M.$



$[Cl^-] = 0{\cdot}366M.$

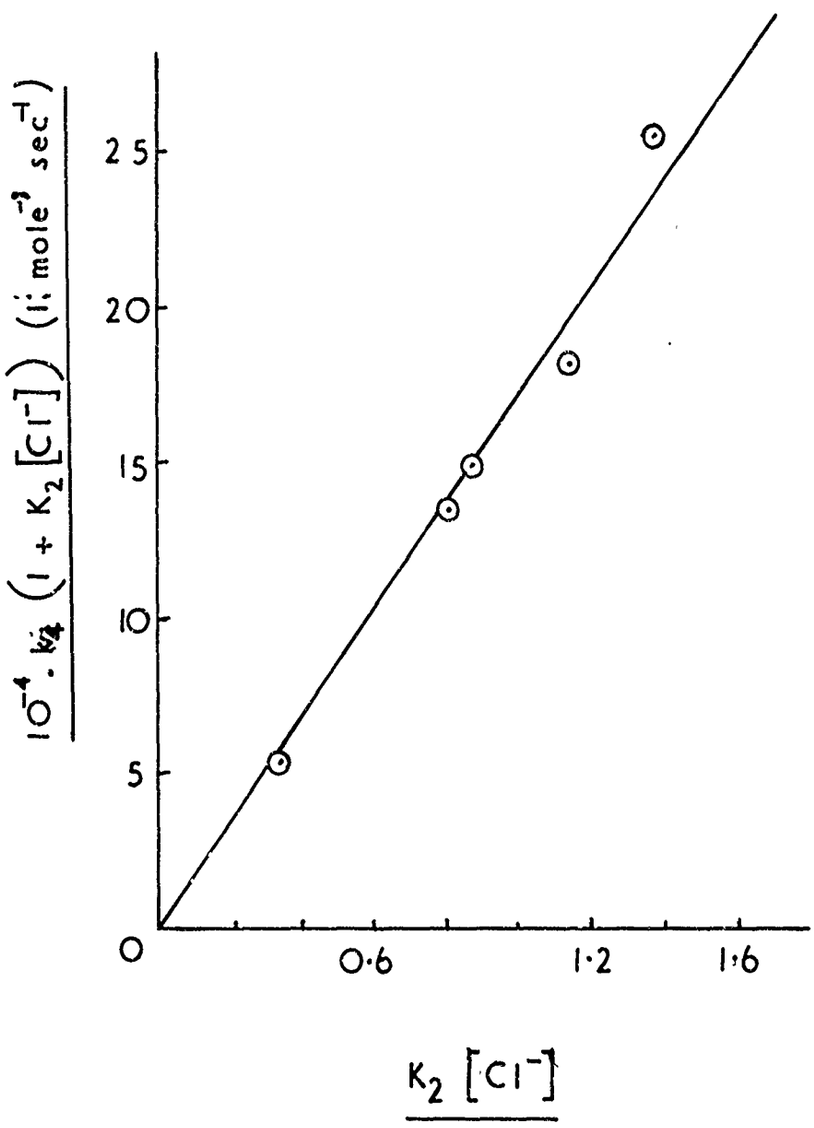
now becomes

$$k_4(1 + K_2[Cl]) = k_{41} + k_{42}[Cl]K_2 \qquad (15)$$

Since k_4 can readily be calculated from the rates of polymerisation measured in the presence of varying chloride ion concentrations, a plot of the l. h. s. of eqn. (15) against $K_2[Cl]$ should give a straight line with an intercept equal to k_{40} and slope equal to k_{42}. Such a plot is shown in Fig. 13, although it is clear that the intercept is too small for an accurate evaluation of it to be made. However, from this graph k_{42} has been found to be $(1.75 \pm 0.19) \times 10^5$ l./mol. sec., and k_{41} computed from the value of the composite termination coefficient (k_4) quoted earlier for those experiments carried out with no added chloride ion viz. 7.41×10^4 l./mol. sec.

The value of k_{41} obtained was $(2.4 \pm 0.30) \times 10^3$ l./mol. sec. which is not very different from that quoted for $Fe^{3+}aq$ for the ferric perchlorate terminated reaction (i. e. 2.8×10^3 l./mol. sec.). It would appear, therefore, that the outer sphere complexes existing in perchloric and hydrochloric acid media have about the same terminating efficiencies, although $Fe6H_2O^{3+}Cl^-$ is apparently also capable of initiation whereas $Fe6H_2O^{3+}ClO_4^-$ is not.

FIG.13. DETERMINATION OF k_{40} AND k_{42} FROM RATE MEASUREMENTS AT VARYING CHLORIDE ION CONCENTRATIONS



Kinetics of termination by ferric sulphate

It has been reported that sulphuric acid has a retarding effect on the polymerisation of acrylamide in aqueous solution, decreasing the rate by 30%.[4] However, in the case of the present series of experiments, the mean value of the constant $R_p/[m_1][cat]^{\frac{1}{2}}$ obtained for varying concentrations of sulphuric acid (0.05 to 0.5 mole/l) was found to be $(9.59 \pm 0.53) \times 10^{-2} l^{\frac{1}{2}}./mol.^{\frac{1}{2}} min.^{\frac{1}{2}}$ as compared with a value of $(10.2 \pm 1.2) \times 10^{-2}$ for the polymerisation of acrylamide in the absence of acid. These results show that sulphuric acid has no significant effect on the kinetics of polymerisation of the system studied in this investigation. Several experiments were also carried out to measure any polymerisation due to initiation by ferric sulphate but no detectable quantities of polymer were obtained, even at 35°C.

At 25°C., mean values of the constant $R_p[Fe(III)]/[m_1][cat]$ were $(9.92 \pm 0.68) \times 10^{-5}$/min. for the experiments with variable ferric sulphate concentration and $(10.91 \pm 1.20) \times 10^{-5}$/min. for those with variable initiator concentration. The exponents for the two concentrations, computed by the method of least squares, were $[initiator]^{0.98}$ and $[Fe_2(SO_4)_3]^{-1.04}$. This shows that termination of growing polymer chains occurs by reaction with the ferric salt, i.e. linear and not mutual termination predominates.

As reported above the specific rate constant for the initiation reaction, k_i, involving A.C.V. is increased slightly in the presence

of ferric perchlorate, and even more in the presence of ferric chloride. Consequently, a determination of k_4 will only be possible if k_i is known, as it cannot be assumed that this will be the same as that for either the ferric perchlorate or the ferric chloride retarded reactions.

Since ferric sulphate does not initiate the polymerisation of acrylamide, ferrous ions will be produced only in the termination reaction, so that under steady state conditions

$$\frac{d[Fe^{11}]}{dt} = k_i\,[cat]$$

and this should be independent of the ferric sulphate concentration. This was found to be so, a ten fold increase in ferric salt concentration from 10^{-4} to 10^{-3} mole/l. producing no discernable difference in the rate of production of ferrous ion.

For an initiator concentration of 2.0×10^{-4}M., we find the rate of production of ferrous ions to be 8.5×10^{-8}mole/l. min. at 25°C. so that k_i is, therefore, 7.08×10^{-6}/sec. Using a value for k_p of 1.8×10^{4}l./mol. sec. and this value of k_i we have calculated the composite termination coefficient, k_4, to be 7.14×10^{4}l./mol. sec.

From a study of the association of ferric ions and sulphate ions in perchloric acid solution at varying ionic strengths, Willix[18] deduced that $FeSO_4^+$ is an inner sphere complex. From the relationship given, the equilibrium constant, for the formation of the $FeSO_4 4H_2O^+$ complex at the ionic strength used in our investigation

has been calculated, the relationship of Milburn and Vosburg[6] being used to estimate the concentration of the $FeOH^{2+}$ species. With this information, the fraction existing as $FeSO_4^+$ was shown to represent 96.2% of the total ferric salt while the fraction existing as $FeOH^{2+}$ was only 0.09% and consequently could be ignored.

Comparison of effects of anions

It has been shown previously that the value of the termination coefficient for the outer sphere complex $Fe6H_2O^{3+}.Cl^-$ is the same (within experimental error) as that for the outer sphere perchlorate complex.

Since the sulphate and perchlorate anions are structurally similar it is reasonable to assume that the ferric sulphate outer sphere complex will have the same value for its termination coefficient as the two other outer sphere complexes.

With this assumption a value for the termination coefficient of the ferric sulphate inner sphere complex, k_{43}, has been calculated from our kinetic data and found to be 7.92×10^4 l./mol. sec. This value is much closer to that for the ferric chloride inner sphere complex, $FeCl^{2+}$, than to that for the outer sphere complexes, the appropriate rate constants being summarised in Table 6.

Table 6

	Termination coefficient at 25°C l./mol. sec.
Fe^{3+} as outer sphere complex with ClO_4^-, Cl^-, (SO_4^{2-})	2.8×10^3
$FeOH^{2+}$ inner sphere complex	21.2×10^3
$FeCl^{2+}$ " " "	172×10^3
$FeSO_4^+$ " " "	79.2×10^3

The decreased terminating efficiency of the ferric sulphate complex, relative to that of the chloro complex, could possibly be due to the much greater size of the sulphate ion as compared with that of the chloride ion, and to the fact that in the first case oxidation of the polymeric radical requires an electron to be transferred to a singly charged entity, whereas in the latter case an electron transfer occurs to a doubly charged entity. From electrostatic considerations the electron transfer in the second case seems to be more favourable energetically.

Values of k_i obtained for the polymerisation of acrylamide, initiated by A. C. V. in the presence of ferric perchlorate, ferric sulphate and ferric chloride are listed below, together with the value of k_i obtained in the absence of metal salts.

Table 7

$10^7 k_i$ sec^{-1}	Metal Salt	% sal as inner sphere complex
1.29	none	-
4.62	$Fe(ClO_4)_3$	little
23.7	$FeCl_3$	44%
70.8	$Fe_2(SO_4)_3$	96%

The effect of the added ferric salt is to increase the value of the initiation coefficient, presumably by facilitating the decomposition of the initiator. It is known that in D.M.F. solution, A.C.V. is readily decarboxylated by ferric chloride at 60°C.,[11] a reaction which may be connected with the capacity of ferric salts to facilitate the initiation of polymerisation by A.C.V. This property seems to depend primarily on the presence of an inner sphere anionic complex since the accelerating effect of a given ferric salt parallels the proportion of it present in this form.

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List of Symbols

ACV	4-4'-Azo-bis-4-cyanopentanoic acid.
[cat]	concentration of catalyst or initiator.
E	energy of activation (reaction indicated by subscript).
f_i	efficiency of initiation of chains
K	equilibrium constant (reaction indicated by subscript).
k_f	velocity coefficient for transfer reaction.
k_i	velocity coefficient for thermal initiation by ACV.
k_i'	velocity coefficient for initiation by metal salt.
k_p	velocity coefficient for propagation.
k_t	" " " mutual termination of chains.
k_4	composite velocity coefficient for termination by metal salt.
k_{40}	velocity coefficient for termination by aquated ferric ions.
k_{41}	" " " " by the outer sphere complex, $Fe.\underline{6}H_2O^{3+}Cl^-$.
k_{42}	velocity coefficient for termination by the inner sphere complex $Fe.(5H_2O)Cl^{2+}$.
k_{43}	velocity coefficient for termination by $FeSO_4^+$.
k_{11}	velocity coefficient for initiation by outer sphere complex.
k_{12}	" " " " by inner sphere complex.
$[m_1]$	concentration of monomer.
$[m^*]$	stationary concentration of radicals.
R_i	total rate of initiation

R_i'	rate of initiation by metal salt.
R_p	rate of propagation.
R_p^o	rate of propagation with [ACV] = O (initiation by metal salt).
$\bar{r}_n$	number average degree of polymerisation.
$\bar{r}_v$	viscosity average degree of polymerisation.
T	any transfer agent.
α	degree of hydrolysis
β	degree of association
$[\eta]$	limiting viscosity number
ΔH	heat of reaction
mμ	milli-microns; 10^{-7} cm. (wavelength).

List of diagrams.

Fig. 1 Arrhenius plot of rates of polymerisation obtained with no metal present.

2 Effect of initiator concentration on rate of polymerisation with ferric perchlorate present.

3 Effect of ferric perchlorate concentration on rate of polymerisation.

4 Arrhenius plot of initiation coefficient k_i.

5 Arrhenius plot of rates of polymerisation obtained with vanadyl perchlorate present.

6 Plot of the reciprocal of the number average degree of polymerisation against vanadyl perchlorate concentration.

7 Rate of polymerisation initiated by uranyl perchlorate as a function of uranyl salt concentration.

8 Effect of uranyl perchlorate concentration on rate of polymerisation initiated by ACV.

9 Arrhenius plot of rates of polymerisation obtained with uranyl perchlorate present.

10 Variation of rate of polymerisation with initiator concentration in the presence of ferric chloride.

11 Effect of ferric chloride concentration on rate of polymerisation.

Fig.12 Plots of the rates of polymerisation against the reciprocal of the ferric chloride concentrations for different amounts of added potassium chloride.

13 Graphical determination of velocity coefficients for termination by inner and outer sphere ferric-chloride ionic complexes.

14 Variation of rate of polymerisation with catalyst concentration in the presence of uranyl perchlorate.