Termination mechanisms of the radical polymerisation of acrylamide.

By
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Abstract
A kinetic study of the polymerisation of acrylamide initiated by 4-4'-azo-bis-4-cyanopentanoic acid has shown that up to 10% conversions, the rate of polymerisation is directly proportional to the concentration of monomer and to the square root of the concentration of initiator. Molecular weight measurements indicate that non-degradative transfer to monomer occurs and that mutual termination is probably by disproportionation.

The addition of ferric salts greatly reduces the overall rate of polymerisation, the chloride being more effective in this respect than the perchlorate. At sufficiently high concentrations of ferric salts, the order of the polymerisation reaction approximates to one with respect to initiator and minus one with respect to the ferric salt. It has been shown that under these conditions, radical chains are being terminated by electron transfer, involving the reduction of the iron salt to the ferrous state.

Introduction
In the presence of a suitable initiator, acrylamide readily undergoes polymerisation in aqueous solution even at room temperature, although the rate of reaction display an extreme sensitivity to traces of certain impurities. Particularly effective in retarding polymerisation are salts of metals of variable valency and it is with the effect of such salts on the kinetics and mechanism of the termination reaction in the radical polymerisation of acrylamide, that this investigation is primarily concerned.

The initiator chosen for the present series of experiments was the water-soluble, thermal catalyzed, 4-4'-azo-bis-4-cyanopentanoic acid, a substance which had not previously been used to initiate polymerisation of acrylamide. A preliminary study of the kinetics of the reaction was, therefore, undertaken to ensure that the mechanisms of initiation and propagation were free from undesirable complications.
Kinetics of polymerisation with no metal salt present

Rates of polymerisation obtained with varying concentrations of monomer and of catalyst are summarised in Tables I and II. Analysis of these kinetic data by the method of least squares has shown that for conversions of up to 10%, the rate of polymerisation ($R_p$) of acrylamide, under the conditions prevailing in our experiments, is proportional to \( [\text{monomer}]^{1.64} \) and to \( [\text{catalyst}]^{0.49} \). We may conclude, therefore, that apart from transfer processes, the principal reactions involved in the polymerisation are as follows:

**Initiation**

\[
\text{Cat} \rightarrow 2Q^- \\
Q^- + m_1 \rightarrow m_1^{\#} \quad \text{Rate} = f_1 k_1 [\text{Cat}] 
\]

**Propagation**

\[
m_j^\# + m_1 \rightarrow m_j^{\#} + m_1 \\
\text{Rate} = k_2 [m_j^\#][m_1^\#] 
\]

**Termination**

\[
m_r^\# + m_s \rightarrow P_r + P_s \\
\text{Rate} = (k_t + k_l)[m_r^\#][m_s^\#] 
\]

where \( m_j^\# \) represents a live polymeric radical consisting of \( j \) monomeric segments \( (m_1) \) and a single initiator fragment \( (Q^-) \), \( P_r \) a dead polymer molecule having \( r \) monomer units, \( k_t \) and \( k_l \) the velocity coefficients for termination by disproportionation and by combination respectively. With the usual simplifying assumptions, this kinetic scheme requires \( k_2 f_1 k_1/(k_t + k_l) \frac{1}{2} \) to equal \( R_p/m_j^\#[\text{Cat}]^\frac{1}{2} \), the average value of which from all our kinetic experiments was found to be \( (1.70 \pm 0.17) \times 10^{-5} \) litre mol$^{-1}$ sec$^{-1}$ at 25.0$^\circ$C. However, at this temperature the propagation \( (k_2) \) and termination \( (k_t + k_l) \) coefficients are known to be \( (1.80 \pm 0.15) \times 10^3 \) litre mol$^{-1}$ sec$^{-1}$ and \( (4.45 \pm 0.20) \times 10^2 \) litre mol$^{-1}$ sec$^{-1}$ respectively.

---

Table I

<table>
<thead>
<tr>
<th>[catalyst] = 1.94 x 10$^{-4}$ M.</th>
<th>Temp. = 25.00 $\pm$ 0.01$^\circ$C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[monomer] = 10$^{-4}$ $R_p$</td>
<td>10$^2$ $R_p/([m_1][\text{Cat}])^{\frac{1}{2}}$</td>
</tr>
<tr>
<td>mol. 1$^{-1}$ min$^{-1}$</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>0.313</td>
<td>3.78</td>
</tr>
<tr>
<td>0.419</td>
<td>4.52</td>
</tr>
<tr>
<td>0.528</td>
<td>6.42</td>
</tr>
<tr>
<td>0.630</td>
<td>6.86</td>
</tr>
<tr>
<td>0.640</td>
<td>6.90</td>
</tr>
<tr>
<td>7.90</td>
<td>9.6</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Monomer</th>
<th>Temp.</th>
<th>(10^4 R_p )</th>
<th>(10^2 R_p/m_1 ) Cat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.096</td>
<td>25.30</td>
<td>1.78</td>
<td>10.9</td>
</tr>
<tr>
<td>0.436</td>
<td>3.51</td>
<td>4.54</td>
<td>11.9</td>
</tr>
<tr>
<td>0.548</td>
<td>2.32</td>
<td>5.51</td>
<td>13.7</td>
</tr>
<tr>
<td>0.855</td>
<td>2.32</td>
<td>4.80</td>
<td>11.9</td>
</tr>
<tr>
<td>0.866</td>
<td>2.32</td>
<td>4.80</td>
<td>11.9</td>
</tr>
<tr>
<td>1.44</td>
<td>6.53</td>
<td>12.0</td>
<td>12.9</td>
</tr>
<tr>
<td>3.54</td>
<td>9.24</td>
<td>12.0</td>
<td>12.9</td>
</tr>
<tr>
<td>3.53</td>
<td>12.0</td>
<td>12.0</td>
<td>12.9</td>
</tr>
<tr>
<td>5.89</td>
<td>12.6</td>
<td>12.6</td>
<td>12.9</td>
</tr>
<tr>
<td>12.9</td>
<td>20.8</td>
<td>20.8</td>
<td>12.9</td>
</tr>
</tbody>
</table>

Our experimental data may, therefore, be used to evaluate the initiation coefficient \( (k_t k_i) \), which was found to be 

\[
(1.29 \pm 0.29) \times 10^{-7} \text{ sec}^{-1}
\]

and it is this value which has been used to compute kinetic chain lengths \((\lambda)\) given in Table III, where

\[
\lambda = \frac{k_t m_1}{(k_t + k_i) F_r k_i \text{ Cat}^{0.2}}
\]

(1)

Molecular weights of polymers

The average degree of polymerisation \( (F_r) \) of the polymers produced are summarised in Table III. They were calculated from limiting viscosity numbers by means of Scholten's relation, which for polymer concentrations expressed in gms. per 100 ml. is

\[
F_r = 6.31 \times 10^{-5} (71.1 F_r) 0.80
\]

(2)

Over the range of polyacrylamide concentrations used in our viscosity measurements, the ratio of specific viscosity to polymer concentration was itself found to vary linearly with polymer concentration, so that limiting viscosity numbers were obtained by graphical extrapolation.

However, average degrees of polymerisation so obtained, which are close to weight-average values, are significantly smaller than would be expected from the corresponding kinetic chain lengths, indicating that non-degradative chain transfer processes are relatively important in the polymerisation of acrylamide under our experimental conditions. Now, in aqeuous solution the most likely transfer reactions seem to be:-

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Table II

\[
\begin{array}{ccc}
10^4 \text{[catalyst]} & 10^4 R_p \text{mol.}^{-1} \text{min}^{-1} & 10^2 R_0 \text{[m]} \text{[Cat]}^{\frac{1}{2}} \\
0.096 & 1.78 & 10.9 \\
0.236 & 3.31 & 13.7 \\
0.547 & 4.54 & 11.9 \\
0.835 & 3.31 & 9.0 \\
0.856 & 4.80 & 9.0 \\
1.64 & 4.92 & 10.0 \\
3.24 & 6.23 & 5.7 \\
3.53 & 9.24 & 9.6 \\
5.89 & 12.8 & 12.9 \\
12.9 & 12.6 & 5.9 \\
& 20.8 & 11.0 \\
\end{array}
\]

Our experimental data may, therefore, be used to evaluate the initiation coefficient \(k_i k_t\), which was found to be \((1.29 \pm 0.29) \times 10^{-7} \text{ sec}^{-1}\) and it is this value which has been used to compute kinetic chain length \(\bar{\nu}\) given in Table III, where

\[
\bar{\nu} = \frac{k_i [m]}{(k_t + k_t f_k k_t \text{[Cat]})^{\frac{1}{2}}}
\]

Molecular weights of polymers

Average degrees of polymerisation \((\bar{\nu})\) of the polymers produced are summarised in Table III. They were calculated from limiting viscosity numbers \([\eta]\) by means of Scholten’s relation, which for polymer concentrations expressed in gm. per 100 ml. is

\[
[\eta] = 6.31 \times 10^{-5} (71.1 \bar{\nu})^{0.80}
\]

Over the range of polyacrylamide concentrations used in our viscosity measurements, specific viscosity was found to vary linearly with polymer concentration, so that limiting viscosity numbers were obtained by graphical extrapolation.

However, average degrees of polymerisation so obtained, which are close to weight-average values, are significantly smaller than would be expected from the corresponding kinetic chain lengths, indicating that non-degradative chain transfer processes are relatively important in the polymerisation of acrylamide under our experimental conditions. Now, in aqueous solution the most likely transfer reactions seem to be:-

\[\text{pp}\]
Table III

<table>
<thead>
<tr>
<th>(10^{9} [Ca^+] )</th>
<th>Kinetic chain length ((n)) (\times 10^{-4})</th>
<th>Degree of polymerisation, (10^{5} (\Delta = 2/V - 1/\bar{V}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.9</td>
<td>19.3</td>
<td>9.04</td>
</tr>
<tr>
<td>5.89</td>
<td>28.6</td>
<td>9.60</td>
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<tr>
<td>3.53</td>
<td>36.9</td>
<td>9.35</td>
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<td>3.36</td>
<td>38.0</td>
<td>9.04</td>
</tr>
<tr>
<td>1.64</td>
<td>54.1</td>
<td>7.91</td>
</tr>
<tr>
<td>0.84</td>
<td>75.8</td>
<td>7.02</td>
</tr>
</tbody>
</table>

\[ m^u_j + m_1 \rightarrow P_3 + m^u_i \quad \text{Rate} = k_{ct}[Ca][m^u_j]\]

\[ m^u_j + Ca \rightarrow P_3 + Q^u \quad \text{Rate} = k_{fo}[Ca][m^u_j]\]

The inclusion of such reactions in the overall scheme leads to the following relationship for the number average degree of polymerisation (\(\bar{V}\))

\[
\frac{1}{\bar{V}} = \frac{k_t + k_{1/2}^u}{k_p}[m^u_j] = \frac{k_{ct}}{k_p}[Ca] + \frac{k_{fo}}{k_p}[Ca]
\]

However, the values of the individual termination coefficients, \(k_t\) and \(k_{1/2}^u\), are not known. We have, therefore, assumed for present purposes that termination proceeds predominantly by disproportionation, i.e., \(k_{1/2}^u \approx 0\), and that the average degree of polymerisation computed using Scholten's equation are twice the number average values, and we have evaluated the L.H.S. of equation (3), which now equals \(\delta\), accordingly. It is clear from the figures given in Table III that \(\delta\) does not increase with increasing catalyst concentration as required by equation (3). On the contrary, there is a marked tendency for it to increase as the catalyst concentration is diminished. This behaviour suggests the existence of an additional transfer reaction involving a substance, the concentration of which is an inverse function of that of the catalyst. The substance concerned, which could be an impurity, possibly a decomposition product either of the catalyst itself or of the monomer, must be capable of being rendered inactive as far as transfer is concerned by a reversible reaction with the catalyst. Indeed our experimental data are represented fairly well by the empirical relationship

\[
\delta = 1.6 \times 10^{-5} + 1 \times 10^{-9}/[Ca]
\]

in which the constant term, \(1.6 \times 10^{-5}\), presumably corresponds to 241

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the transfer constant for monomer \( \text{k}_{\text{tr}} \), for which Dalton and Tordoff\(^1\) obtained a value of \( \text{1.2} \times \text{10}^{-5} \text{ at 25.0}^\circ \text{C} \).

Experimental confirmation of the assumption that termination of polymerization is primarily by disproportionation seems to be limited to an observation of residual unsaturation in the polymer\(^2\). Attempts in the present investigation to determine the terminal carboxyl groups by titration were unsuccessful, so that conclusive evidence for the mechanism of termination is not yet available.

**Effect of ferric perchlorate on kinetics of polymerization**

Commercial acrylamide is said to contain some 50 parts per million of iron\(^{3+}\), probably as sulphate. A consideration of the effect of added ferric salts is therefore an appropriate point at which to start. The perchlorate appears to be the least complicated of all ferric salts in aqueous solutions. Its effect on the X- and γ-ray initiated polymerisation of acrylamide has been investigated by Gollinson, Dalton and McNaughton\(^4\), so that a comparison is possible between the results obtained in the present investigation and those given by an independent method.

The most obvious effect of the addition of ferric perchlorate is the reduction in the overall rate of polymerisation, the extent of which increases with an increasing concentration of ferric salt, as illustrated by the data given in Table IV. Perchloric acid, itself, has no detectable effect on the rate of polymerisation and no significant amount of polymer was produced by ferric perchlorate and perchloric acid in the absence of the initiator. However, for the range of concentrations examined, the rate of polymerisation was found to be directly proportional to \( \text{[catalyst]}^{0.77} \) but inversely proportional to \( \text{[ferric salt]}^{-0.74} \). In addition, we have shown using o-phenanthroline that the ferric salt is continuously reduced to the ferrous state during the course of the polymerisation. These observations are all consistent with the conclusion that in the presence of ferric perchlorate, the following alternative mechanism of termination is operative:

\[
\text{Fe}^{3+} + \text{Fe}^{3+}_{\text{aq.}} + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{Fe}^{2+}_{\text{aq.}} + \text{H}_2\text{O}
\]

\[
\text{Rate} = k_H[\text{Fe}^{3+}_{\text{aq.}}][\text{m}^3]
\]

in addition to the normal bimolecular termination reaction discussed above. Infra-red absorption studies have shown that polyacrylamide produced in the presence of ferric perchlorate contains some vinyl groups\(^5\), an observation which suggests that the polymeric carbocation, produced by loss of an electron to the ferric ion, stabilises itself by proton transfer to a solvent molecule. The implications of including this additional mode of chain termination in the overall kinetic scheme are such that the termination coefficient \( (k_t) \) for this reaction may be calculated from the equation

\[
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\]

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Table IV

\[
\text{[monomer]} = 1.00 \text{M}; \quad [\text{HClO}_4] = 0.11 \text{M}; \quad \text{Temp.} = 25.00 \pm 0.01^\circ \text{C}.
\]

(a) Variation of \( R_p \) with concentration of ferric perchlorate

\[
10^5 \left[ \text{Fe(OClO}_4\text{)}_2 \right] \quad \text{(catalyst)} = 4.00 \times 10^{-5} \text{M}
\]

\[
\begin{array}{c|c|c}
10^4 \text{ } R_p & 10^{-4} k_p & 10^{-4} k_d \\
\text{mol. } 1^{-1} \text{ min}^{-1} & 1. \text{ mol}^{-1} \text{ min}^{-1} & 1. \text{ mol}^{-1} \text{ min}^{-1} \\
1.39 & 14.3 & 8.7 \\
5.58 & 5.29 & 10.6 \\
9.28 & 3.54 & 9.9 \\
9.28 & 3.48 & 10.1 \\
\end{array}
\]

(b) Variation of \( R_p \) with concentration of catalyst

\[
10^5 \left[ \text{catalyst} \right] \quad \text{[Fe(OClO}_4\text{)}_2] = 9.28 \times 10^{-5} \text{M}
\]

\[
\begin{array}{c|c|c}
10^4 \text{ } R_p & 10^{-4} k_p & 10^{-4} k_d \\
\text{mol. } 1^{-1} \text{ min}^{-1} & 1. \text{ mol}^{-1} \text{ min}^{-1} & 1. \text{ mol}^{-1} \text{ min}^{-1} \\
2.60 & 2.96 & 7.7 \\
2.60 & 2.98 & 7.6 \\
4.00 & 3.48 & 10.1 \\
4.00 & 3.94 & 9.9 \\
4.51 & 5.06 & 7.8 \\
6.00 & 5.62 & 9.2 \\
\end{array}
\]

\[
k_d = \frac{f_1 R_p}{k_p [\text{Fe(OClO}_4\text{)}_2]} = \frac{k_t R_p}{k_p [\text{catalyst}] [\text{Fe(OClO}_4\text{)}_2]}
\]  \( (5) \)

The mean value of \( k_d \) so obtained from the data given in Table IV was \((1.49 \pm 0.17) \times 10^{3} \text{ litre mole}^{-1} \text{ sec}^{-1}\).

However, ferric salts are known to be subject to a series of complex hydrolytic reactions in aqueous solutions, of which the following are said to be the most important:

\[
\begin{align*}
\text{Fe}^{3+}_{\text{aq.}} + 2\text{H}_2\text{O} & \rightleftharpoons \text{Fe(OH)}^{2+} + \text{H}_3\text{O}^+ & K_1 \\
\text{Fe(OH)}^{2+} + 2\text{H}_2\text{O} & \rightleftharpoons \text{Fe(OH)}^{3+} + \text{H}_3\text{O}^+ & K_2 \\
2\text{Fe(OH)}^{2+} & \rightleftharpoons \text{Fe}_2(\text{OH})_{4}^{2+} & K_4
\end{align*}
\]
The termination coefficient $k_t$ is, therefore, a composite quantity, which under appropriate experimental conditions might be expected to vary with the total concentration of ferric salt present, particularly as the relative terminating efficiencies of the ionic species $\text{Fe}^{2+}$, $\text{FeOH}^{3+}$, $\text{Fe(OH)}_3^+$, and $\text{Fe}_3(\text{OH})_2^{10-}$ are known to be in the ratio $1:5.5:50:200$. This variation is not observed in the present series of experiments, however, partly because of low concentrations of ferric salt employed and partly because of the low pH of the solutions. However, in order to illustrate the relative importance of the various ionic species present, we have calculated their concentrations (Table V) from the values of $k_1$ and $k_2$ given by Millburn and Voeburg and from that for $k_3$ obtained by Nedderman, $k_4$ being assumed to vary with ionic strength in the same way that $k_3$ does. It is clear that despite their greater terminating

$$\begin{align*}
[R_{\text{ClO}_4}] &= 0.11\mu; \quad [\text{Fe(OH)}_3^+] = 9.28 \times 10^{-5} \mu; \quad \text{Temp.} = 25.0^\circ \text{C.}
\end{align*}$$

$\begin{align*}
k_1 &= 2.83 \times 10^{-3} \\
k_2 &= 1.2 \times 10^{-3} \\
k_3 &= 192 \\
k_4 &= 9.04
\end{align*}$

Table V: efficiencies, the effect of both the second hydrolysis product and of the dimer on the kinetics of termination may be neglected. In addition, it should be noted that the high concentration of acid used ensures that relative proportions of $\text{Fe}^{3+}$ and $\text{FeOH}^+$ are independent of the total concentration of ferric perchlorate, so that the absolute value of the termination coefficient for the equated ferric ion ($k_{40}$) may be evaluated from the reaction

$$k_{40} = k_{40}(1-a) + k_{40}a$$

(6)

in which $k_{40}$ is the termination coefficient for $\text{FeOH}^+$ and $a$ is the degree of hydrolysis, viz. $0.0251$ for $[\text{H}_3\text{O}^+] = 0.11\mu$. After making due allowance for the relatively large uncertainty in the value of the reaction coefficient $(f_1k_1)$, we find $k_{40}$ to be $(1.3 \pm 0.4) \times 10^5$ litre mole$^{-1}$ sec$^{-1}$ compared with values of $(2.0 \pm 0.6) \times 10^5$ and $(2.2 \pm 0.3) \times 10^5$ reported by other investigators.

Effect of ferric chloride on kinetics of polymerisation

The chloride ion is known to catalyse electron transfer reactions involving ferric ions$^{2+}$, $^{10}$. It is not surprising, therefore,
that for a given concentration of ferric chloride the reduction in the rate of polymerisation observed is significantly larger than for the same concentration of ferric perchlorate. The appropriate kinetic data are summarised in Tables VI and VII and for the range of concentrations studied we have found that $R_p$ is directly proportional to $[\text{catalyst}]^{0.30}$ and inversely proportional to $[\text{ferric chloride}]^{0.39}$. However, by restricting attention to sufficiently high concentrations of ferric salt and low concentrations of catalyst, both exponents can be made to approach unity more closely.

We have again found that with ferric chloride present, polymerisation is accompanied by the production of ferrous ions. Hydrochloric acid by itself had no effect on the rate of polymerisation and no significant amount of polymer was produced in solutions of monomer containing ferric chloride and acid in the absence of the initiator. Evidently linear termination of radical chains by an electron transfer process involving the ferric salt is again operative in addition to the normal bimolecular mode of mutual termination of chains. The essential difference in behaviour with chloride ions present is that the rate of linear termination is faster than with perchlorate ions.

Table VI

<table>
<thead>
<tr>
<th>[catalyst] $10^{-4}$</th>
<th>$10^{-3} R_p$</th>
<th>$10^{-4} k_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>2.14</td>
<td>14.5</td>
</tr>
<tr>
<td>1.00</td>
<td>2.17</td>
<td>14.3</td>
</tr>
<tr>
<td>2.00</td>
<td>4.12</td>
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</tr>
<tr>
<td>2.00</td>
<td>3.34</td>
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<td>4.17</td>
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<td>4.00</td>
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<td>18.8</td>
</tr>
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<td>4.00</td>
<td>5.57</td>
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</tr>
<tr>
<td>5.00</td>
<td>9.56</td>
<td>14.6</td>
</tr>
<tr>
<td>5.00</td>
<td>8.02</td>
<td>17.7</td>
</tr>
<tr>
<td>5.08</td>
<td>8.59</td>
<td>16.5</td>
</tr>
</tbody>
</table>

The greater efficiency of ferric chloride as a chain terminator is undoubtedly due to the greater complexity of its solutions as compared with those of ferric perchlorate. This complexity arises from the tendency for ionic association to occur in aqueous solutions in addition to the usual hydrolytic reactions common to all ferric salts, and the following equilibria have been recognised and investigated by several authors.

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Table VII

\[
\text{mole litre}^{-1} \text{ min}^{-1}
\]

\[
\text{litre mole}^{-1} \text{ min}^{-1}
\]

\[
\text{catalyst} = 8.01 \times 10^{-4} M
\]

\begin{align*}
3.60 & \quad 10.0 & \quad 16.4 \\
6.00 & \quad 6.26 & \quad 17.0 \\
6.00 & \quad 5.88 & \quad 16.2
\end{align*}

\[
\text{catalyst} = 5.08 \times 10^{-4} M
\]

\begin{align*}
2.58 & \quad 8.39 & \quad 16.5 \\
4.20 & \quad 6.79 & \quad 13.6 \\
5.15 & \quad 4.94 & \quad 16.0 \\
6.00 & \quad 4.35 & \quad 12.8 \\
6.00 & \quad 4.07 & \quad 15.9 \\
7.72 & \quad 3.03 & \quad 17.9 \\
7.72 & \quad 3.84 & \quad 13.8
\end{align*}

\[
\begin{align*}
\text{Fe}^{3+} + \text{Cl}^- & \rightleftharpoons \text{FeCl}^{2+} \quad K_3 \\
\text{FeCl}^{2+} + \text{Cl}^- & \rightleftharpoons \text{FeCl}^+ \quad K_4
\end{align*}

However, the use of decimolar hydrochloric acid in the present experiments ensures that the only hydrolysis product which need be considered is \text{Fe(OH)}^{2+}, and also that the relative proportions of all ionic species present, including \text{FeCl}^{2+} and \text{FeCl}^+, are independent of the total ferric chloride concentration since this is very small compared with that of hydrochloric acid.

by means of the semi-empirical relationship of Rabicowitch and Stockmayer\textsuperscript{13}, the constants appropriate to the ionic strengths of the solutions used in kinetic measurements, for each of the above equilibria, have been evaluated and are given in Table VIII, together with proportions of the total ferric chloride present in the different forms.

The average value of the composite termination coefficient \((k_4')\) evaluated from the experimental data given in Tables VI and VII by means of equation (5) was found to be \((2.65 \pm 0.27) \times 10^3 \text{ litre mole}^{-1} \text{ sec}^{-1}\). Although \(k_4'\) is related to the individual coefficients of the various ionic species present by the expression

\[
k_4' = (1 - a - b - \gamma)k_{40} + \alpha k_{41} + \beta k_{42} + \gamma k_{44} \quad (7)
\]

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Table VIII

\[ \left[ \text{HOCl} \right] = 0.122 \text{M} \quad \text{Temp.} = 25.0^\circ \text{C} \]

\[ K_1 = 2.76 \times 10^{-5}; \quad K_3 = 7.73; \quad K_4 = 2.5 \]

<table>
<thead>
<tr>
<th>Species</th>
<th>Fraction of total FeCl(_3)</th>
<th>Rate coefficient symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl(_2^+)</td>
<td>( a = 0.010 )</td>
<td>( k_{41} )</td>
</tr>
<tr>
<td>FeCl(_3^+)</td>
<td>( b = 0.403 )</td>
<td>( k_{43} )</td>
</tr>
<tr>
<td>FeCl(_4^-)</td>
<td>( c = 0.127 )</td>
<td>( k_{44} )</td>
</tr>
</tbody>
</table>

It is not possible at this stage without more experimental data to evaluate \( k_{43} \) and \( k_{44} \) separately. We hope to obtain the necessary additional experimental information by measuring the rate of polymerisation in the presence of different concentrations of chloride ion. At the moment it is only possible to evaluate an average value for the termination coefficients of the ions, FeCl\(_2^+\) and FeCl\(_3^+\), viz. \( (sk_{43} + yk_{44})/(a + y) \), and this turns out to be \( 3.7 \times 10^{-3} \text{ litre mole}^{-1} \text{ sec}^{-1} \). These ions therefore terminate radical chains at about three times the rate of the uncharged ferric ion.

One final question still to be settled is whether termination of polymer chains by species such as FeCl\(_2^+\) involves the incorporation of chloride into the polymer molecule produced,

\[
\text{FeCl}_2^+ + \text{m} \rightarrow \text{P}_{\text{m}} \rightarrow \text{P}_{\text{m}}\text{Cl} + \text{FeCl}^{2+}
\]

instead of producing a molecule having a terminal vinyl linkage as with ferric perchlorate. There is evidence that in non-hydroxyllic media, e.g., dimethyl formamide, the termination of polymerisation of some vinyl monomers by ferric salts does sometimes involve the incorporation of the anion concerned into the resulting polymer \(^{12,13}\). As far as the aqueous polymerisation of acrylamide is concerned, this point has still to be settled.

Bibliography