POLYMERIZATION OF VINYL MONOMERS

II. Ceric-Formaldehyde Redox System

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INTRODUCTION

Apart from their use in the oxidation of numerous inorganic and organic substrates, ceric salts in aqueous acidic solutions have been found to initiate vinyl polymerization either alone or in combination with reducing agents. The reducing agents employed have invariably been alcohols and the initiation of polymerization has been assumed to take place via the free radicals produced by the decomposition of the ceric-alcohol complex. We have investigated the kinetics of polymerization of methyl acrylate using the ceric perchlorate-formaldehyde redox system; it is proposed to present here the results of our experiments with this redox system and compare them with those obtained earlier in this laboratory with ceric perchlorate-methyl acrylate system. The choice of formaldehyde as the reducing agent has been made for the following reasons: (1) the kinetics of ceric perchlorate-formaldehyde reaction has been studied in detail by Hargreaves and Sutcliffe; (2) formic acid which is formed as product is not further easily oxidised under our experimental conditions; and (3) the concentration of formaldehyde can be conveniently measured during the course of the reaction.

EXPERIMENTAL

Methyl acrylate is a Rohm and Haas (U.S.A.) product containing 2% hydroquinone. After removal of the inhibitor by shaking the commercial monomer with 5% sodium hydroxide solution, the monomer is dried over anhydrous sodium sulphate, repeatedly distilled in nitrogen atmosphere and stored in a refrigerator at 5°C. Ceric perchlorate has been obtained as a 0.65 M solution in 2 M perchloric acid from G. Frederick Smith Chemical Company (U.S.A.). Perchloric acid is an E. Merck Guaranteed Reagent containing ca. 60% HClO₄. Formaldehyde is a B.D.H. Analar reagent containing 36% formaldehyde in water and is more than 98% pure. Stock solutions...
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of suitable strengths have been made from this solution. Water, doubly distilled over alkaline permanganate in all-glass Pyrex unit and passed through the ion-exchange resin, 'Biodiminrolit', has been used for the preparation of reagents and solutions. Other reagents like ferrous ammonium sulphate, ceric ammonium sulphate, sodium hydroxide, o-phenanthroline, etc., are either B.D.H. Analar or E. Merck G.R. products. Solvents like acetone, methanol, etc., have been distilled before use. Deaeration of the reaction mixture has been done by nitrogen freed from oxygen by passage through Fieser's solution.

The estimation of ceric ion concentration has been done by adding a known excess of ferrous ammonium sulphate solution in sulphuric acid, to the ceric solution and back-titrating against standard ceric sulphate solution, using ferroin indicator. The strength of acid in stock ceric solutions is estimated with standard alkali after reducing the ceric to cerous state, precipitating cerium as cerous oxalate and filtering off the precipitate. Formaldehyde concentration in stock solutions (> 0.1 M) has been estimated by the hypoidite method; for lower concentrations (1 × 10⁻⁴ − 1 × 10⁻² M) the chromotropic acid method has been employed, and absorption measurements have been made at λ = 585 mμ in the Hilger 'Uvispek' spectrophotometer H-700.

The reaction vessel is an 8" long Pyrex tube fitted with a B-24 socket carrying a B-24 cone with an inlet and outlet tube for nitrogen. Appropriate quantities of the monomer and formaldehyde solution are taken in the reaction vessel and kept at 25 ± 0.1° C. in a thermostat, housed in a dark chamber. The mixture is deaerated for about 15–20 minutes at the end of which the ceric perchlorate solution (0.5–1.0 ml.) is added through a long thin glass funnel inserted through the outlet tube. The polymerization starts immediately without any induction period. After the specified time interval, the reaction is arrested by addition of a known excess of ferrous solution. The polymer is filtered off, washed well with water, dried to constant weight under vacuum and the rate of monomer disappearance is calculated from the weight of the polymer. The rate of ceric disappearance has been calculated from the final concentration of the ceric ion in the filtrate (by titrimetry) after removal of the polymer. In some cases, the rate of formaldehyde disappearance has been found out by estimation of the formaldehyde concentration in the filtrate (by chromotropic acid method). The chain-lengths of the purified polymethyl acrylates have been determined viscometrically, using a P.C.L. Ubbelohde suspended level dilution viscometer. The following
Mark-Houwink type relationship has been employed for polymethyl acrylate in acetone at 25°C: \[ n = 11.2 [\eta]^{1.28}. \]

RESULTS AND DISCUSSION

A. Kinetic Scheme and Rate Expressions

The following scheme embodies the sequence of reactions which have been found to explain satisfactorily the kinetic results obtained:

(a) \[ \text{Ce}^{4+} + F \xrightarrow{k_1} \text{Ce}^{3+} + H^+ + F. \]

(b) \[ \text{Ce}^{4+} + F \xrightarrow{k_2} \text{Ce}^{3+} + H^+ + H\text{.COOH} \]

(c) \[ \text{Ce}^{4+} + M \xrightarrow{k_i} \text{Ce}^{3+} + \text{R. (radical ion)} \]

(d) \[ F + M \xrightarrow{k_i'} \text{R.'} \]

(e) \[ \text{R. or R.'} + M \xrightarrow{k_p} (\text{M.})_2 \]

(f) \[ (\text{M.})_{n-1} + M \xrightarrow{k_p} (\text{M.})_n \]

\[ (\text{M.})_n + \text{Ce}^{4+} \xrightarrow{k_t} \text{P}_n + \text{Ce}^{3+} + H^+ \]

F represents formaldehyde and F. the radicals derived from it. The primary radicals R and R.' may be treated without distinction for kinetic purposes. The active form of ceric ion in this study has been assumed to be the Ce\(^{4+}\) ion in the unhydrolysed form in accordance with the observations by Hargreaves and Sutcliff as well as by ourselves. Applying the stationary state principle for the free radical concentrations F. and M., we get the following rate expressions:

Rate of ceric disappearance,

\[ -\frac{d [\text{Ceric}]}{dt} = 2 [\text{Ce}^{4+}] (k_1 [F] + k_i [M]). \]
Rate of monomer disappearance,

\[ \frac{d[M]}{dt} = \left( \frac{k_p}{k_i} \right) [M]^2 \left( k_i + \frac{k_1 [F]}{[M] + \left( \frac{k_1}{k_i} \right) [Ce^{4+}]} \right). \]  

(2)

Chain-length,

\[ n = \frac{k_p [M]}{k_t [Ce^{4+}]} \].

(3)

The reaction scheme pictured above is analogous to that obtained by Katai, Kulshrestha and Marchessault in their study on the polymerization of acrylonitrile initiated by ceric sulphate-ethylene glycol redox system. They have however included complex formation between ceric ion and the alcohol in their scheme whereas complex formation between ceric ion and formaldehyde is neither supported by previous work nor found necessary to explain our kinetic data.

B. Rate of Ceric Disappearance

A first-order dependence of the rate of ceric disapperance on the [Ce^{4+}] has been obtained (Fig. 1, Curve A). The rate has also been found to increase linearly with increasing [F] (Fig. 1, Curve B). It has been observed that the rate in the ceric-methyl acrylate system forms only about 10% of that obtained in the ceric-formaldehyde-methyl acrylate system, under identical conditions. Moreover, the rate in the latter case is almost equal to that in the ceric-formaldehyde reaction reported by Hargreaves and Sutcliff, and the stoichiometry \( \Delta [Ce^{4+}] / \Delta [F] \) is only slightly greater than two. These observations point out the fact that the amount of ceric ion consumed for polymerization is small compared to the ceric consumption by formaldehyde in steps (a) and (b). This is further supported by the experimental finding that increase of the monomer concentration causes only a negligible increase in the rate of ceric disapperance, indicating that \( k_1 [F] \gg k_i [M] \) in equation (1). As there is appreciable polymerization even in the absence of formaldehyde, we are led to conclude that only a small percentage of the radicals \( F_0 \) take part in the initiation step (d), while the bulk is consumed by ceric ion in reaction (b). Although the dependence of the rate on monomer concentration is not pronounced in the presence of formaldehyde, the validity of equation (1) can be verified.
from experiments carried out in absence of the aldehyde where it has been found that the rate increases steadily with increasing [M] (Fig. 2, Curve A).

C. Rate of Monomer Disappearance

Figure 2 (Curve B) shows the dependence of the rate of monomer disappearance on the square of the monomer concentration. The second-order dependence has also been observed in the absence of formaldehyde. These observations are in accordance with the requirements of equation (2), provided \((k_2/k_1') [Ce^{4+}]\) in the denominator is considerably higher than [M]. An order of two for the monomer concentration has also been obtained by Katai et al.\(^6\) They have however been unable to verify the same dependence in the absence of the reducing agent owing to (according to them) experimental difficulties. It is to be noted that the second-order dependence is not possible if termination of the chain radicals takes place by the mutual type, whereas it is easily reconciled if termination is effected by ceric ions. There is good amount of evidence for this kind of linear termination by metal ions.\(^3-6,12\) The rate of monomer disappearance has been found to increase with the formaldehyde concentration and decrease with ceric ion concen-
Fig. 2. Effect of monomer concentration on (A) rate of ceric disappearance and (B) rate of monomer disappearance.

tration (Table I), thus satisfying the demands of equation (2). It is of interest to note that the rate is independent of the ceric ion concentration in the absence of formaldehyde.⁴

D. Chain-lengths

In accordance with equation (3), the chain-lengths of the polymethyl acrylates obtained have been found to increase with the monomer concentration and decrease with the ceric ion concentration (Table II).

E. Rate Constants

From the slopes of the plots of $-d[Ceric]/dt$ against [M] and [F], the values of $k_i$ and $k_1$ respectively have been calculated and found to be $2 \times 10^{-4} \text{lm}^{-1} \text{s}^{-1}$ and $0.26 \text{lm}^{-1} \text{s}^{-1}$ at $25^\circ \text{C}$. (The value of $k_1$ obtained from Fig. 1 has been corrected for initial rate values which are approximately
TABLE I

Rate of monomer disappearance at different ceric and formaldehyde concentrations

\[
\frac{d [M]}{dt} = k_p \left( \frac{c}{[M]^2} \right) [M] = k_1 \left( \frac{c}{[M]} \right) [M]
\]

\[
\frac{d [CH_2O]}{dt} = 5 \times 10^{-3} \text{ m.} / \text{l.}
\]

<table>
<thead>
<tr>
<th>[Ceric] × 10^3 m./l.</th>
<th>(- \frac{d [M]}{dt} \times 10^4) m./l./s.</th>
<th>([CH_2O] \times 10^3) m./l.</th>
<th>(- \frac{d [M]}{dt} \times 10^4) m./l./s.</th>
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<td>0.5</td>
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<td>2.236</td>
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<tr>
<td>1.0</td>
<td>3.328</td>
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<td>3.0</td>
<td>2.854</td>
<td>4.0</td>
<td>3.042</td>
</tr>
<tr>
<td>4.0</td>
<td>2.787</td>
<td>8.0</td>
<td>3.163</td>
</tr>
</tbody>
</table>

* [CH_2O] = 5 × 10^{-3} m./l. ; † [Ceric] = 5 × 10^{-3} m./l.

TABLE II

Variation of chain-length with monomer and ceric concentrations

<table>
<thead>
<tr>
<th>[M] m./l.</th>
<th>Chain-length</th>
<th>[Ceric] × 10^4 m./l.</th>
<th>Chain-length</th>
</tr>
</thead>
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</tr>
<tr>
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<td>6730</td>
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<td>0.2210</td>
<td>2900</td>
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<td>4965</td>
</tr>
<tr>
<td>0.2650</td>
<td>3526</td>
<td>6.0</td>
<td>4255</td>
</tr>
<tr>
<td>0.4420</td>
<td>3701</td>
<td>8.0</td>
<td>2436</td>
</tr>
</tbody>
</table>

twice those obtained after the experimental time interval of ten minutes.) The value of \(k_p/k_t\) can be obtained from experiments conducted in the absence of formaldehyde, where \(- \frac{d [M]}{dt} = (k_1k_p/k_t) [M]^2\). This value has been found to be 1.643. The values of \(k_1\) and \(k_t\) can be substituted in the ratio
between the rate of polymerization in the presence ($R_{p_1}$) and absence ($R_{p_2}$) of formaldehyde, to get the average value of $k_2/k_1'$:

$$\frac{R_{p_1}}{R_{p_2}} = 1 + \frac{k_1 [F]}{k_1 [M] + \left(\frac{k_2}{k_1'}\right)[Ce^{4+}]}.$$

It is found that $k_2/k_1' \approx 150$, so that the value of $(k_2/k_1')[Ce^{4+}]$ is much greater than $[M]$, in equation (2), thus supporting the experimentally observed order of two for $[M]$ in the rate expression for monomer disappearance.

**SUMMARY**

The kinetics of the polymerization of methyl acrylate initiated by the ceric perchlorate-formaldehyde redox system has been investigated. The rate of monomer disappearance has been found to be proportional to (a) the square of the monomer concentration, (b) the formaldehyde concentration and (c) the reciprocal of ceric ion concentration. The rate of ceric disappearance is found to be proportional to the ceric, monomer and formaldehyde concentrations. The chain-lengths have been found to increase with the monomer concentration and decrease with the ceric ion concentration. A kinetic scheme has been proposed whereby both ceric ions and the radicals produced from oxidation of formaldehyde by ceric ions have been shown to initiate the polymerization, while the termination occurs exclusively by the interaction of the chain radicals with ceric ions. The results obtained in the presence as well as absence of the reducing agent have been compared on the basis of the above kinetic scheme.

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