

Polymerization of Vinyl Monomers in Aqueous Solution by Radicals from Photo-excited Electron Transfer Reaction in the Ion-pair $\text{Fe}^{3+}\text{OH}^-$

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A photochemical method for the preparation of pure vinyl addition polymers is suggested. Polymerization kinetics of reaction of radicals from photo-excited ion-pair, $\text{Fe}^{3+}\text{OH}^-$, with vinyl monomers in aqueous solution are discussed.

FRANCK and Haber¹ were the first to postulate the formation of OH radicals in solution when the aqueous halide and sulphite ions were irradiated. Haber and Willstätter² have indicated that OH and HO_2 radicals are the chain carriers in the catalytic decomposition of hydrogen peroxide. This was followed by a study of the system ferrous or ferric ion-hydrogen peroxide and introduction of the theory of the formation of OH and HO_2 radicals into the field of reaction kinetics in solution by Haber and Weiss^{3,4}. Baxendale, Evans and Park⁵ have shown that free radicals produced in Haber and Weiss's reaction initiate polymerization of vinyl compounds. Rabinowitch and Stockmayer⁶ interpreted the absorption spectra of ferric ion-pair complexes as electron transfer spectra, the primary photochemical process being $\text{Fe}^{3+}x^- \xrightarrow{h\nu} \text{Fe}^{2+}x$ where $x^- = \text{OH}^-$, halide, etc. Rabinowitch⁷ predicted the occurrence of free radicals or atoms in irradiated ferric salt systems. Evans and Uri⁸ showed that the free radicals produced photochemically from ferric ion-pair complexes lead to polymerization of vinyl compounds. Evans, Santappa

and Uri⁹ have reported on the polymerization of vinyl compounds in aqueous solution using $\text{Fe}^{3+}\text{OH}^-$, $\text{Fe}^{3+}\text{Cl}^-$, etc., as photo-sensitizers. Santappa¹⁰ has reported the difference in behaviour between $\text{Fe}^{3+}\text{OH}^-$ or $\text{Fe}^{3+}\text{Cl}^-$ on the one hand and $\text{Fe}^{3+}\text{N}_3^-$ on the other as photo-sensitizers in the polymerization of vinyl compounds.

This paper presents a detailed kinetic study of the system $\text{Fe}^{3+}\text{OH}^-$ vinyl monomers, leading to polymerization of vinyl monomers in aqueous solution.

Experimental procedure

Optical arrangements — A light beam from a 250 watt high pressure mercury vapour lamp (B.T.H.) was rendered parallel by a quartz condenser lens and passed through filters for isolating the mercury lines¹¹: (a) 313 m μ : 0.178 M NiSO_4 in a 5 cm. open quartz cell, Chance OX7; M/40 potassium biphthalate in 1 cm. open quartz cell; (b) 365 m μ : CuSO_4 in 1 cm. quartz cell; Chance OX1. Most of the experiments were carried out with 313 m μ filter. The light beam passed through an adjustable iris diaphragm into a thermostat and fell on the reaction cell which was mounted in the centre of a thermostat and maintained at a temperature $25^\circ \pm 0.1^\circ\text{C}$. The diameter of the reaction cell was 5 cm., its optical depth 46 mm. and capacity 75 cc. A solution of ferric perchlorate, perchloric acid and vinyl monomer formed the system $\text{Fe}^{3+}\text{OH}^-$ vinyl mono-

mer, for irradiation purposes. By adjusting the pH and ionic strength of the solution⁶, the concentration of $\text{Fe}^{3+}\text{OH}^-$ could be controlled.

Reagents — Ferric perchlorate was prepared from precipitated brown ferric oxide and perchloric acid. Monomers, acrylonitrile, methyl methacrylate, methacrylic acid were freed from stabilizers and purified by repeated distillation under reduced pressure in an atmosphere of oxygen-free nitrogen.

Before irradiation, nitrogen purified in Pieser's solution¹² was bubbled through to displace air.

Estimations — The rate of ferrous ion production ($d\text{Fe}^{2+}/dt$) was determined colorimetrically with *o*-phenanthroline. Concentrations of ferrous ion down to a minimum limit of $5 \times 10^{-7}\text{M}$ could be determined. Monomer disappearance ($-dM/dt$) was followed by the weight of polymers purified after precipitation from acetone solution and dried at 100°C . to constant weight. Chain lengths of methyl methacrylate polymers (n) were determined by measuring the viscosities of the polymers in benzene solution and with the help of the factors given in Baxendale, Bywaters and Evans's¹³ paper. Light absorption fraction (k_e) by the ion-pair $\text{Fe}^{3+}\text{OH}^-$ was calculated¹⁰ or measured spectrophotometrically, taking into account all the equilibria and species of ions present in the system. Light intensity or lamp output (I) was measured actinometrically¹¹ using uranium oxalate solution. Monomer concentration $[M]$ for methyl methacrylate was measured by adding a known amount of bromine to the monomer solution and determining the excess of bromine by iodometry.

Results

(1) k_e — It may be shown that in ferric perchlorate solutions the photochemically active species is the ion-pair complex $\text{Fe}^{3+}\text{OH}^-$. The concentration of $\text{Fe}^{3+}\text{OH}^-$ is dependent on the pH and ionic strength of the solution⁶. It is now well recognized that the purple colour of ferric perchlorate solutions or ferric nitrate solutions in both of which ferric ion does not complex with anion (ClO_4^- or NO_3^-) is due to absorption by hydrated ferric ion itself. Absorption by ferric ion moves to the far U.V. region in concentrated perchloric acid solutions and, therefore, the solution becomes colourless. But as the pH of the solution is increased

the colour of the solution varies from faint yellow to yellow and deep yellow. This variation of colour is attributed to the presence of species like $\text{Fe}^{3+}\text{OH}^-$, $\text{Fe}^{3+}(\text{OH})_2^{2-}$, $\text{Fe}^{3+}(\text{OH})_3^{3-}$, etc. By controlling the acidity and ionic strength of the solution, the concentration of any one type of complex could be increased. At pH = 0, ferric perchlorate solutions are practically colourless showing the absence of $\text{Fe}^{3+}\text{OH}^-$. From the absorption spectra of $\text{Fe}^{3+}\text{OH}^-$ as well as $\text{Fe}^{3+}(\text{aq.})$ and also from the dependence of equilibrium constant (K_H) for $\text{Fe}^{3+}\text{OH}^- \rightleftharpoons \text{Fe}^{3+} + \text{OH}^-$ upon ionic strength of the solution (μ), the concentration of $\text{Fe}^{3+}\text{OH}^-$ as well as $\text{Fe}^{3+}(\text{aq.})$ could be calculated. When the system $\text{Fe}^{3+}\text{OH}^-$ methyl methacrylate or acrylonitrile is irradiated with a light beam of 313 or 365 m μ , there is in the primary photochemical process an electron transfer from the anion to the cation giving Fe^{2+} and OH. The OH radicals polymerize the vinyl monomer. It has been found that ferric salt solutions in the range 10^{-2} to 10^{-6}M and even at 10^{-6}M give rise to active ion-pair sensitizer $\text{Fe}^{3+}\text{OH}^-$. Tables 1 and 2 indicate the concentrations as well as $d\text{Fe}^{2+}/dt$ for $\text{Fe}^{3+}\text{OH}^-$ at various pH levels.

It was interesting to note that between pH 0.86 and 0.56 there was neither polymerization nor ferrous ion production when solution was irradiated for over 12 hr. Also, at a perchloric acid concentration of $\gg 1\text{N}$ and $[\text{Fe}(\text{ClO}_4)_3]$, as high as 10^{-2}M , ferrous ion formation and polymerization were practically negligible. Under the latter conditions the concentration of the species $\text{Fe}^{3+}\text{OH}^-$

TABLE 1 — INFLUENCE OF pH ON LIGHT ABSORPTION

($[\text{Fe}^{3+}] = 10^{-3}$ and 10^{-4}M ; [acrylonitrile] = 1.0M ; intensity = 8.1×10^{-6} Nh/hr.; μ = ionic strength)

$[\text{Fe}^{3+}]$ (molar)	pH	μ	$k_H \times 10^3$ [Fe^{3+}] $\times 10^4$	$[\text{Fe}^{3+}\text{OH}^-]$ $\times 10^4$	k_e	
10^{-3}	0.0	1.070	7.50	99	1.0	0.20
	0.6	0.345	3.28	96	4.0	0.80
	1.0	0.170	3.09	92	8.0	0.90
	1.3	0.120	3.16	88	12.0	0.91

TABLE 2 — INFLUENCE OF pH AND k_e ON THE RATE OF FERROUS ION PRODUCTION

$[\text{Fe}^{3+}]$	pH	k_e	$d\text{Fe}^{2+}/dt$ (moles/hr.) $\times 10^6$
10^{-4}	2.01	0.509	1.610
10^{-4}	1.73	0.356	1.190
10^{-4}	1.50M	0.265	0.631
10^{-4}	1.35	0.194	0.560
10^{-3}	1.01	0.085	0.314
10^{-4}	{0.86 0.56}	Not measurable	

would be minimal. These data show that $\text{Fe}^{3+}\text{OH}^-$ is the photochemically active species. It has also been shown¹⁵ that the rate of monomer disappearance and the chain length (n) of the methyl methacrylate polymer are linear functions of k_6 .

(2) *Light intensity*—The results for $d\text{Fe}^{2+}/dt$ with variation of light intensity with $\text{Fe}^{3+}\text{OH}^-$ acrylonitrile monomer given in Fig. 1 and Table 3 respectively show that light intensity I is a better function of the expression

$$\left(\frac{d\text{Fe}^{2+}}{dt}\right) \left(1 + \frac{k_6[\text{Fe}^{2+}]}{k_i[\text{M}]}\right)$$

than I versus $d\text{Fe}^{2+}/dt$ alone. The significance of this is dealt with later. Further, the rate of monomer disappearance has already been shown¹⁴ to be a linear function of square root of light intensity, and the chain length of methyl methacrylate polymer a linear function of reciprocal square root of light intensity.

(3) *Variation of monomer concentration*—An accurate investigation of the dependence of $d\text{Fe}^{2+}/dt$ on monomer concentration was rather difficult because, at very low concentrations of the monomer or even in the absence of monomer, the free radicals would be consumed, it is presumed, by the organic impurities in the distilled water used. The rate of ferrous ion production, therefore, with small concentration of monomer or even in

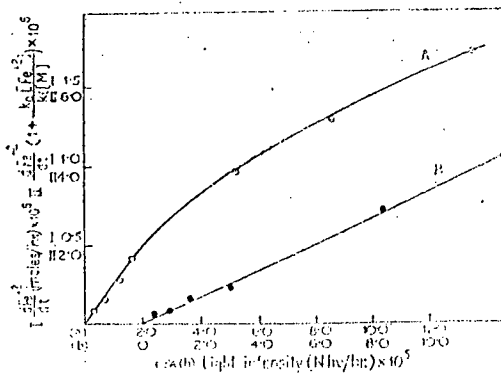


FIG. 1.—RATE OF FERROUS ION PRODUCTION WITH LIGHT INTENSITY [A—Non-linear variation of $\frac{d\text{Fe}^{2+}}{dt}$ with light intensity for the system $\text{Fe}^{3+}\text{OH}^-$, acrylonitrile; $[\text{Fe}^{3+}] = 10^{-3}\text{M}$; $\text{pH} = 1.0$. B—Linear variation of $\frac{d\text{Fe}^{2+}}{dt} \left(1 + \frac{k_6[\text{Fe}^{2+}]}{k_i[\text{M}]}\right)$ with light intensity under conditions as in A.]

TABLE 3.—RATE OF FERROUS ION PRODUCTION WITH LIGHT INTENSITY

($[\text{Fe}^{3+}] = 10^{-3}\text{M}$; $[\text{acrylonitrile}] = 1.2\text{M}$; $\text{pH} = 1.0$)

Intensity N/ohr. $\times 10^5$	$\frac{d\text{Fe}^{2+}}{dt}$ (moles/hr.) $\times 10^5$	MEAN (Fe^{2+}) molar $\times 10^3$	$\frac{d\text{Fe}^{2+}}{dt} \left(1 + \frac{k_6[\text{Fe}^{2+}]}{k_i[\text{M}]}\right)$
8.00	0.970	6.94	1.496
6.80	0.800	5.72	1.450
5.40	0.690	4.93	0.956
3.20	0.450	3.22	0.564
2.01	0.300	2.15	0.350
1.23	0.200	1.43	0.220
0.63	0.155	1.11	0.170

TABLE 4.—RATE OF FERROUS ION PRODUCTION WITH TYPE AND CONCENTRATION OF MONOMER

(For $[\text{Fe}^{3+}] = 10^{-3}\text{M}$, $I = 1.32 \times 10^{-5}$ N/ohr.; and for $[\text{Fe}^{3+}] = 10^{-2}\text{M}$, $I = 6.9 \times 10^{-5}$ N/ohr.)

$[\text{Fe}^{3+}]$ molar	Monomer	[M] molar	$\frac{d\text{Fe}^{2+}}{dt}$ (moles/hr.) $\times 10^5$
10^{-2}	Acrylonitrile	1.00	6.3
10^{-2}	do	0.60	6.5
10^{-2}	do	0.30	6.2
10^{-2}	do	0.10	6.6
10^{-2}	do	0.01	6.8
10^{-2}	Methyl methacrylate	0.10	6.5
10^{-2}	nil	nil	6.0
10^{-2}	Acrylonitrile	0.10	3.1

the absence of any monomer was as high as in the presence of higher monomer concentrations. This aspect of impurities has been dealt with in greater detail elsewhere by the author¹⁵. The experimental results (TABLE 4) obtained with $\text{Fe}^{3+}\text{OH}^-$ show that the values of $d\text{Fe}^{2+}/dt$ are practically independent of the type and concentration of the monomer. The rate of monomer disappearance with methyl methacrylate was found¹⁴ to be a linear function of first power of monomer concentration.

(4) *The effect of ferrous ion* accumulating in the course of the reaction is similar to that of sensitizer ion initially added. Because of secondary dark back reaction between Fe^{2+} and OH^- , it was observed (FIG. 2) that the rate of ferrous ion production decreased with increase in time or increase in mean ferrous ion concentration, i.e. ferrous ion initially added or present plus one-half of ferrous produced during the time interval. For the $\text{Fe}^{3+}\text{OH}^-$ sensitizer and in the presence of an initially added $[\text{Fe}^{2+}]$ as high as 10^{-4}M , the total ferrous ion produced did not exceed $1.3 \times 10^{-4}\text{M}$ and, therefore, it was possible to measure ferrous ion produced during the time interval and subsequently compute mean ferrous ion concentration. The results in Table 5 indicate how $d\text{Fe}^{2+}/dt$ decreases as

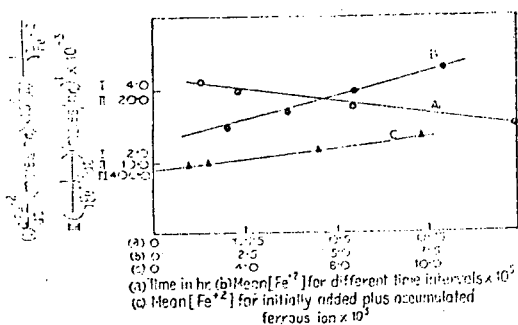


FIG. 2.—RATE OF FERROUS ION PRODUCTION WITH TIME AND MEAN FERROUS ION CONCENTRATION. A—Decrease of rate of ferrous ion production with time; $[Fe^{3+}] = 10^{-2}M$, acrylonitrile; $I = 0.77 \times 10^{-4}Nh\nu/hr.$ B—Increase of $\frac{d[Fe^{2+}]}{dt}$ with mean ferrous ion concentration computed at different intervals. C—Increase of $\frac{d[Fe^{2+}]}{dt}$ with mean ferrous ion concentration computed from initially added ferrous ion plus half ferrous ion produced during the time interval; $[Fe^{3+}] = 10^{-2}M$; $I = 1.32 \times 10^{-4}Nh\nu/hr.$; $pH = 1.3$

TABLE 5.—EFFECT OF INITIALLY ADDED FERROUS ION UPON RATE OF FERROUS ION PRODUCTION ($[Fe^{3+}OH] = 10^{-2}M$; $pH = 1.3$; intensity $= 1.32 \times 10^{-4}Nh\nu/hr.$; monomer, acrylonitrile)

Added $[Fe^{2+}]$ molar $\times 10^3$	TOTAL $[Fe^{2+}]$ MEASURED MOLES $\times 10^3$	$[Fe^{2+}]$ PRODUCED molar $\times 10^3$	MEAN $[Fe^{2+}]$ molar $\times 10^3$	$d[Fe^{2+}]/dt$ (mole./hr.) $\times 10^4$	$1/d[Fe^{2+}]/dt$ (mole./hr.) $\times 10^4$
nil	3.5	3.5	1.75	4.85	2.00
10^{-5}	3.5	3.4	1.80	4.75	2.10
10^{-4}	4.3	3.3	2.65	4.70	2.13
5×10^{-3}	8.1	3.2	6.60	4.54	2.20
10^{-2}	13.0	3.0	11.50	4.20	2.38

TABLE 6.—EFFECT OF MEAN FERROUS ION CONCENTRATION ON THE RATE OF FERROUS ION PRODUCTION ($[Fe^{3+}] = 10^{-2}M$; [acrylonitrile] = 1.2M; $pH = 1.0$)

Intensity $Nh\nu/hr. \times 10^2$	MEAN $[Fe^{2+}]$ moles $\times 10^3$	$d[Fe^{2+}]/dt$ (mole./hr.) $\times 10^4$	RECIPROCAL QUANTUM YIELD
13.20	3.50	1.75	58.82
8.20	2.70	1.35	47.17
3.20	1.94	0.97	21.10
1.85	0.80	0.40	36.62
1.25	0.70	0.35	27.86
0.55	0.50	0.25	17.18
3.00	0.28	0.14	16.72

mean $[Fe^{2+}]$ increase or $1/d[Fe^{2+}]/dt$ increases with added ferrous ions. The mean ferrous ion concentration could also be computed at various intensities and the same uniform variation between mean $[Fe^{2+}]$ and $1/d[Fe^{2+}]/dt$ is observed (TABLE 6).

(5) Quantum yields — The quantum yields with respect to ferrous ion $\gamma_{Fe^{2+}}$ have been found to be dependent on (i) concentration of $Fe^{3+}OH^-$ and, therefore, upon pH of the system and (ii) wavelength. $\gamma_{Fe^{2+}}$ was practically equal at 313 and 365 $m\mu$ though it dropped steeply when the limit of the visible was reached. $\gamma_{Fe^{2+}}$ was found to be independent of (i) the intensity of light and (ii) type and concentration of monomer. The quantum yield with regard to monomer disappearance γ_M was found to be dependent on the concentration and type of the monomer used. A maximum value of ≈ 300 for γ_M for high light intensity and concentration of the monomer and a minimum value ≈ 5 to 10 for low light intensity were observed. The lower values of γ_M for higher intensities of the order of 1.3 to $1.5 \times 10^{-4}Nh\nu/hr.$, $[Fe^{3+}] = 10^{-2}$ to 10^{-3} and for $[M] = 1.0$ to 0.10 were occasionally observed. This must be attributed to the scattering of light by the polymer. The ideal conditions for minimizing the scattering of light were found for a light intensity 6 to $8 \times 10^{-5}Nh\nu/hr.$ and for a $[Fe^{3+}] = 4 \times 10^{-5}M$ concentration were determined. The quantum yields for ferrous ion at various pH levels, ferric ion concentrations and light intensities are given in TABLE 7.

Discussion

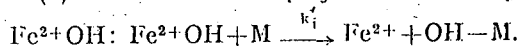
The light absorption process is connected with the change $Fe^{3+}OH^- \rightleftharpoons Fe^{2+}OH$. The energetics of the system and the mechanism of how $Fe^{2+}OH$ dissociates into Fe^{2+} and OH because of non-equilibrium configuration of hydrated $Fe^{2+}OH$ have already been discussed^{9,10}. The resulting OH free radicals initiate polymerization. The experimental results have been examined in the light of the following reaction mechanism to arrive at the actual mechanism of polymerization.

TABLE 7.—QUANTUM YIELDS FOR FERROUS ION AND MONOMER DISAPPEARANCE

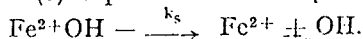
pH	$\gamma_{Fe^{2+}}$ at Fe^{3+}			γ_M	
	$10^{-2}M$	$10^{-3}M$	$10^{-4}M$	At intensity $8.1 \times 10^2 Nh\nu/hr.$	At intensity $1.32 \times 10^4 Nh\nu/hr.$
2.00	0.080	—	0.040	0.06	0.06
1.70	0.055-0.06	—	0.016	—	—
1.50	0.050	—	0.022	0.05	0.05
1.30	0.050	—	0.022	—	—
1.00	0.050	0.050	0.030	0.03	0.03
0.83	0.050	0.012	0.005	—	—
0.54	0.039	—	—	—	0.04
0.34	0.017	—	—	0.03	—

(1) Light absorption process and primary dark back reaction: $\text{Fe}^{3+} + \text{OH}^- \xrightleftharpoons[k_d]{h\nu} \text{Fe}^{2+} + \text{OH}^-$.

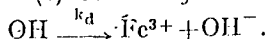
(2) Initiation of polymerization by



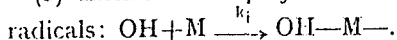
(3) Separation of the primary product:



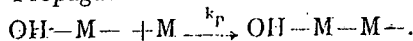
(4) Secondary dark back reaction: $\text{Fe}^{2+} +$



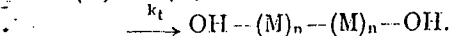
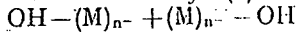
(5) Initiation of polymerization by OH



(6) Propagation:



(7) Termination by (a) recombination:



or (b) disproportionation by the radicals $\text{Fe}^{2+} + \text{OH}^-$ or OH^- represented by the rate constants k_{t1} and k_{t2} respectively.

In the above scheme, the concentrations of the radicals OH^- , $\text{Fe}^{2+} + \text{OH}^-$ or $\text{OH}^- + (\text{M})_n \cdot$ are assumed to be constant and stationary.

(i) If $\text{Fe}^{2+} + \text{OH}^-$ radicals alone initiate polymerization and the radical chains terminate by disproportionation, then it is easy to show that

$$\frac{d\text{Fe}^{2+}}{dt} = k_e I k_i [\text{M}] / k_d$$

$$\text{and } \frac{d\text{M}}{dt} = k_p k_i [\text{M}]^2 / k_{t1}$$

(ii) If $\text{Fe}^{2+} + \text{OH}^-$ radicals initiate polymerization and termination is brought about by recombination of the radical chains, then

$d\text{Fe}^{2+}/dt$ will be same as in (i);

$$\text{but } \frac{d\text{M}}{dt} = k_p [\text{M}]^{3/2} (k_i k_e I / k_t k_d)^{1/2}$$

(iii) On the other hand, if OH radicals alone initiate polymerization and the radical chains terminate by disproportionation, then

$$(a) \frac{d\text{Fe}^{2+}}{dt} = \frac{k_s k_e I}{k_d + k_s} \left(\frac{k_i [\text{M}]}{k_i [\text{M}] + k_o [\text{Fe}^{2+}]} \right)$$

and (b) $d\text{M}/dt = k_p k_i [\text{M}]^2 / k_{t2}$.

(iv) If OH radicals initiate the polymerization and termination of radical chains is by recombination of the radical chains, then

$d\text{Fe}^{2+}/dt$ will be same as in (iii);

$$\text{but } \frac{d\text{M}}{dt} = k_p [\text{M}] \left\{ \frac{k_s k_e I}{k_i (k_s + k_d)} \right\}$$

(v) If both $\text{Fe}^{2+} + \text{OH}^-$ and OH radicals initiate polymerization and termination of the radical chains is by disproportionation as well as by recombination, then

$$\frac{d\text{Fe}^{2+}}{dt} = \frac{k_s k_e I}{k_d + k_s + k_i [\text{M}]} \times \left\{ \frac{k_i [\text{M}]}{k_s} + \frac{k_i [\text{M}]}{k_i [\text{M}] + k_o [\text{Fe}^{2+}]} \right\}$$

and for $d\text{M}/dt$ expressions involving $[\text{M}]^2$ will be obtained for both types of terminations.

If polymerization is to be initiated by $\text{Fe}^{2+} + \text{OH}^-$ radicals then according to (i) the quantum yield with regard to ferrous ion production must go on increasing as the monomer concentration is increased and not reach a constant value below unity. On the other hand, if OH radicals initiate, then according to (iii), production of ferrous ions must increase with monomer concentration and at high concentrations, i.e. when $k_i [\text{M}] \gg k_o [\text{Fe}^{2+}]$ the quantum yield will be represented by $k_s / (k_s + k_d)$ which is a constant and which is also independent of monomer concentration. When $\text{Fe}^{2+} + \text{OH}^-$ as well as OH radicals are assumed as initiators, then according to (v) the quantum yield cannot be represented by any constant quantity.

According to the experimental results presented in this paper, the quantum yield for ferrous ion attained a constant value of 0.05 (TABLE 7) both at lower as well as higher monomer concentrations and sometimes even in the absence of the monomer. This must be attributed to the reactions of free radicals with the organic impurities in the reaction system. Further, a plot of reciprocal ferrous ion production against mean ferrous ion (FIG. 2, graph C) gives the expected linearity. The slope of this graph gave $k_o/k_i = 4 \times 10^3$ for acrylonitrile and the intercept confirmed the quantum yield for ferrous ion to be ≈ 0.05 . The non-linearity of ferrous ion production with light intensity is attributed to the dark back reaction $\text{Fe}^{2+} + \text{OH}^- \xrightarrow{k_o} \text{Fe}^{3+} + \text{OH}^-$. If this dark back reaction is considerable, the actual rate of ferrous ion production is then

given by $(d\text{Fe}^{2+}/dt) \left(1 + \frac{k_o [\text{Fe}^{2+}]}{k_i [\text{M}]} \right)$ and a

plot of the latter quantity against light intensity must be linear. This has been found to be the case (FIG. 1).

It is also found that $d[\text{Fe}^{2+}]/dt$ is a linear function of k_e as well as $p\text{H}$. These facts point to OH radicals being the initiators and, therefore, the correct expression for ferrous production would be represented by (iii).

In case of termination of the polymer chain by disproportionation by either Fe^{2+}OH or OH radicals, the rate of monomer disappearance will be proportional to square of monomer concentration $[\text{M}]^2$. If Fe^{2+}OH is the initiator and the chains are terminated by recombination, then $d\text{M}/dt$ must vary linearly with $[\text{M}]$. On the other hand, if OH radicals initiate the reaction, then $d\text{M}/dt$ must vary with $[\text{M}]$ for termination by recombination. It has been found that $d\text{M}/dt$ varies linearly with $[\text{M}]$ proving thereby that the termination reaction is one of mutual recombination of active particles. Further details in support of the termination reaction for the sensitizer $\text{Fe}^{3+}\text{Cl}^-$ whose behaviour is similar to that of $\text{Fe}^{3+}\text{OH}^-$ are given elsewhere¹¹.

Summary

A method for photochemical initiation of polymerization of vinyl monomers in aqueous solution making use of the ion-pair complex $\text{Fe}^{3+}\text{OH}^-$ is described. The light absorption process by the ion-pair leads to an electron transfer causing the reduction of the cation and oxidation of OH^- to a free radical OH which initiates polymerization. Kinetics of the reaction between OH and vinyl monomer were studied from (a) the dependence of a rate of ferrous production; (b) overall rate of polymerization; and (c) chain length of polymethyl methacrylate (viscometric me-

thod) upon (i) light absorbed by the ion-pair; (ii) intensity of light; (iii) monomer concentration and (iv) accumulated or initially added ferrous ion. From the results obtained it is shown that polymerization reaction is initiated by OH radicals and termination of polymerization is by mutual recombination of the active radical chains.

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