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Photopolymerization of Acrylonitrile by Potassium Trisoxalatocobaltate(III) in Aqueous Perchloric Acid

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ABSTRACT

Results of a kinetic study on photopolymerization of acrylonitrile by potassium trisoxalatocobaltate(III) in aqueous perchloric acid medium (pH = 1) by use of light of 365 nm wavelength at 30 ± 0.1°C are presented. All reactions were carried out under completely deaerated conditions. Certain important features of the photopolymerization are described. The rate of polymerization R_p was followed by gravimetric estimation of polymer formed and rate of disappearance of complex $-R_c$ by spectrocolorometric estimation of complex disappearing. R_p was found to be directly proportional to $[M]^{3/2}$, $k_\epsilon^{1/2}$, and $I^{1/2}$, where $[M]$, k_ϵ, and I refer to concentration of acrylonitrile, light absorption fraction of the complex, and light intensity, respectively. $-R_c$ was found to be directly proportional to k_ϵ and I. A reaction scheme is drawn and kinetic expressions derived on the basis of that scheme are given.

INTRODUCTION

Photodecomposition of potassium trisoxalatocobaltate(III) has been widely studied by a number of investigators [1-12]. The absorption spectrum of $Co(Ox)_3^{3-}$, (where Ox = $C_2O_4^{2-}$) consists of three bands with maxima lying at 254, 420, and 596 nm [13]. The UV band is strong, while the other two bands in the visible region are weak. The UV band is due to charge transfer and the visible bands are due to ligand field transitions [14]. From the study of photolysis of the complex it has been inferred that even when the irradiation is performed in the ligand field bands the primary photochemical act involves a charge transfer from oxalato ligand to cobalt central ion. Appreciable quantum yield of 0.25 was reported by Porter et al. [9] for this complex in acetate buffer at 365 nm, corresponding to the ligand field region of its spectrum.

Potassium trisoxalatocobaltate (III) was used as initiator in the thermal polymerization of methyl methacrylate monomer at 45-70°C by Biswas and Mukherjee [15]. Ghosh et al. [16] used this complex for photoinitiation of methyl methacrylate polymerization in aqueous medium and reported the results of endgroup analysis of the resultant polymers by the dye partition technique. In these two papers it was suggested that the initiating species, namely $C_2O_4^{\cdot -}$, $CO_2^{\cdot -}$ or $\cdot OH$ would be obtained by the thermal or photochemical degradation of $Co(Ox)_3^{3-}$. $Co(Ox)_3^{3-}$ has also been employed by Takemura et al. [17] as sensitizer for photopolymerization of acrylamide at wavelengths of 420 and 600 nm; the rate of photopolymerization of acrylamide was found to be proportional to the square root of light intensity. However, no detailed kinetic study is available in the literature on the photopolymerization of acrylonitrile by $Co(Ox)_3^{3-}$. The present paper reports the results of a kinetic study of photopolymerization of acrylonitrile by potassium trisoxalatocobaltate(III) in aqueous perchloric acid (pH = 1) by use of light of wavelength 365 nm from a high-pressure mercury-vapor lamp at 30 ± 0.1°C.

EXPERIMENTAL

Materials

Acrylonitrile (American Cyanamid Co.) was freed from inhibitor by washing with 5% alkali followed by 10% orthophosphoric acid, washed well with water, dried over anhydrous calcium chloride, and distilled under reduced pressure. The middle fraction was stored at 5°C.

Potassium trisoxalatocobaltate(III) was prepared by the standard procedure [18] and its purity ascertained by comparison of the spectrum with that reported by Copestake and Uri [7]. All other chemicals were either B. D. H, A R, or E. Merck grade.

Estimations

Concentrations of acrylonitrile monomer [M], concentration of the complex [C], pH, and light intensity I were varied in the following ranges: [M], 0.3-0.9 mole/liter; [C], 5×10^{-4}-1×10^{-2} mole/liter; pH, 0.4-1.3; I, 0.9×10^{-8}-2.7×10^{-8} Nhν/liter-sec. The kinetics of the reaction was followed by determining the rate of monomer (acrylonitrile) disappearance, -d[M]/dt by gravimetry and the rate of complex disappearance $-R_c$ spectrocolorimetrically. After reaction the precipitated polymers were filtered, washed, and dried at 60°C in air oven for about 10 hr. From the weight of the dried polymers R_p was calculated. The rate of monomer disappearance -d[M]/dt was assumed to be equal to the rate of polymerization R_p. The rate of complex disappearance $-R_c$ was determined by measuring optical densities of reaction solution at 420 nm before and after irradiation. Change in concentration of complex was obtained from a Beer's law curve constructed at 420 nm for potassium trisoxalatocobaltate (III).

Light intensities were measured by the potassium ferrioxalate actinometry [19].

RESULTS AND DISCUSSION

Features of the Photopolymerization

The photopolymerization of acrylonitrile photoinitiated by potassium trisoxalatocobaltate(III) in aqueous perchloric acid medium at 365 nm should be free radical in nature because long induction periods were noticed in the presence of dissolved atmospheric oxygen. Hence all our experiments were conducted by flushing the reaction solution consisting of $Co(Ox)_3^{3-}$ and acrylonitrile in aqueous perchloric acid with pure, dry nitrogen gas.

Polymerization occurred immediately when the reaction mixture was deaerated and irradiated with light of 365 nm wavelength. Polymerization also took place in presence of sunlight.

No thermal polymerization was noticed up to 40°C for a period of over 12 hr with the deaerated reaction solution.

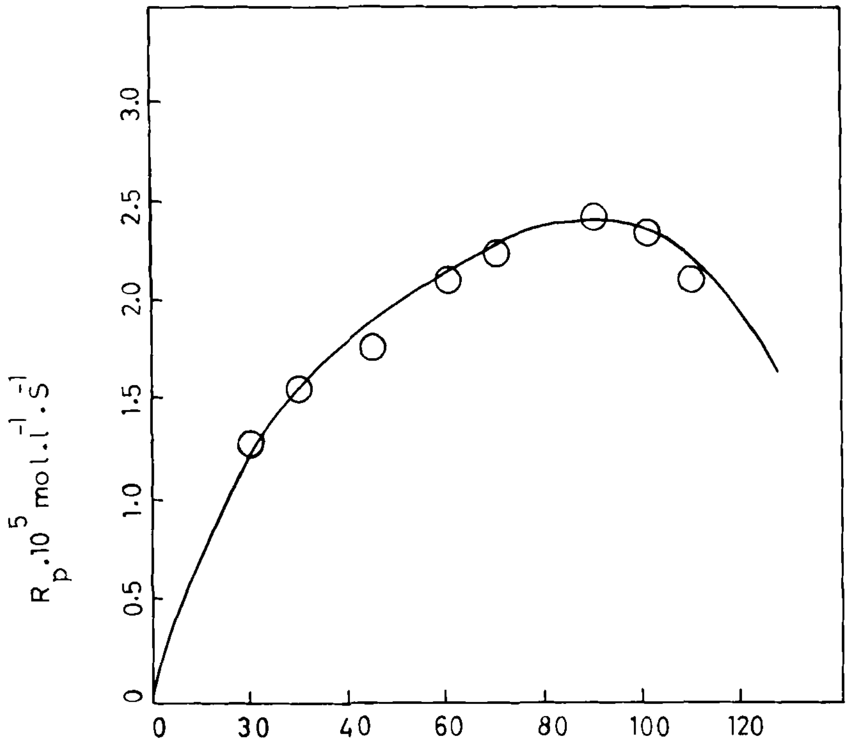


FIG. 1. Plot of $R_p \times 10^5$ vs time (in minutes) for photopolymerization of acrylonitrile in aqueous perchloric acid medium with the use of light of 365 nm wavelength. Initiator: Potassium trisoxalatocobaltate (III).

An aliquot of irradiated solution of the complex in concentrated hydrochloric acid showed an absorption at 690 nm which is characteristic of Co(II) ion. Hence photoredox decomposition of the complex can be inferred.

Kinetic Orders

The steady state for the reaction was reached in about 75 min (Fig. 1). The light absorption fraction of the complex k_ϵ is proportional to [C] in the concentration range employed by us. The rate of

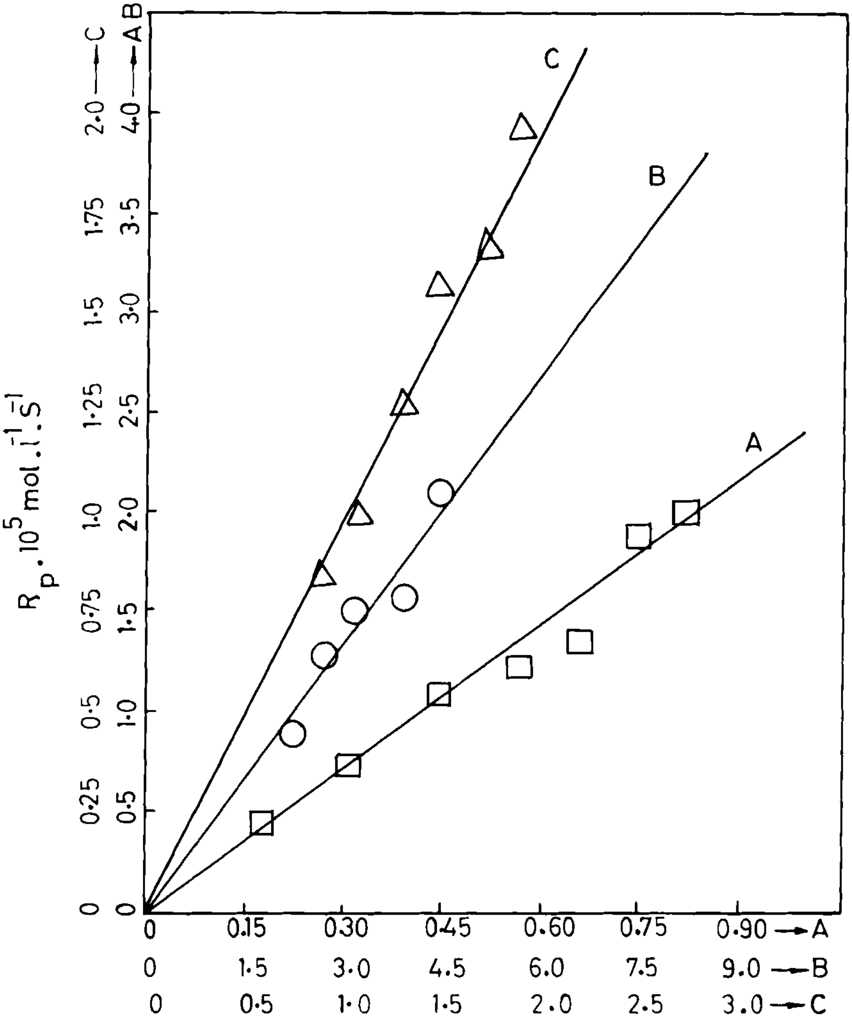


FIG. 2. Photopolymerization of acrylonitrile in aqueous perchloric acid medium with the use of light of 365 nm wavelength and potassium trisoxalatocobaltate (III) initiator: (A) plot of $R_p \times 10^5$ vs. $[M]^{3/2}$ (mole/liter-sec)$^{3/2}$ at constant $[C] = 2 \times 10^{-3}$ mole/liter, $I = 2.652 \times 10^{-8}$ Nhν/liter-sec and $[HClO_4] = 0.1$ mole/liter; (B) plot of $R_p \times 10^5$ vs. $[C]^{1/2} \times 10^2$ (mole/liter-sec)$^{1/2}$ at constant $[M] = 0.9122$ mole/liter, $I = 2.652 \times 10^{-8}$ Nhν/liter-sec, and $[HClO_4] = 0.1$ mole/liter; (C) plot of $R_p \times 10^5$ vs. $I^{1/2} \times 10^4$ (Nhν/liter-sec)$^{1/2}$ at constant $[M] = 0.9122$ mole/liter, $[C] = 4 \times 10^{-3}$ mole/liter, and $[HClO_4] = 0.1$ mole/liter.

polymerization R_p was found to be proportional to $[M]^{3/2}$ (Fig. 2A) under constant $[C] = 2 \times 10^{-3}$ mole/liter and light intensity $I = 2.65 \times 10^{-8}$ Nhν/liter-sec. R_p was proportional to $[C]^{1/2}$ in the concentration range 5×10^{-4} to 1×10^{-2} mole/liter under constant $[M] = 0.6081$ mole/liter and $I = 2.65 \times 10^{-8}$ Nhν/liter sec (Fig. 2B). R_p also depended on the square root of light intensity, I under constant $[M] = 0.9122$ mole/liter and $[C] = 4 \times 10^{-3}$ mole/liter (Fig. 2C). The rate of complex disappearance, $-R_c$, was directly proportional to the first powers of complex concentration (Fig. 3A) and light intensity (Fig. 3B).

Reaction Scheme

The following reaction scheme may explain our experimental results.

Light absorption and excitation of the complex:

$$[\mathrm{Co(III)}(C_2O_4^{2-})_3]^{3-} \xrightarrow[k_\epsilon,\, I]{h\nu} [\mathrm{Co(II)}(C_2O_4^{2-})_2(C_2O_4^{-})^*]^{3-} \tag{1}$$

$[\mathrm{Co(II)}(C_2O_4^{2-})_2(C_2O_4^{-})^*]^{3-}$ is the excited complex formed through light absorption.

Dark back reaction:

$$[\mathrm{Co(II)}(C_2O_4^{2-})_2(C_2O_4^{-})^*]^{3-} \xrightarrow{k_d} [\mathrm{Co(III)}(C_2O_4^{2-})_3]^{3-} + \Delta \tag{2}$$

This is the reverse of step (1) denoting dark back reaction of the excited complex leading to original ground-state complex with liberation of heat energy.

Redox decomposition:

$$[\mathrm{Co(II)}(C_2O_4^{2-})_2(C_2O_4^{-})^*]^{3-} \xrightarrow{k_r} [\mathrm{Co(II)}(C_2O_4^{2-})_2]^{2-} + C_2O_4^{-} \tag{3}$$

The excited complex decomposes yielding initiating radical anion, $C_2O_4^{-}$.

Radical scavenging by the complex:

$$C_2O_4^{-} + [\mathrm{Co(III)}(C_2O_4^{2-})_3]^{3-} \xrightarrow{k_1} [\mathrm{Co(II)}(C_2O_4^{2-})_2]^{2-} + C_2O_4^{2-} + 2CO_2 \tag{4}$$

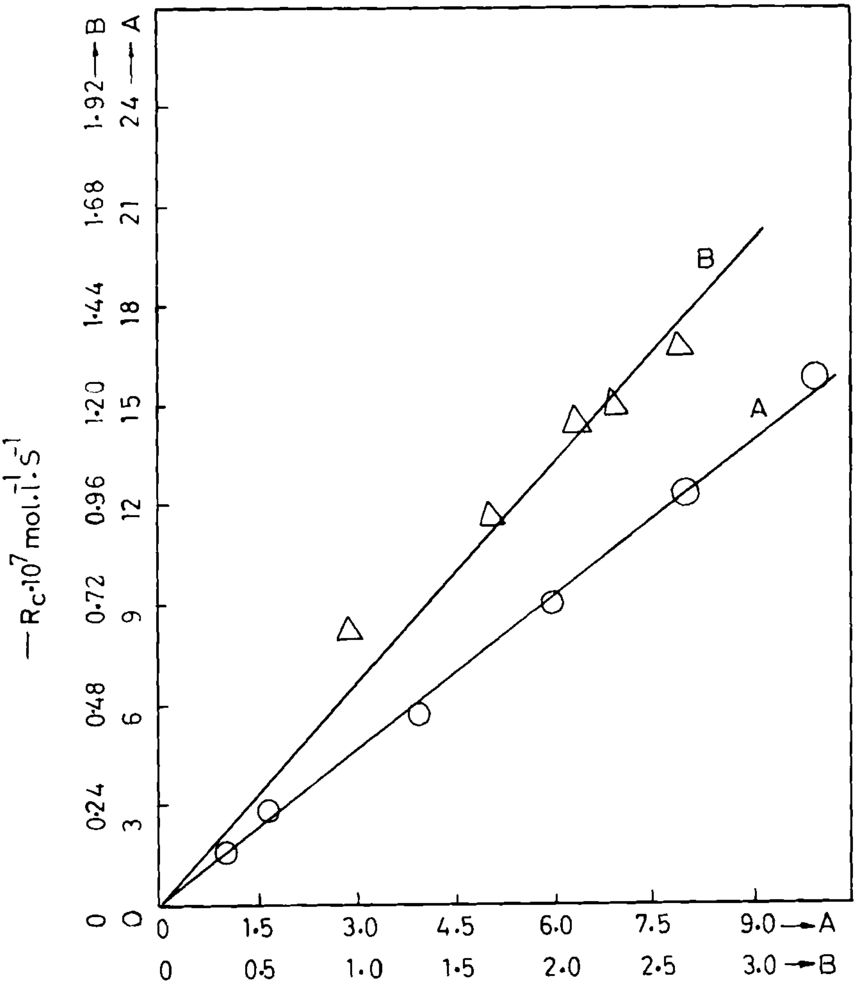


FIG. 3. Photopolymerization of acrylonitrile in aqueous perchloric acid medium with the use of light of 365 nm wavelength and potassium trisoxalatocobaltate (III) initiator: (A) plot of $-R_c \times 10^7$ vs. $[C] \times 10^3$ (mole/liter) at constant $[M] = 0.6081$ mole/liter, $I = 2.652 \times 10^{-8}$ Nhν/liter-sec, and $[HClO_4] = 0.1$ mole/liter, (B) plot of $-R_c \times 10^7$ vs. $I \times 10^8$ Nhν/liter-sec at constant $[M] = 0.9122$ mole/liter, $[C] = 4 \times 10^{-3}$ mole/liter, and $[HClO_4] = 0.1$ mole/liter.

$C_2O_4^-$ radical anions partly interact with the ground state complex itself and are said to be scavenged by the complex.

Initiation:

$$C_2O_4^- + M \xrightarrow{k_i} M\cdot \tag{5}$$

$C_2O_4^-$ radical anions also initiate the polymerization reaction.

Propagation:

$$\begin{array}{l} M\cdot + M \xrightarrow{k_p} M_2\cdot \\ M_2\cdot + M \xrightarrow{k_p} M_3\cdot \\ \vdots \qquad\qquad\quad \vdots \\ M_{n-1}\cdot + M \xrightarrow{k_p} M_n\cdot \end{array} \tag{6}$$

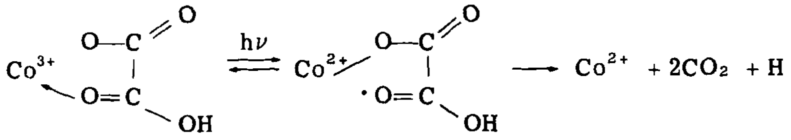
Various stages of the propagation reaction are shown in step (6).

Termination:

$$M_n\cdot + M_m\cdot \xrightarrow{k_t} M_{n+m} \text{ or } M_n + M_m \tag{7}$$

This is mutual type of termination between growing polymer chain radicals.

The radical scavenging step [20, 21] is included in order to explain the dependence of R_p on $[M]^{3/2}$. R_p also depends on square roots of $[C]$ (or k_ϵ) and I which lends support to the occurrence of mutual type of termination. From the fact that $-R_c$ is directly proportional to the first powers of both $[C]$ (or k_ϵ) and I, we can infer that the primary light absorbing species is the complex. The pH of aqueous perchloric acid medium was varied, and the rates R_p and $-R_c$ were found to increase with increasing hydrogen ion concentration (Fig. 4A). This observation may be explained by considering protonation of one of the oxalato ligands in Co $(Ox)_3^{3-}$ followed by the reaction producing hydrogen atoms in acidic solutions [22].



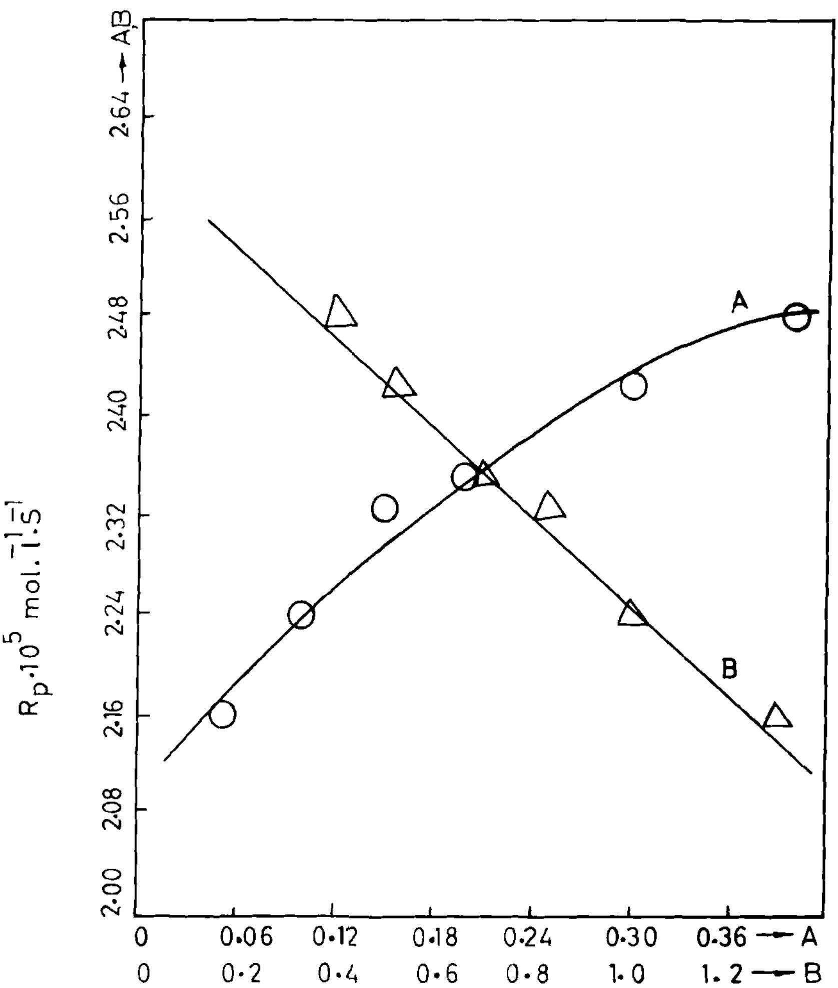


FIG. 4. Photopolymerization of acrylonitrile in aqueous perchloric acid medium with the use of light of 365 nm wavelength and potassium trisoxalatocobaltate (III) initiator: (A) plot of $R_p \times 10^5$ vs. $[H^+]$ (mole/liter); (B) plot of $R_p \times 10^5$ vs. pH at constant $[M] = 0.6081$ mole/liter, $[C] = 2 \times 10^{-3}$ mole/liter, $I = 2.652 \times 10^{-8}$ Nhν/liter-sec.

The hydrogen atoms then account for the additional amount of polymerization which increases as the pH of the solution decreases (Fig. 4B).

Steady-state kinetic treatment of the above mentioned reaction scheme gives the kinetic expressions (8) and (9).

$$R_p = -d[M]/dt$$

$$= \frac{k_p}{k_t^{1/2}} \left[\left(\frac{k_r}{k_r + k_d}\right) \frac{k_i k_\epsilon I}{(k_1[C] + k_i[M])} \right]^{1/2} [M]^{3/2} \qquad (8)$$

$$-R_c = \left(\frac{k_r}{k_r + k_d}\right) \left[\frac{2k_1[C] + k_i[M]}{k_1[C] + k_i[M]} \right] k_\epsilon I \qquad (9)$$

Our studies on photopolymerization of acrylonitrile by $Co(Ox)_3^{3-}$ complex provides further evidence for the occurrence of photoredox reactions in this complex and production of significant concentrations of $C_2O_4^-$ radical anions.

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