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G. Muralidharan[a]; Q. Anwaruddin[a]; L. V. Natarajan[ab]
[a] Department of Chemistry, New College, Madras, India [b] Department of Chemistry, Amherst College, Amherst, Massachusetts

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Tris-o-phenanthrolineiron(III) Complex as a Photoinitiator of Acrylamide Polymerization

G. MURALIDHARAN, Q. ANWARUDDIN, and L. V. NATARAJAN*

Department of Chemistry
New College
Madras 60014, India

ABSTRACT

The blue Tris-o-phenanthrolineiron(III) complex, $Fe(phen)_3^{3+}$, formed in aqueous solution by oxidation of the red ferrous phenanthroline complex by nitric acid, is found to be a good photoinitiator of acrylamide (A.AM) polymerization. Systematic study of the kinetics of polymerization of acrylamide by $Fe(phen)_3^{3+}$ in aqueous nitric acid solution in the presence of light of λ = 365 nm at room temperature showed that the rate of polymerization R_p was dependent on $[A.AM]^{1.5}$, $[C]^{0.5}$, $I^{0.5}$, and [HCOOH], and the rate of $Fe(phen)_3^{3+}$ disappearance, $-R_c$, was found to be proportional to [A.AM], [C], I, and [HCOOH], where [A.AM], [C] and [HCOOH] refer to the concentrations of acrylamide, $Fe(phen)_3^{3+}$, and formic acid, respectively, and I refers to light intensity. The kinetic observations are consistent with the interaction of the excited $Fe(phen)_3^{3+}$ with acrylamide molecule to produce a radical R. capable of initiation and also reduction of $Fe(phen)_3^{3+}$, to the stable $Fe(phen)_3^{2+}$. The results of the present study differ from those reported for photoinitiation by ion pairs of the type $Fe^{3+}X^{n-}$ where X = Cl^-, Br^-, $C_2O_4^{2-}$,

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*Present address: Department of Chemistry, Amherst College, Amherst, Massachusetts 01002.

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OH^-, etc., which may be attributed to differences in the photobehavior of the two systems.

INTRODUCTION

Ion pairs of the type $Fe^{3+}X^{n-}$, where X = Cl^-, Br^-, $C_2O_4^{2-}$, etc., are well-known photoinitiators of vinyl polymerization [1-4]. In these labile ion pairs light absorption leads to charge transfer from the anion X^{n-} to Fe^{3+} followed by dissociation to Fe^{2+} and X capable of initiating polymerization. The photochemistry of the nonlabile Tris-o-phenanthrolineiron(III) complex, $Fe(phen)_3^{3+}$, was studied in detail by Baxendale and Bridge [5]. The blue ferric complex is formed in solution by careful oxidation of the red $Fe(phen)_3^{2+}$. $Fe(phen)^{3+}$ is unstable and converts to the ferrous complex in a few hours even in the dark [5-7]. The photobehavior of $Fe(phen)_3^{3+}$ is different from $Fe^{3+}X^{n-}$ ion pairs. Whereas electron transfer from X^{n-} to Fe^{3+} followed by dissociation with high quantum yields occurred in light, no such electron transfer took place from the ligand and no separation of the ligand radical was observed in $Fe(phen)_3^{3+}$. The absence of photodissociation is consistent with the reaction of the excited complex with a ground state $Fe(phen)_3^{3+}$ leading to $Fe(phen)_3^{2+}$ and probable oxidation of the phenanthroline ligand to give ultimate hydroxylation without dissociating from the complex. The quantum yields of photoreduction were low but increased with an increase in $Fe(phen)_3^{3+}$ concentration, an increase of pH, a decrease of the wavelength of the incident light, and also with the addition of oxidizable substrates such as formic acid.

With knowledge of the differences in photochemistry between the ion pairs $Fe^{3+}X^{n-}$ and $Fe(phen)_3^{3+}$, it would be interesting to explore the photoinitiation by $Fe(phen)_3^{3+}$ and compare it with that known for $Fe^{3+}X^{n-}$. In this paper we report the results of photopolymerization of acrylamide in aqueous nitric acid solution by $Fe(phen)_3^{3+}$ by irradiation with light of λ = 365 nm.

EXPERIMENTAL

Materials

Acrylamide (Sarabhai, E. Merck grade) was recrystallized from chloroform. Potassium ferrioxalate for actinometry was prepared by the procedure given by Parker and Hatchard [8]. $Fe(phen)_3^{3+}$ was prepared by oxidizing the red $Fe(phen)_3^{2+}$ of known concentrations by

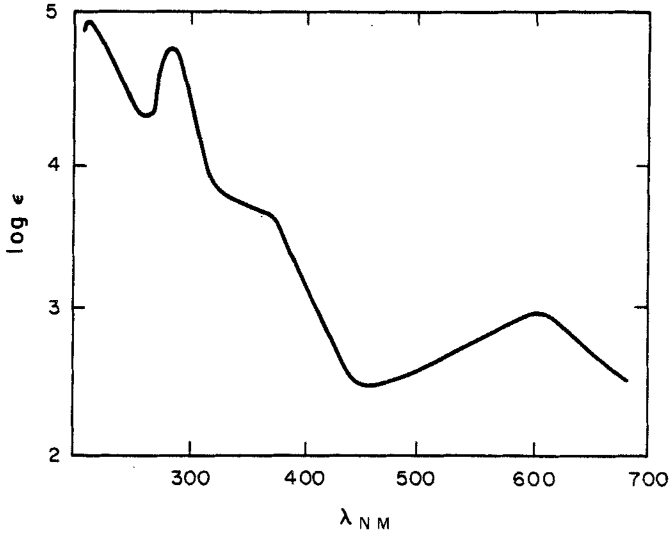

FIG. 1. Absorption spectrum of Tris-o-phenanthrolineiron(III) complex in aqueous solution.

suitable additions of concentrated nitric acid. Increasing the pH decreased the stability of the complex. The complex solutions were freshly prepared before each experiment because the solutions are not stable for more than a few hours. All other chemicals were either BDH (A.R.) or E. Merck grade.

Estimations

The rate of polymerization R_p was equal to the rate of monomer disappearance and was followed by pipetting out aliquots of the reaction solution before and after irradiation and estimating the monomer concentration by the usual bromometry. The rate of complex disappearance $-R_c$ was calculated by measuring the optical densities of the reaction solution before and after irradiation at a peak of 600 nm (Fig. 1). Changes in the concentration of the complex were deduced from the Beer's law curve at 600 nm. Light intensities were measured by potassium ferrioxalate actinometry [8]. The irradiation source was a medium pressure 125 W, 365 nm (Phillips, Holland) lamp. All experiments were conducted at 25°C.

RESULTS AND DISCUSSION

Features of the Photopolymerization

The blue $\mathrm{Fe(phen)_3}^{3+}$ complex is characterized by a high intensity UV absorption band at 270 nm, a moderate intensity band at 350 nm, and a weak absorption at 600 nm (Fig. 1). Irradiation of $\mathrm{Fe(phen)_3}^{3+}$ at 365 nm produced $\mathrm{Fe(phen)_3}^{2+}$. In the presence of acrylamide, polymerization took place without an induction period in deaerated solution. No thermal polymerization was detected in the dark. The steady state was reached in about 60 min with 20% conversion of the monomer. The red $\mathrm{Fe(phen)_3}^{2+}$ complex was stable photochemically and did not initiate polymerization.

Kinetic Orders

The rate of polymerization R_p was proportional to $[\mathrm{A.AM}]^{1.5}$, $[\mathrm{Fe(phen)_3}^{3+})]^{0.5}$, $I^{0.5}$, and [HCOOH] (Fig. 2). The rate of complex

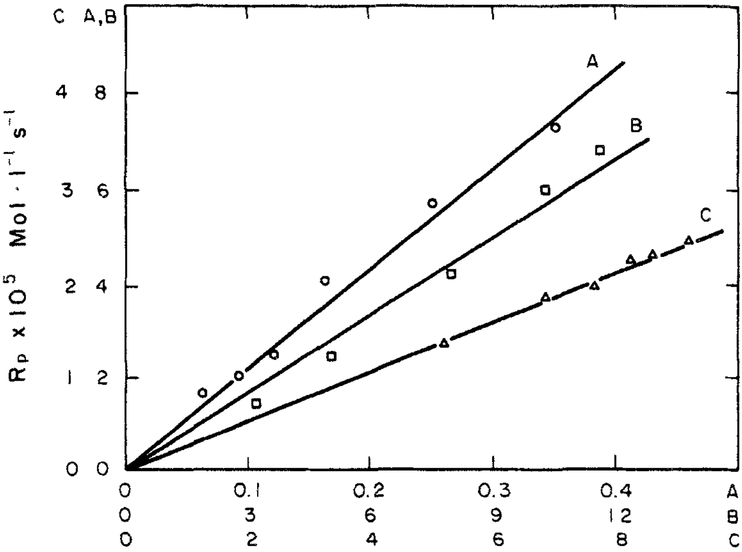

FIG. 2. Photopolymerization of acrylamide in aqueous solution by Tris-o-phenanthrolineiron(III) complex as initiator. (A): Plot of R_p vs $[\mathrm{A.AM}]^{1.5}$ $(\mathrm{mol/L})^{1.5}$. (B): Plot of R_p vs [formic acid] × 10^3 (mol/L). (C): Plot of R_p vs $I^{0.5} \times 10^5$ $(Nh\nu/L{\cdot}s)^{0.5}$.

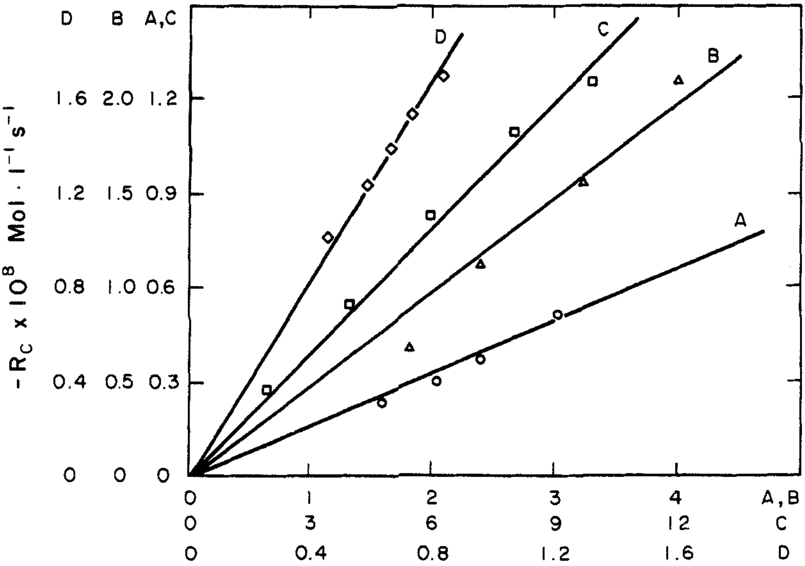

FIG. 3. Photopolymerization of acrylamide in aqueous solution by Tris-o-phenanthrolineiron(III) complex as initiator. (A): Plot of $-R_c$ vs [A.AM] × 10^1 (mol/L). (B): Plot of $-R_c$ vs [$Fe(phen)_3^{3+}$] × 10^4 (mol/L). (C): Plot of $-R_c$ vs [formic acid] × 10^3 (mol/L). (D): Plot of $-R_c$ vs light intensity I × 10^8 (Nhν/L·s).

$Fe(phen)_3^{3+}$ disappearance $-R_c$ was directly dependent on [A.AM], $[Fe(phen)_3^{3+})]^3$, I, and [HCOOH] where [A.AM], [$Fe(phen)_3^{3+}$], and [HCOOH] denote the concentrations of the monomer, complex, and formic acid, respectively, and I refers to the light intensity (Fig. 3).

Reaction Scheme

The following reaction scheme may explain our experimental results.

(a) Light absorption and excitation of the complex:

$$Fe(phen)_3^{3+} \underset{k_d}{\overset{h\nu,\ k_\epsilon I}{\rightleftharpoons}} (Fe(phen)_3^{3+})^* \tag{1}$$

k_d refers to the radiationless deactivation to the ground state. k_ϵ is the light absorption fraction of the complex, and is assumed to be proportional to the complex concentration in the range of concentration studied by us. The very low quantum yields observed for photoreduction implies the predominance of the deactivation process.

(b) Redox reaction. Abstraction of an electron from the π bond of acrylamide by the excited complex to give radical R:

$$(\mathrm{Fe(phen)_3}^{3+})^* + \mathrm{CH_2{=}CH{-}CONH_2} \xrightarrow{k_r} (\mathrm{Fe(phen)_3}^{2+}) + \mathrm{R} \qquad (2)$$

Reaction of the excited complex with a ground state complex ion:

$$(\mathrm{Fe(phen)_3}^{3+})^* + \mathrm{Fe(phen)_3}^{3+} \xrightarrow{k_c} \mathrm{Fe(phen)_3}^{2+} + \text{products} \qquad (3)$$

Radical scavenging by the ground state complex ion:

$$\mathrm{Fe(phen)_3}^{3+} + \mathrm{R}^{\cdot} \xrightarrow{k_s} (\mathrm{Fe(phen)_3}^{2+}) + \text{products} \qquad (4)$$

(c) Initiation of polymerization:

$$\mathrm{R}^{\cdot} + \mathrm{M} \xrightarrow{k_i} \mathrm{M}^{\cdot} \qquad (5)$$

(d) Propagation.

$$\mathrm{M}^{\cdot} + \mathrm{M} \xrightarrow{k_p} \mathrm{M_2}^{\cdot} \qquad (6)$$

$$\mathrm{M_2}^{\cdot} + \mathrm{M} \xrightarrow{k_p} \mathrm{M_3}^{\cdot}$$

$$\vdots$$

$$\mathrm{M}^{\cdot}_{n-1} + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_n^{\cdot}$$

(e) Mutual type of termination between growing polymer chain radicals:

$$\mathrm{M}_n^{\cdot} + \mathrm{M}_m^{\cdot} \longrightarrow \mathrm{M}_{n+m} \text{ or } \mathrm{M}_n + \mathrm{M}_m \qquad (7)$$

The reduction of $(\mathrm{Fe(phen)_3}^{3+})^*$ by the ground state complex (Eq. 3) will be less significant in the presence of the reactive reducing monomer. Likewise $k_r[\mathrm{A.AM}] \gg k_s[\mathrm{Fe(phen)_3}^{3+}]$.

Steady-state kinetic treatment of the above reaction scheme gives the kinetic expressions

$$R_p = k_p/k_t^{0.5}\left(\frac{k_r k_\epsilon I}{k_d + k_s + k_r[M]}\right)^{0.5}[M]^{1.5} \qquad (8)$$

$$-R_c = (k_r/k_d + k_s + k_c)k_\epsilon I[M] \qquad (9)$$

The reactions of the excited $Fe(phen)_3^{3+}$ with acrylamide to produce R' (Eq. 2) is supported by the kinetic observations; namely, the dependence of R_p on $[A.AM]^{1.5}$ and of $-R_c$ on [A.AM]. Baxendale and Bridge [5] observed that the quantum yields for photoreduction increased significantly with an increase in formic acid concentrations. They proposed that the reaction of the excited complex with formic acid to give the products predominated. The results of the polymerization of acrylamide in the presence of formic acid follows the same trend (Figs. 2 and 3). R_p and $-R_c$ varied linearly with formic acid concentrations, implying the formation of radicals from formic acid capable of initiation. The increase of R_p with pH up to 3 is consistent with increasing quantum yields for photoreduction. The pH dependence of the photoreduction has been accounted for in terms of the ability of the complex ion to function as a base to give the ion $H(Fe(phen)_3^{4+})$ which may differ in photoreactivity [5].

The results of the present study are not very similar to the well-known $Fe^{3+}X^{n-}$ photoinitiators [1-4]. In the case of $Fe^{3+}X^{n-}$ initiated photopolymerization of vinyl monomers, R_p varied linearly with [M]. X', formed by photodissociation of $Fe^{2+}X^{n-}$, initiated the polymerization. Monomer had no influence on the rate of dissociation of the ion pairs. Thus the differences in kinetics between the two photoinitiating systems $Fe^{3+}X^{n-}$ and $Fe(phen)_3^{3+}$ may be attributed to differences in the primary photochemical reactions.

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