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Kinetics of Vinyl Polymerization. 1. Ceric Ion Induced Polymerization of Acrylonitrile in the Presence of Butane-1,4-diol

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ABSTRACT

The kinetics of acrylonitrile polymerization initiated by butane-1,4-diol-Ce(IV) redox system have been studied in aqueous sulfuric acid in the range 30 to 40°C under nitrogen. There is no experimental evidence for the formation of a complex between diol and oxidant; the kinetics are consistent with a linear mode of termination. The effect of certain neutral salts, acids, water-miscible organic solvents, and temperature on the rate of polymerization and the rate of metal ion disappearance have also been investigated. Various rate and energy parameters have been evaluated.

INTRODUCTION

Certain transition metals in their higher valence states, when coupled with easily oxidizable organic substrates, act as initiators for the redox polymerization of vinyl monomers [1-5]. We have

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earlier reported [6-8] work on several initiating systems involving tetravalent ceric ion coupled with various organic substrates. Ceric ion has previously been used for the oxidation of many organic substrates [9-11] and the mechanism of such reactions has been well explained by various authors. There is evidence that no single mechanism holds good for all "metal ion/alcohol" redox systems and that the radical generating step in such systems is not generally straightforward [5]. Hence a detailed study of the aqueous polymerization of acrylonitrile (AN) initiated by the ceric ion-butane-1,4-diol system was undertaken. From the experimental observations, a suitable reaction scheme for the polymerization has been suggested and the kinetic parameters evaluated.

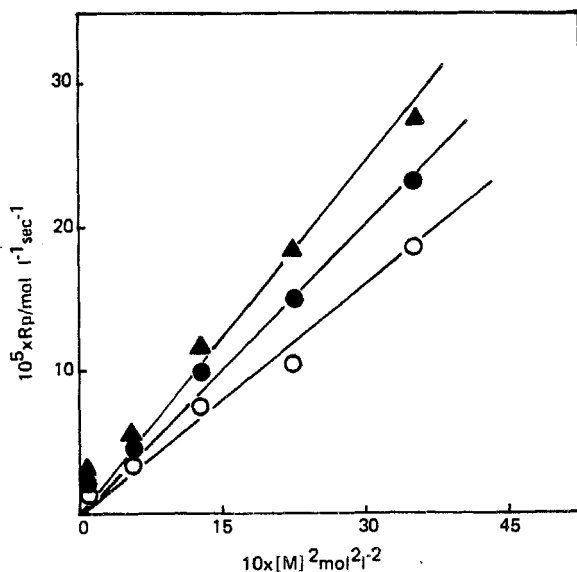


FIG. 2. Variation of rate of polymerization (R_p) of acrylonitrile (M) with $[M]$. $[H_2SO_4] = 0.4 \text{ mol/L}$, $\mu = 1.39 \text{ mol/L}$, $[Ce(IV)] = 0.005 \text{ mol/L}$. $[A] = 0.565 \text{ mol/L}$ at 30 (○), at 35 (●), and at 40°C (▲).

nearly linear and passed through the origin (Fig. 2) and hence a plot of $\log R_p$ vs $\log [M]$ was expected to give a slope of 2. But in prac-

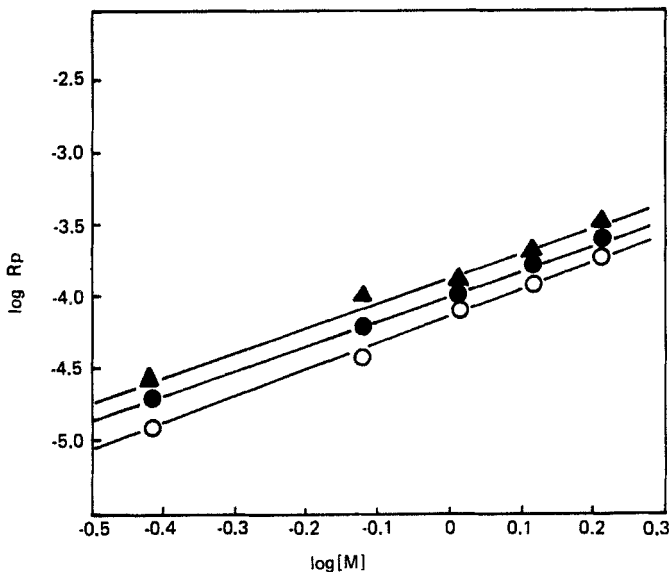


FIG. 3. The rate of polymerization of acrylonitrile (M) as a function of $[M]$. $[Ce(IV)] = 0.005$ mol/L, $\mu = 1.39$ mol/L, $[H_2SO_4] = 0.4$ mol/L. $[A] = 0.565$ mol/L at 30 (○), at 35 (●), and at 40°C (▲).

at low $[Ce(IV)]$ is higher than R_p at high $[Ce(IV)]$. This finding rules out mutual termination and points to the possibility of linear termination as a major process.

Rate of Disappearance of $Ce(IV)$ ($-R_{Ce}$)

The plot for ceric ion disappearance as a function of alcohol concentration $[A]$ is shown in Fig. 6. The step rise of the plot with increasing $[A]$ indicates that the major consumption of this species is due to the reaction of $Ce(IV)$ with butane-1,4-diol. The change in $[Ce(IV)]$ due to initiation and termination polymerization is found to be negligible at $[A] = 0$. The absence of complex formation between the substrate and ceric ion was revealed by consideration of Michaelis-Menten kinetics [13]. The effect of monomer concentration on ceric ion reduction is illustrated by the data of Table 2. It is clearly seen that consumption due to monomer is relatively small compared to that due to butane-1,4-diol. The plots of rate of disappearance of ceric ion vs $[M]$ in the presence of substrate are shown in Fig. 7. The slight rise in the straight line plots shows that an increase in

TABLE 1. Rate of Polymerization of AN in the Presence and the Absence of Butane-1,4-diol

Temperature (°C)	[M] (mol/L)	$10^5 R_p'$ (without substrate)	$\frac{R_p'}{[M]^2} \times 10^5$	$10^5 R_p'$ (from extrapolation)	$10^5 R_p$ (with substrate)	$\frac{R_p}{[M]^2} \times 10^5$	$\frac{R_p}{R_p'}$
30	0.7510	1.5660	2.7765	1.50	3.3050	5.8599	2.1104
	1.1265	3.1937	2.5167		7.3310	5.7769	2.2954
35	0.7510	2.1564	3.8233	2.00	4.6894	8.3145	2.1746
	1.1265	3.9533	3.1152		10.0071	7.8857	2.5313
40	0.7510	2.4684	4.3765	2.40	5.6031	9.9290	2.2686
	1.1265	2.4272	3.3311		12.0121	9.4562	2.8338

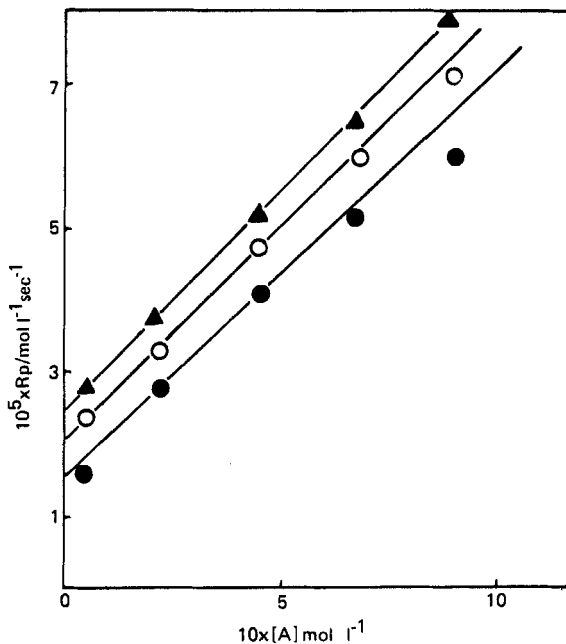


FIG. 4. Variation of rate of polymerization (R_p) with butane-1,4-diol concentration $[A]$ at $[H_2SO_4] = 0.4$ mol/L, $\mu = 1.09$ mol/L, $[M] = 0.75$ mol/L, $[Ce(IV)] = 0.005$ mol/L at 30 (●), at 35 (○), and at 40°C (▲).

$[M]$ does not produce any appreciable effect on the rate of disappearance of ceric ions. The result implies that ceric ions are not involved in reactions of the type $M + Ce(IV)$.

At the highest monomer concentration (1.8775 mol/L) the ceric ion reduction due to acrylonitrile alone is about 58.4% of the total reduction. The rate of disappearance of ceric ion concentration in the absence of alcohols at an initial monomer concentration is shown in Fig. 8. The curving off of the linear plot at higher monomer concentration could be due to increasing heterogeneity of the propagation and termination reactions at higher monomer concentration.

Plots of $-R_{Ce}$ vs $[Ce(IV)]$ are shown in Fig. 9. A first-order dependence of this rate is deduced from the linear plots of $-R_{Ce}$ vs $[Ce(IV)]$ passing through the origin.

Effect of Acids and Salts

R_p was found to decrease with increasing $[H_2SO_4]$ (0.1-1.7 mol/L). The ionic strength was adjusted by adding $NaHSO_4$.

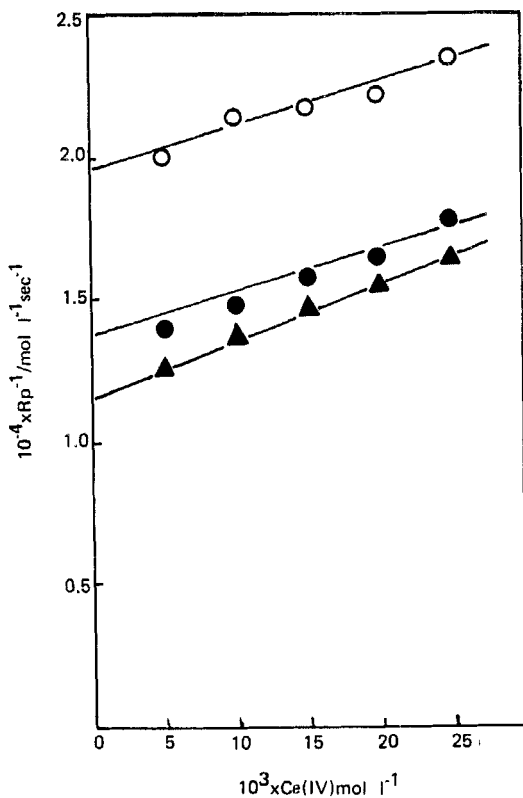


FIG. 5. Variation of $1/R_p$ with $[\text{Ce(IV)}]$ at $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol/L}$, $[\text{A}] = 0.0565 \text{ mol/L}$, $\mu = 1.7 \text{ mol/L}$, $[\text{M}] = 0.751 \text{ mol/L}$ at 30 (○), at 35 (●), and at 40°C (▲).

Rate Dependence on Temperature

In general, it was found that R_p increased with an increase of temperature (30–40°C). Similar effects were noted by Rout [14] and Whitby [15].

Effect of Organic Solvent

The effect of a small amount (5% v/v) of an organic solvent (acetone, methanol, and dioxane) depressed the initial rate of polymerization. A similar effect has been noted by Mishra et al. [16]. It is

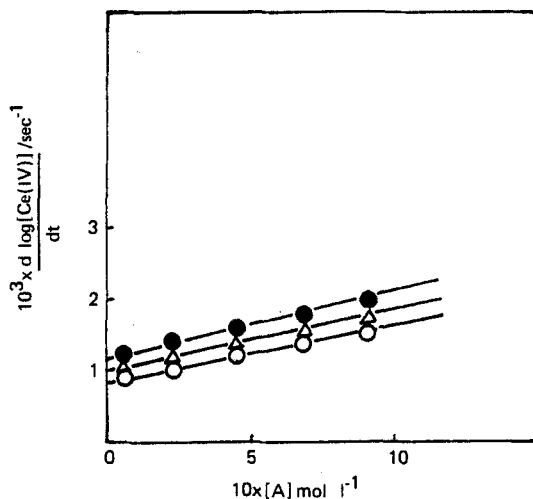


FIG. 6. Rate of ceric ion consumption ($-R_{\text{Ce}}$) as a function of butane-1,4-diol concentration $[A]$ at $\text{H}_2\text{SO}_4 = 0.4 \text{ mol/L}$, $[\text{Ce(IV)}] = 0.005 \text{ mol/L}$, $[M] = 0.751 \text{ mol/L}$, $\mu = 1.09 \text{ mol/L}$ at 30°C (\circ), at 35°C (\triangle), and at 40°C (\bullet).

TABLE 2. Decrease in Ceric Ion Concentration for Comparable Systems (reaction time 140 min)

$[M]$ mol/L	$-R_{\text{Ce}} \times 10^6$		[Sum of reductions due to M only + $2.3809] \times 10^6$
	$[A] = 0$	$[A] = 0.565$ mol/L	
0.0000	0.0000	2.3809	2.3809
0.0751	1.7850	4.1755	4.1659
0.2253	2.1726	4.5643	4.5535
0.3755	2.6873	5.0595	5.0682
0.7510	2.9886	5.5095	5.3695
1.1265	3.4226	5.8630	5.8035
1.5020	3.3630	5.9226	5.7439
1.8755	3.5505	6.0714	5.9314

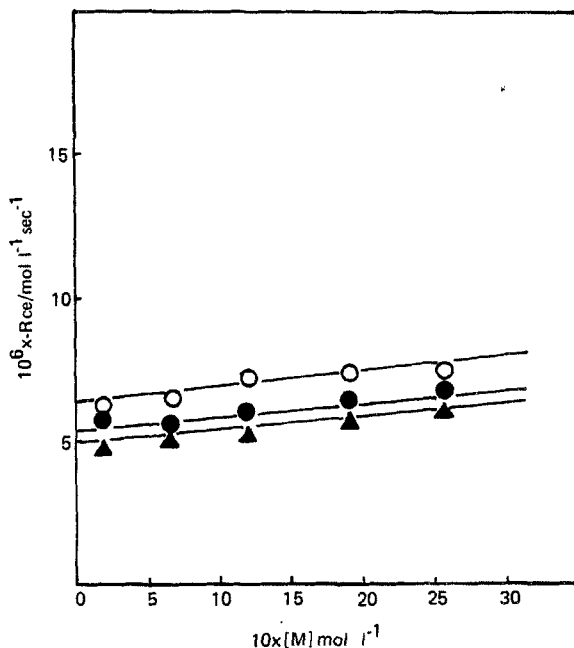


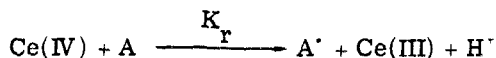
FIG. 7. Variation of $-R_{Ce}$ with $[M]$ at $[H_2SO_4] = 0.4$ mol/L, $[Ce(IV)] = 0.005$ mol/L, $[A] = 0.565$ mol/L, $\mu = 1.39$ mol/L at 30 (▲), at 35 (●), and at 40°C (○).

explained by assuming increased radical formation which simultaneously renders the termination rate relatively faster than the rate of growth of the polymer chain.

Reaction Mechanism and Rate Law

From the proportionality obtained between various measurable parameters and variables and the kinetic analysis of the experimental data, the following reaction scheme is suggested involving initiation by organic free radicals produced by interaction of Ce(IV) with butane-1,4-diol and termination by ceric ions. Termination of vinyl polymerization by metal ions is well recognized [17, 18]. Mino et al. [2-4] have also provided convincing evidence that the termination reaction involves ceric ions.

Primary Radical Formation:



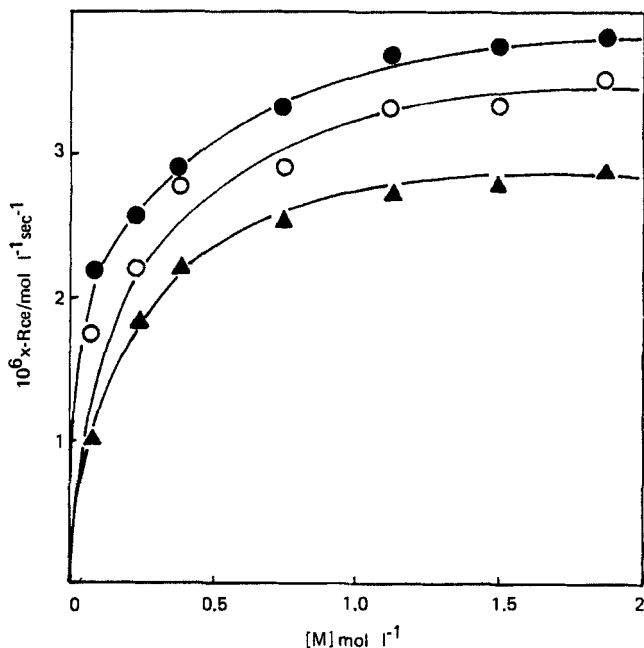
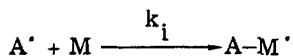


FIG. 8. Dependence of the rate of ceric ion reduction on the concentration of monomer in the absence of butane-1,4-diol [A].
 $[Ce(IV)] = 0.005 \text{ mol/L}$, $[H_2SO_4] = 0.4 \text{ mol/L}$, $\mu = 1.09 \text{ mol/L}$ at 30 (▲), at 35 (○), and at 40°C (●).

where A is the reducing agent (butane-1,4-diol) and A' is the primary radical.

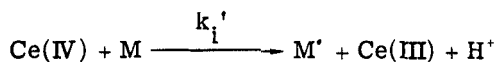
Initiation:

(a) By primary radical:



where M is monomer and A-M' is the radical formed by reaction of primary radical with monomer:

(b) By ceric ion:



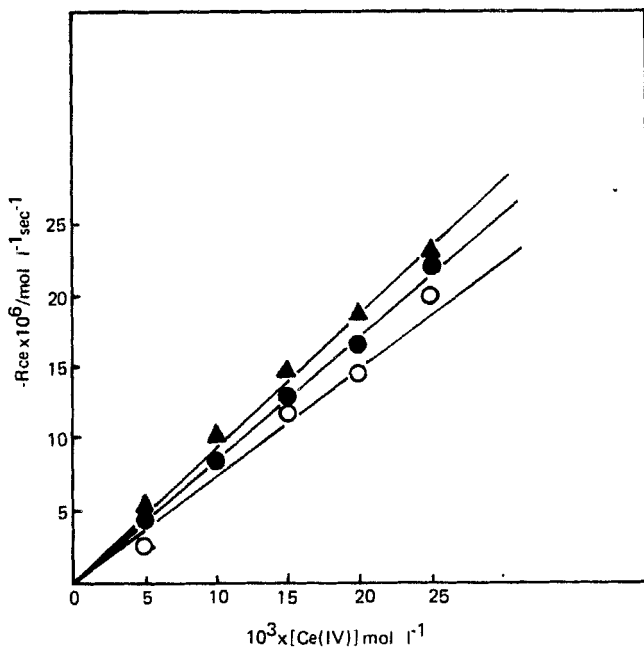
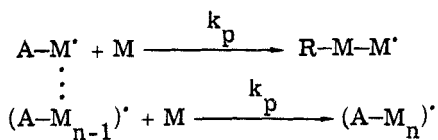


FIG. 9. Variation of the rate of Ce(IV) disappearance ($-R_{\text{Ce}}$) with $[\text{Ce(IV)}]$ at $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol/L}$, $\mu = 1.7 \text{ mol/L}$, $[\text{A}] = 0.0565 \text{ mol/L}$, $[\text{M}] = 0.751 \text{ mol/L}$ at 30 (○), at 35 (●), and at 40°C (▲).

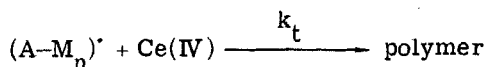
Propagation:



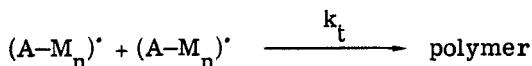
where $(\text{A-M}_n)'$ is the growing polymer radical.

Termination:

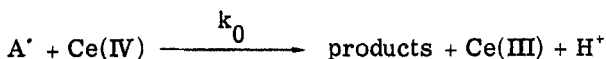
(a) Linear termination by ceric ions:



(b) Mutual termination by ceric ions:



Oxidation:



Applying the steady-state assumption to both $[M^{\cdot}]$ and $[A^{\cdot}]$ separately and assuming that no complex between the ceric ion and alcohol forms under the experimental conditions, the following expressions for the rate of polymerization (R_p) and the rate of disappearance of ceric ions ($-R_{\text{Ce}}$) is obtained:

$$R_p = \frac{k_p}{k_i} [M]^2 \left\{ k_i' + \frac{k_r[A]}{[M] + \frac{k_0}{k_i} [\text{Ce(IV)}]} \right\} \quad (1)$$

$$-R_{\text{Ce}} = 2[\text{Ce(IV)}] \left\{ k_r[A] + k_i'[M] \right\} \quad (2)$$

It is seen from the above expression that R_p is proportional to $[M]^2$ when $[A] = 0$. But when $[A] \neq 0$, the extent of deviation of R_p from square dependence will be determined by the magnitude of $[M]$ vs $(k_0/k_i)[\text{Ce(IV)}]$. This situation is realized in the graphs of Figs. 2 and 3.

Infrared Spectra

The IR spectrum of the isolated polymer was determined according to the method of Horback et al. [19] to detect endgroups in a double beam Perkin-Elmer Model 337 spectrophotometer. A shell thickness of 1 mm was used in order to get suitable absorbance of the nitrile band. The spectra showed aliphatic hydroxyl absorption 3400 cm^{-1} along with peaks, characteristic of the homopolymer of AN. The heavy quenching of the $-\text{C}\equiv\text{N}$ intensity at 2100 cm^{-1} is explained [20] as due to the introduction of an oxygenated group into the molecule. The shifting of the narrow high intensity band at 3600 cm^{-1} to a wide high intensity band at 3400 cm^{-1} due to $-\text{OH}$ stretching is explained as being due to hydrogen bond formation. This observation confirms the proposed kinetic scheme that under the experimental conditions the initiation of polymerization occurs by the interaction of Ce(IV) with butane-1,4-diol. Termination is by ceric ions.

TABLE 3. Rate Constants

Temperature (°C)	$10^3 \times k_r$ from $-R_{Ce}$ vs [Ce(IV)]	k_t/k_p from $1/R_p$ vs [Ce(IV)]	k_0/k_i from $1/R_p$ vs [Ce(IV)]	$10^3 \times K_i'$ from $-R_{Ce}$ vs [M] in the absence of alcohol
30	7.285	6.1620	6.1620	9.9050
35	7.813	4.5581	10.9236	9.6153
40	8.849	4.2241	16.6888	8.0000

Evaluation of Rate Constants

The values of the second-order rate constant K_r were obtained from plots of $-R_{Ce}$ vs [Ce(IV)] (from the initial slopes). The values of k_0/k_t , k_0/k_i were obtained by our previous methods [7]. The values of k_i' were obtained from the slopes of the plot of $-R_{Ce}$ vs [M] in the absence of alcohol.

It is seen from Table 3 that the values of k_0/k_i are considerably greater than unity. This ensures that the term (k_0/k_i) [Ce(IV)] is always greater than [M] in Eq. (1). Hence the square dependence of R_p on monomer as observed experimentally is assured. However, this dependence is not expected to hold good at high monomer concentration or at extremely low ceric ion concentration.

Although the reaction scheme envisages termination by ceric ions, there is always the probability of termination by species other than Ce(IV) because numerous molecular complexes of the metal ion with alcohol are possible. Hence, with an increase in the $[A]/[Ce(IV)]$ ratio, the probability of departure from the linear mode of termination increases. The nonrealization of the predicted slope of 2 in the plot of $\log R_p$ vs $\log [M]$ (Fig. 3) is attributed to the presence of alcohols.

Evaluation of Energy Parameters

The values of E_r , $E_t - E_p$, and $E_0 - E_i$ were computed as before [7]. E_r , $E_t - E_p$, $E_0 - E_i$, and E_t values were found to be 16.58, 9.94, 9.48, and 14.34 kcal/mol, respectively. The corresponding entropies of activation for K_r , k_t/k_p , and k_0/k_i were -16.49, -31.45, and -25.03 e.u., respectively.

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