Retardation of Cerium(IV)-Initiated Polymerization of Acrylonitrile by Cinnamic Acid

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ABSTRACT

The kinetics and the mechanism of retarding action of cinnamic
acid on the Ce(IV)-initiated polymerization of acrylonitrile were
studied in the temperature range 35-45°C. The rate of polym-
erization R_p was measured with respect to its dependence on
time, monomer, metal ion, cinnamic acid, perchloric acid,
acetic acid, sodium perchlorate, sodium sulfate, and manganese
sulfate. The most significant observation was the rate mech-
anism. The process of polymerization was initiated by Ce(IV)
alone and terminated essentially by the free radical produced
by the interaction of Ce(IV) with cinnamic acid, which seems
to be a general observation for all retarding substrates.

The mechanism and the kinetics of action of stabilizers and anti-
oxidants have been the subject of study by several research workers
because of their commercial importance. This area of investigation
is closely related to that of inhibited or retarded polymerization in
which Bird and Russell [1], Tüdös, Simonyi, Pospisil and Foldes-
Berezhnykh [2, 3] have made very significant contributions.
    As a part of the investigation of the retarding action of different
substrates on the rate of polymerization, it was considered worthwhile

to study the retarding action of cinnamic acid on the Ce(IV)-initiated polymerization of acrylonitrile. There were several reasons which prompted us to use cinnamic acid as the substrate.

In the course of an extensive program in this laboratory, on studies relating to oxidation reactions involving structure-reactivity correlation, organic compounds containing carboxyl group adjacent to a –CH=CH– group, e. g., cinnamic acid [4] were used as substrates for oxidation by Ce(IV). On the basis of the experimental data, a free-radical mechanism for the Ce(IV) oxidation of cinnamic acid has been proposed. The mechanism was also consistent with other experimental findings: stoichiometry and product analysis. Ce(IV) in the absence of cinnamic acid brought about polymerization of acrylonitrile, whereas decrease in the rate of polymerization was observed when cinnamic acid was added to the Ce(IV)-acrylonitrile system. This indicated that cinnamic acid retards polymerization of acrylonitrile by Ce(IV). Inhibited or retarded polymerization of acrylonitrile un-equivocally established involvement of a free-radical mechanism. Similar retarding action was also observed in case of polymerization of acrylonitrile by Ce(IV) in presence of chalcone, and a similar mech-anism has been suggested [5].

In view of the above, it was considered worthwhile to carry out more elaborate investigations on the retarding action of cinnamic acid on the Ce(IV)-initiated polymerization of acrylonitrile and suggest a reaction mechanism consistent with the experimental results. On the basis of the experimental data, it has now been postulated that the polymeriza-tion is initiated by ceric ions and terminated essentially by the pri-mary radical produced from the interaction of Ce(IV) with cinnamic acid. It was interesting that the rate of polymerization consistently decreased with increase in the concentration of cinnamic acid.

The rate expression used in the present investigation for evaluating the composite rate constant is different from the rate expression used by previous workers.

On the basis of experimental data, the expression for R_p is given by Eq. (1):

$$R_p = \frac{k_p k_i k_0 \, [M]^2 \, [Ce(IV)]}{k_t k [R] - k_t k_i [M]} \tag{1}$$

By suitable rearrangement of Eq. (1) it was found that:

$$\frac{[M]}{R_p} = \frac{k \, k_t \, [R]}{k_i k_p k_0 [Ce(IV)][M]} - \frac{k_t}{k_0 k_p [Ce(IV)]} \tag{2}$$

By plotting $[M]/R_p$ versus $1/[M]$, the composite rate constants were

calculated. But a very significant observation in the present study was that this plot gave a negative intercept. Similar observation was reported by us in the case of Ce(IV)-initiated polymerization of acrylonitrile in the presence of chalcone [5]. This is certainly very interesting and significant.

EXPERIMENTAL

Acrylonitrile used was an American Cyanamid product containing 2% hydroquinone. After removal of the inhibitor by shaking the commercial monomer with 5% sodium hydroxide solution and 3% orthophosphoric acid followed by repeated washing with conductivity water, the monomer was dried over anhydrous calcium chloride and stored at 5°C. Reagents like ceric ammonium nitrate, perchloric acid, cinnamic acid, acetic acid, etc. were either BDH, AnalaR or E. Merck G. R. products. Water, doubly distilled over alkaline permanganate in an all-glass Pyrex unit, was used for preparation of reagents and solutions. Deaeration of the reaction mixture was done by passing nitrogen freed from oxygen.

The requisite quantity of monomer and the solution of cinnamic acid in acetic acid were taken in the appropriate reaction vessel (Pyrex tube fitted with a B24/29 socket carrying a B24/29 cone with an inlet and outlet tube for nitrogen) deaerated for 20 min and kept at a desired temperature in a thermostat. An appropriate amount of ceric ammonium nitrate solution was then added, and after a specified time interval, the polymerization was stopped by addition of a known excess of ferrous ammonium sulfate solution. The polymer was filtered off, washed well with conductivity water, and dried to constant weight. The rate of polymerization was determined gravimetrically.

DISCUSSION

Relation between Conversion and Reaction Time

The percentage of conversion of monomer to polymer in the presence of cinnamic acid increases with the reaction time, and a steady state of consumption of monomer is attained within 80 min.

Reaction Mechanism

Ce(IV) alone is capable of initiating the polymerization of acrylonitrile. Since cinnamic acid retards the polymerization of acrylonitrile by Ce(IV), one would infer that the radical produced from cinnamic acid by interaction with Ce(IV) does not play an effective role in the initiation step but is involved in the termination step.

The schemes summarized in Eqs. (3)-(10) embody the sequence of reactions proposed to explain satisfactorily the kinetic results obtained.
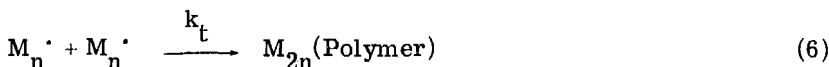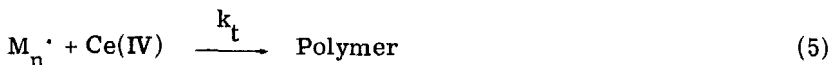
Unretarded Polymerization:
Initiation by ceric ion:

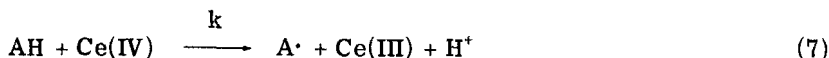$$Ce(IV) + M \xrightarrow{k_i} M\cdot + Ce(III) \tag{3}$$

Propagation:

$$M\cdot + M \xrightarrow{k_p} M_2\cdot$$

$$\vdots$$

$$M_{n-1}^{\cdot} + M \xrightarrow{k_p} M_n^{\cdot} \tag{4}$$

Termination by metal ion (linear) and by combination (mutual):

$$M_n^{\cdot} + Ce(IV) \xrightarrow{k_t} Polymer \tag{5}$$

$$M_n^{\cdot} + M_n^{\cdot} \xrightarrow{k_t} M_{2n}(Polymer) \tag{6}$$

Retarded Polymerization:
In presence of cinnamic acid (AH) as retarder:

$$AH + Ce(IV) \xrightarrow{k} A\cdot + Ce(III) + H^+ \tag{7}$$

where $A\cdot$ is the resonance stabilized radical.
Termination:

$$A\cdot + M_n^{\cdot} \xrightarrow{k_t} M_n A \tag{8}$$

$$M_n^{\cdot} + AH \xrightarrow{k_t} M_n H + A\cdot \tag{9}$$

Reaction of primary radical with $Ce(IV)$:

$$A\cdot + Ce(IV) + H_2O \xrightarrow{k_0} Oxidation\ product + Ce(III) + H^+ \tag{10}$$
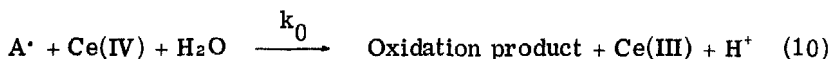
At higher concentration of the retarder, reactions (5) and (6) are neglected. In presence of $Ce(IV)$, reaction (9), i. e., chain transfer is neglected.

By applying the steady-state principle for free-radical concentra-
tions, the following rate expression for R_p is obtained:

$$R_p = \frac{k_p k_0 k_i [M]^2 [Ce(IV)]}{k k_t [AH] - k_i k_t [M]}$$

The other modes of termination, namely linear and mutual, were
excluded on the basis that the expressions for R_p involved proportion-
alities which were not experimentally realized.

Effect of Variables on Rate

Effect of Monomer.

The rate of polymerization R_p in-
creased with monomer concentration (0.15 M - 1.5 M). Linear plots
were obtained, when R_p was plotted against $[M]^2$ with zero intercept
at three different temperatures (Fig. 1). The order with respect fo
$[M]$ was, therefore, two.

Effect of Ceric Ion.

The rate of polymerization increases
initially with increase in ceric ion concentration (0.005 M to 0.02 M).
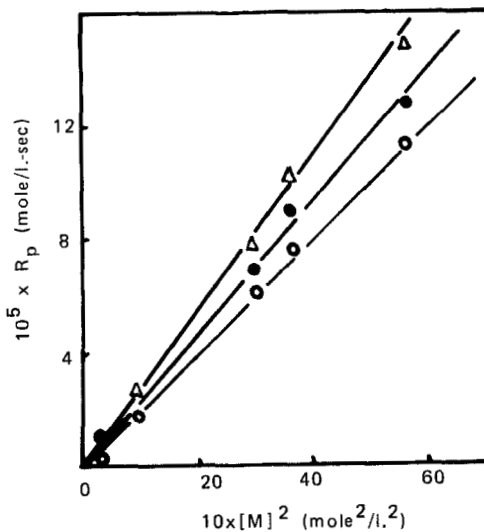At higher concentrations of ceric ions, R_p decreases (Fig. 2). The

FIG. 1. Variation of R_p with $[M]^2$: ($\circ$) 35°C; ($\bullet$) 40°C; ($\triangle$) 45°C.
$[Ce(IV)]$ = 1×10^{-2} mole/liter; $[AH]$ = 5×10^{-4} mole/liter; AcOH =
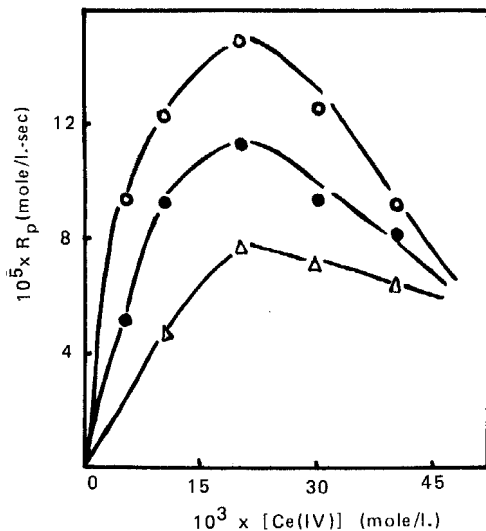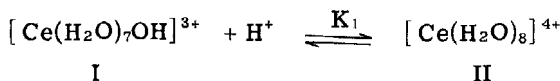30% (v/v); $[HClO_4]$ = 0.8 mole/liter; μ = 0.95 mole/liter.

FIG. 2. Variation of R_p with $[Ce(IV)]$: ($\triangle$) 35°C; ($\bullet$) 40°C; ($\circ$) 45°C. $[AH] = 5 \times 10^{-4}$ mole/liter; $[HClO_4] = 0.8$ mole/liter; AcOH = 30% (v/v), $[AN] = 0.754$ mole/liter; $\mu = 0.95$ mole/liter.

maxima in the curve reflects a sudden change in the reaction mechanism beyond a particular limit of ceric ion concentration.

Effect of Cinnamic Acid.   The rate of polymerization R_p consistently decreases with increase in cinnamic acid concentration (0.0005 M-0.025 M) (Fig. 3). Similar observations were obtained by Simonyi et al. [2] and Bird et al. [1] in the study of the effect of phenols in the polymerization of vinyl acetates. The chain-terminating process is brought about by the resonance-stabilized free radical (produced from cinnamic acid by interaction with ceric ion) which rapidly combines with a growing polymer chain resulting in prematured termination. There is no evidence of complex formation between ceric ion and cinnamic acid, as found from the oxidation studies of cinnamic acid by Nanda [6].

Effect of Perchloric Acid.   The rate of polymerization increases with increased concentration of perchloric acid (0.2 M to 1.2 M). Depending on the concentration of perchloric acid, ceric ion may be present in this medium [7] as $[Ce(H_2O)_8]^{4+}$ and $[Ce(OH)(H_2O)_7]^{3+}$. Since the predominant species is monomeric in perchloric acid range (0.2 M to 2.0 M), the equilibrium can be written as follows:
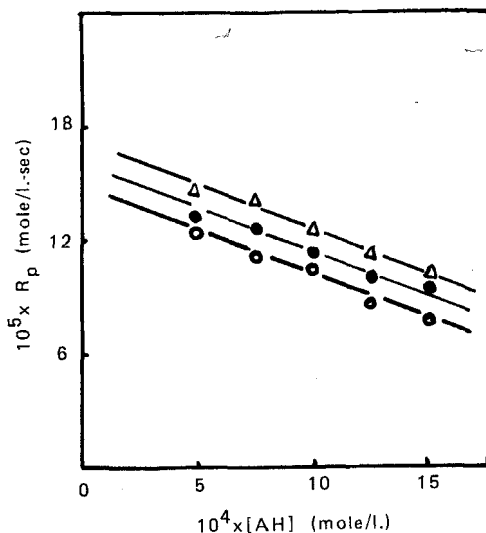
$$[Ce(H_2O)_7OH]^{3+} + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} [Ce(H_2O)_8]^{4+}$$

I   II

FIG. 3. Variation of R_p with cinnamic acid concentration $[AH]$:
(○) 35°C; (●) 40°C; (△) 45°C. $[Ce(IV)] = 1 \times 10^{-2}$ mole/liter;
$[HClO_4] = 0.8$ mole/liter; AcOH = 30% (v/v); $[AN] = 0.754$ mole/
liter; $\mu = 0.95$ mole/liter.

Since the rate increases with increasing acid concentration, the un-
hydrolyzed species (II) would be the active one.

Effect of Salts. The rate of polymerization is retarded by
the addition of anions like SO_4^{2-} and ClO_4^- and accelerated by the
addition of Mn^{2+} ions. The decrease in the rate may be accounted for
by the destruction of active cerium species by complexation or due
to greater consumption of Ce(IV) by the oxidation process.

Mn(II), on the other hand, is known to enhance the rate of oxidation
due to the formation of an active Mn(III) species:

$$Mn(II) + Ce(IV) \longrightarrow Mn(III) + Ce(III)$$

$$Substrate + Mn(III) \longrightarrow Product + Mn(II)$$
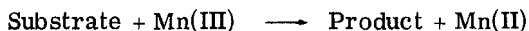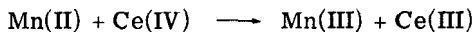
Thus the observed increase in R_p in presence of Mn(II) could either
be due to fast removal of the retarding substrate or due to the accel-
erating effect of Mn(III) on the polymerization.

Influence of Organic Solvent. As cinnamic acid is not
soluble in water, 30% acetic acid was used as the solvent for carrying

out the polymerization. The increase in the percentage of acetic acid (30% to 60%) in the reaction medium is found to decrease the rate of polymerization appreciably. This decrease can be attributed to increased production of radicals with increase in the solvent molecules, which, in turn, renders the termination rate faster than the rate of growth of polymer chains as reported by Kern et al. [8].

ACKNOWLEDGMENTS

REFERENCES

[1] R. A. Bird and K. E. Russell, Can. J. Chem., 43, 2123 (1965).
[2] F. Tüdös, M. Simonyi, and J. Pospisil, Eur. Polym. J., 3, 101 (1967).
[3] T. Foldes-Berezhnykh and F. Tüdös, Eur. Polym. J., 2, 229 (1966).
[4] M. K. Rout, unpublished results.
[5] R. K. Satapathy, S. N. Patnaik, B. K. Misra, S. P. Rout, and M. K. Rout, J. Macromol. Sci.–Chem., A13, 273 (1979).
[6] C. N. Nanda, Ph. D. thesis, Utkal University, 1976.
[7] M. G. Adamson, F. S. Dainton and P. Glentwork, Trans. Faraday Soc., 61, 689 (1965).
[8] R. Schulz, G. Renner, A. Henglein, and W. Kern, Makromol. Chem., 12, 20 (1954).