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Retardation of Cerium(IV)-Initiated Polymerization of Acrylonitrile by Chalcone

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ABSTRACT

The present investigation describes the kinetics and the mechanism of the inhibiting action of chalcone on the rate of Ce(IV)-initiated polymerization of acrylonitrile in the temperature range 30-40°C. The effect of monomer, metal ion, chalcone, perchloric acid, acetic acid, sodium sulfate, and manganese sulfate on the rate of polymerization has been studied. The most striking observation in the present investigation was the rate mechanism. The plot of $[M]/R_p$ versus $1/[M]$ gave a negative intercept which appears to be a general phenomenon for all inhibiting substrates. The activation parameters were calculated, and a suitable reaction scheme is proposed.

The commercial importance of stabilizers and antioxidants is quite well recognized. Methylene-bisphenols [1] have been found to be quite efficient in the stabilization of oil solutions of carotene at 75°C and in the stabilization of paraffin wax at 163°C. Monohydric phenols have been known to retard and even inhibit completely the autoxidation of olefinic oils and technically important substances [2]. Very much related to this area of investigation is that of inhibited or retarded polymerization. Bird and Russell [3], Tüdös [4, 5], Simonyi [4], Pospisil [4], and Foldes-Berezhnykh [5] have made significant contribution in this field of inhibited or retarded polymerization kinetics.

A program of investigation in the field of retarded or inhibited polymerization kinetics has been under way in this laboratory for some time. Suitable substrates which are expected to inhibit or retard the metal-ion-initiated polymerization of monomers have been chosen.

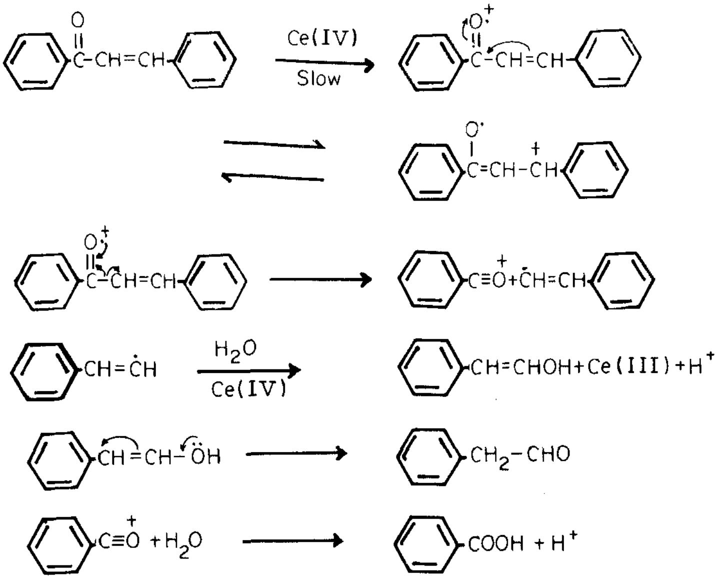
The use of chalcone as the substrate was the consequence of oxidation kinetics carried out in this laboratory with chalcone [6] and several metal ions including Ce(IV). Chalcone has a unique structural feature containing, as it does, a carbonyl function adjacent to a $-CH{=}CH-$ group. The effect of acrylonitrile on the rate of oxidation has been studied. It was found that acrylonitrile facilitated the process of oxidation. To verify if this suggested a free-radical mechanism, polymerization of acrylonitrile was undertaken in the presence of Ce(IV) and chalcone as the substrate. Chalcone retarded the polymerization of acrylonitrile by Ce(IV), thus clearly pointing to a free-radical mechanism. The formation of free radicals in the process of oxidation was supported by the formation of a white precipitate with mercuric chloride. There was, however, no formation of the precipitate in the absence of Ce(IV).

A discussion whether ionization (removal of electron) involved a bonding electron or oxygen lone pair may be of interest. One might anticipate that because carbonyl lone pairs have greater S-character than alcohol or ether oxygen lone pairs, ionization from a carbonyl unshared pair would be more difficult. Nevertheless, it seems clear that it is an oxygen lone-pair electron that is lost on ionization. The ionization potential values of acrolein and propionaldehyde are 10.10 and 9.98 eV, respectively. If the electron had been lost from the pi-system, the ionization potential of acrolein would have been substantially lower, just as the ionization potential of butadiene (9.07 eV) is lower than that of 1-butene (9.58 eV).

The IR analysis of polymer (polyacrylonitrile obtained using chalcone as the substrate) does not show the $>C{=}O$ group absorption at 1665 cm^{-1} and 1220 cm^{-1}, indicating the absence of the $>C{=}O$ group in the radical.

The oxidative mechanism has been assumed to involve the benzoyl cation as shown in Eqs. (1)-(5). This is also consistent with the loss on ionization of an oxygen lone-pair electron. The benzoyl cation species has been confirmed from studies on mass spectra.

Since the oxidative mechanism involved a free-radical intermediate, it was considered worthwhile to study the detailed kinetics of the



(1)

(2)

(3)

(4)

(5)

inhibiting action of chalcone and substituted chalcones to determine a reaction mechanism consistent with the experimental results and to ascertain how far the experimental findings correspond to the trend observed in the oxidation experiments in case of p-methoxychalcone.

The most significant aspect studied is the rate mechanism. On the basis of the experimental data, it has been postulated that the polymerization is initiated by ceric ions and terminated essentially by the primary radical produced from the interaction of Ce(IV) with chalcone. It was interesting that the rate of polymerization consistently decreased with increasing concentration of chalcone.

The rate expression used in the present investigation for the evaluation of the composite rate constant is different from the rate expression used by other workers.

On the basis of the experimental data, the expression for R_p is given by Eq. (6):

$$R_p = k_p k_i k_0 [M]^2 \, [Ce(IV)]/(k_t k \, [R] - k_t k_i \, [M]) \tag{6}$$

Rearrangement of Eq. (6) gives Eq. (7):

$$\frac{[M]}{R_p} = \frac{k \, k_t \, [R]}{k_i k_p k_0 \, [Ce(IV)] \, [M]} - \frac{k_t}{k_0 k_p \, [Ce(IV)]} \tag{7}$$

By plotting $[M]/R_p$ versus $1/[M]$, the composite rate constants were calculated. The plot showed a striking feature. A negative intercept was observed. Since this was contrary to observations with other substrates, it appeared worthwhile to investigate if it was a special characteristic of all substrates having inhibitory action. Our investigation led to a very significant generalization (to be reported elsewhere) that all inhibiting substances give a negative intercept in the plot of $[M]/R_p$ versus $1/[M]$.

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. The reagents like ceric ammonium nitrate, perchloric acid, chalcone, acetic acid, etc. were either BDH AnalaR or E. Merck, GR 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 passage of nitrogen freed from oxygen.

The requisite quantity of monomer and the solution of chalcone in acetic acid were taken in the 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 the desired temperature in a thermostat. An appropriate amount of cerium 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 monomer disappearance was calculated from the initial slope of the time versus yield.

DISCUSSION

Relation between Percentage Conversion and Reaction Time

The conversion was studied at different monomer concentrations and its relation with time is shown in Fig. 1. It is found that the percentage of conversion increases with the passage of reaction time.

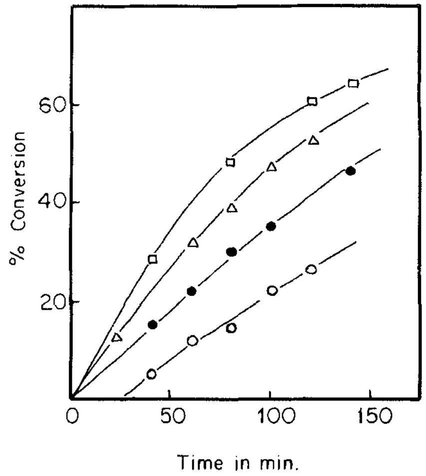


FIG. 1. Relation of percentage conversion with reaction time: (○) [M] = 0.375 mole/liter; (●) [M] = 0.751 mole/liter, (△) [M] = 1.126 mole/liter, (□) [M] = 1.502 mole/liter. [Ce(IV)] = 1 × 10^{-2} mole/liter; [$HClO_4$] = 0.8 mole/liter; [chalcone] = 5 × 10^{-4} mole/liter; AcOH = 30% (v/v); 35°C.

The percentage of conversion has also been studied at different substrate (chalcone) concentrations and was found to decrease with increase of chalcone concentration. This has been attributed to the inhibiting action of chalcone on the rate of polymerization.

Effect of Monomer on Rate

The rate of polymerization increased with increase of acrylonitrile concentration (0.375 M to 1.877 M). The rate also increases with temperature as expected. Good linear plots were obtained, when R_p was plotted against $[M]^2$ at three different temperatures, (Fig. 2). This indicates that the order of the reaction with respect of [M] is two.

Reaction Mechanism and Kinetic Scheme

Ce(IV) alone can initiate the polymerization of acrylonitrile. Since chalcone inhibits the polymerization of acrylonitrile by Ce(IV), it is

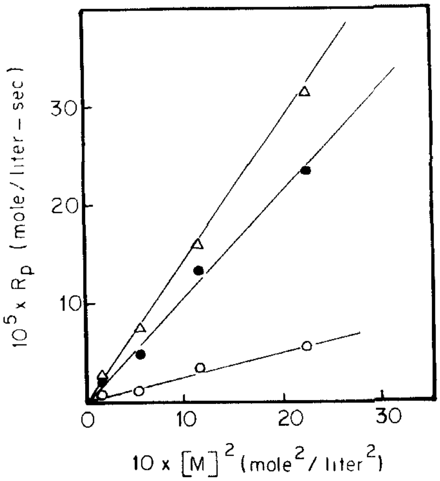


FIG. 2. Variation of R_p with $[M]^2$: (○) 30°C; (●) 35°C; (△) 40°C. $[Ce(IV)] = 1 \times 10^{-2}$ mole/liter; $[HClO_4] = 0.8$ mole/liter; $[\text{chalcone}] = 5 \times 10^{-4}$ mole/liter; AcOH = 30% (v/v).

suggested that the radical produced from chalcone by the interaction of Ce(IV) may not be taking part in the initiation step, but is involved in the termination step (primary radical termination). IR analysis of the polymer (polyacrylonitrile obtained using chalcone as the substrate) does not show the presence of a $>C{=}O$ group absorption in the IR at 1665 and 1200 cm^{-1}, indicating the absence of a $>C{=}O$ group in the radical.

The scheme proposed appears to explain satisfactorily all the kinetic results obtained.

Uninhibited Polymerization

Initiation by ceric ion:

$$Ce(IV) + M \xrightarrow{k_i} M^{\bullet} + Ce(III) \tag{8}$$

Propagation:

$$M^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet} \tag{9}$$

$$\vdots$$

$$M_{n-1}^{\bullet} + M \xrightarrow{k_p} M_n^{\bullet} \tag{10}$$

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

$$M_n^{\bullet} + \text{Ce(IV)} \xrightarrow{k_t} \text{Polymer} \tag{11}$$

$$M_n^{\bullet} + M_n^{\bullet} \xrightarrow{k_t} M_{2n}\text{(Polymer)} \tag{12}$$

Inhibited Polymerization

In the presence of chalcone (AH) as inhibitor:

$$\text{AH} + \text{Ce(IV)} \rightleftharpoons [\text{Complex}] \xrightarrow{k} A^{\bullet} + \text{Ce(III)} + H^{+} \tag{13}$$

where $A^{\bullet}$ is the resonance-stabilized radical.

Termination:

$$A^{\bullet} + M_n^{\bullet} \xrightarrow{k_t} M_nA \tag{14a}$$

$$\text{AH} + M_n^{\bullet} \xrightarrow{k_t} M_nH + A^{\bullet} \tag{14b}$$

Reaction of primary radical with Ce(IV):

$$A^{\bullet} + \text{Ce(IV)} + H_2O \xrightarrow{k_0} \text{Oxidation product} + \text{Ce(III)} + H^{+} \tag{15}$$

At high concentration of the inhibitor, reactions (11) and (12) are neglected. In the presence Ce(IV), reaction (14b), that is, chain transfer is neglected.

By applying steady-state kinetics, the expression (16) for the rate of polymerization R_p is obtained:

$$R_p = k_pk_0k_i\,[M]^2\,[\text{Ce(IV)}]/(kk_t[\text{AH}] - k_ik_t\,[M]) \tag{16}$$

The termination step is assumed to be exclusively by the radical formed by the interaction of Ce(IV) with the substrate (chalcone). The rate expression proposed satisfactorily explains all the kinetic results obtained.

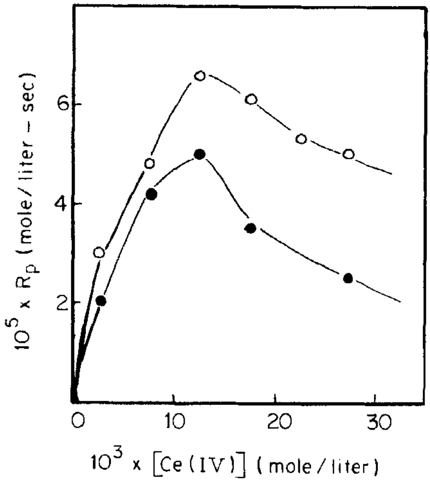


FIG. 3. Variation of R_p with [Ce(IV)]: (●) 35°C; (○) 40°C. [Chalcone] = 5×10^{-4} mole/liter; [$HClO_4$] = 0.8 mole/liter; [AN] = 0.751 mole/liter; AcOH = 30% (v/v).

Effect of Ceric Ion on Rate

With increased concentration of ceric ion (0.0025 to 0.0175 M), the rate of polymerization increases initially, but at higher concentrations, the rate of polymerization decreases (Fig. 3). The maxima in the curve undoubtedly reflect a sudden change in the reaction mechanism beyond a particular limit of ceric ion concentration.

Effect of Substrate (Chalcone) on Rate

The rate of polymerization R_p decreases with increasing concentration of the substrate (chalcone) (Fig. 4). Similar observations have been reported by Simonyi et al. [4] and Bird et al. [3] in the study of the effect of phenols in the polymerization of vinyl acetates. In the present work, the retarding action of chalcone can be accounted for in a manner similar to that proposed by Bartlett et al. [7] to explain the observed kinetic results for the polymerization of allyl acetates. The termination of the propagating polymer chain is caused by the resonance-stabilized free radical produced from chalcone by interaction with Ce(IV). The formation of Ce(IV)-Chalcone complex has

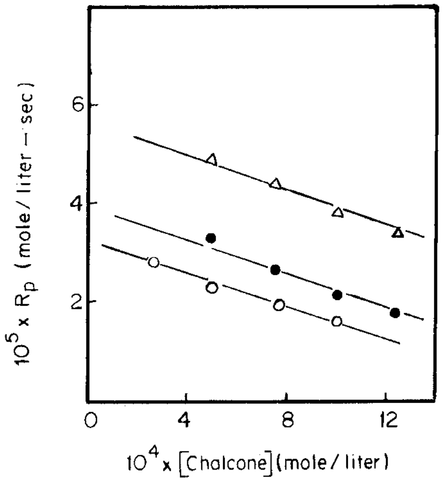


FIG. 4. Variation of R_p with [chalcone]: (○) 30°C; (●) 35°C; (△) 40°C. [Ce(IV)] = 1×10^{-2} mole/liter; [$HClO_4$] = 0.8 mole/liter; [AN] = 0.751 mole/liter; AcOH = 30% (v/v).

been reported by Acharya [8], and it has been proved beyond doubt from the IR spectra of a precipitate obtained after the lapse of a good deal of time, when chalcone and Ce(IV) are mixed in 1:2 molar proportion. The IR spectrum of the complex has all the features of a chalcone molecule and the precipitate gives the test for Ce(IV).

Effect of Perchloric Acid on Rate

The rate of polymerization increases with increasing concentration of perchloric acid (0.5 M to 2 M). Depending on the concentration of perchloric acid, ceric ion is believed to be present in this medium [9] as $[Ce(H_2O)_8]^{4+}$ and $[Ce(OH)(H_2O)_7]^{3+}$. As the effective species is monomeric in perchloric acid medium (0.2 M to 2.0 M), the equilibrium can be written as follows:

$$\underset{\text{I}}{[Ce(H_2O)_7OH]^{3+}} + H^+ \overset{K_1}{\rightleftharpoons} \underset{\text{II}}{[Ce(H_2O)_8]^{4+}} \qquad (17)$$

The increase of rate with increased perchloric acid concentration has been attributed to the unhydrolyzed species (II), which is the active one.

Effect of Salts

The rate of polymerization, R_p, decreased with the addition of salts like sodium sulfate. This decrease in the rate may be accounted for by the destruction of the active cerium species or by the greater consumption of Ce(IV) by the oxidation process. However, with the addition of $MnSO_4$, there was complete inhibition and no polymerization was observed.

Bamford et al. [10] have reported that ions which are capable of existing in more than one valence state may behave as retarders under certain conditions by entering into an oxidation-reduction type of mechanism. In case of chalcone, since complex formation takes place with Ce(IV), Ce(IV) is not available adequately for converting Mn(II) into Mn(III) which acts as an accelerator because of its ability to initiate polymerization. In case of cinnamic acid, no complex formation takes place, and conversion of Mn(II) to Mn(III), which is an initiating species, is possible and hence acceleration is observed.

Effect of Organic Solvent on Rate

The polymerization experiments were carried out in 30% acetic acid due to the insolubility of chalcone in the aqueous media. Increase in the percentage of acetic acid (30% to 60%) in the reaction media is found to decrease the rate of polymerization to a considerable extent. This can be explained by the increased production of radicals with the increase in the solvent molecules which prematurely terminates the growing polymer chains. Similar observations were reported by Kern et al. [11].

Activation Parameters

The composite rate constants at 30, 35, and 40°C were used in the calculation of activation parameters.

The energy of activation, entropy of activation, and enthalpy of activation were computed to be 15.54 kcal/mole, -49.10 kcal/degree-mole and 14.9 kcal/mole, respectively.

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