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## Retardation of $V^{5+}$ -Cyclohexanone Initiated Polymerization of Acrylonitrile by Phenol

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### ABSTRACT

Studies have been made on the kinetics and mechanism of the retardation of  $V^{5+}$ -cyclohexanone initiated polymerization of acrylonitrile by phenol in the temperature range 45-50°C. The effects of metal ion, monomer, phenol,  $H_2SO_4$ , some inorganic salts, and some organic solvents have also been studied. The unique observation in this investigation is the positive intercept obtained from the plot of  $[M]/R_p$  vs  $1/[M]$ . This type of observation is significantly different from previous studies on retarded polymerization. The values of composite rate constants  $k_0 k_t / k_i k_p K$  were calculated from plots of  $[M]/R_p$  vs  $[M]^{-1}$ . A suitable mechanism is put forth and the rate law based on the proposed mechanism is derived.

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## INTRODUCTION

Studies on vinyl polymerization initiated by metal ion-organic substrate redox systems have been carried out by various workers. Polymerization of acrylonitrile (AN) initiated by  $V^{5+}$ -cyclohexanone as the redox system has been reported by Mohanty et al. [1]. Phenol has proven to be a very good retarder in vinyl polymerization. Rout et al. [2] have worked on the retarded polymerization of AN by chalcone. Pospisil et al. [3] have reported the stabilization of paraffin wax at 163°C and of an oil solution of carotene at 75°C by methylene bisphenols. Waters et al. [4] have reported the inhibiting action of monohydric phenols on the autooxidation of olefinic oil. We [7] have also reported the retarded polymerization of AN by phenol with permanganate as the initiator. Until now no one seems to have reported the retardation kinetics with an initiator involving a metal ion like  $V^{5+}$  which cannot itself initiate polymerization, but can do so in the presence of an organic substrate. The present work reports the results on the retardation of  $V^{5+}$ -cyclohexanone initiated polymerization by phenol.

## EXPERIMENTAL

Acrylonitrile (American Cyanamid) was washed with 5% NaOH and 3% o-phosphoric acid followed by repeated washing with conductivity water. Ammonium metavanadate (A.R.), cyclohexanone (A.R., BDH), and  $H_2SO_4$  (18 M; A.R., BDH) were used. Conductivity water was prepared by redistilling distilled water over alkaline  $KMnO_4$  in an all-glass Pyrex unit. The monomer (AN) was made moisture-free by drying over anhydrous  $CaCl_2$ . The polymerization was studied under atmospheric condition.

The required amounts of monomer,  $H_2SO_4$ , and phenol solution in water were taken in the reaction vessel (Pyrex vessel fitted with a B<sub>24/29</sub> socket carrying a B<sub>24/29</sub> cone with inlet and outlet tube) and thermostated at the desired temperature. A required amount of  $V^{5+}$  solution (prepared in 1 M  $H_2SO_4$ ) was added and the time was noted. After a specified time the polymerization was arrested by adding a known excess of ferrous ammonium sulfate solution. The polymer formed was filtered, washed repeatedly with water, and dried to constant weight. The percentage conversion and the rate of polymerization were calculated by using the following formulas:

$$\% \text{ conversion} = \frac{\text{weight of polymer}}{\text{weight of monomer}} \times 100$$

$$\text{Rate of polymerization } (R_p) = \frac{1000 \times W}{V \times t \times M}$$

where  $W$  = weight of polymer

$V$  = volume of reaction mixture in milliliters (20 mL here)

$t$  = time in seconds

$M$  = molecular weight of monomer (for AN,  $M = 53.04$ )

## RESULTS AND DISCUSSION

### Relation between Percentage Conversion and Reaction Time

The percentage conversion was studied at the control condition (without retarder) and with the retarder (Fig. 1). A very interesting observation is that the percentage conversion without retarder increases with the passage of reaction time and the steady state was attained within 90 min. The percentage conversion was found to de-

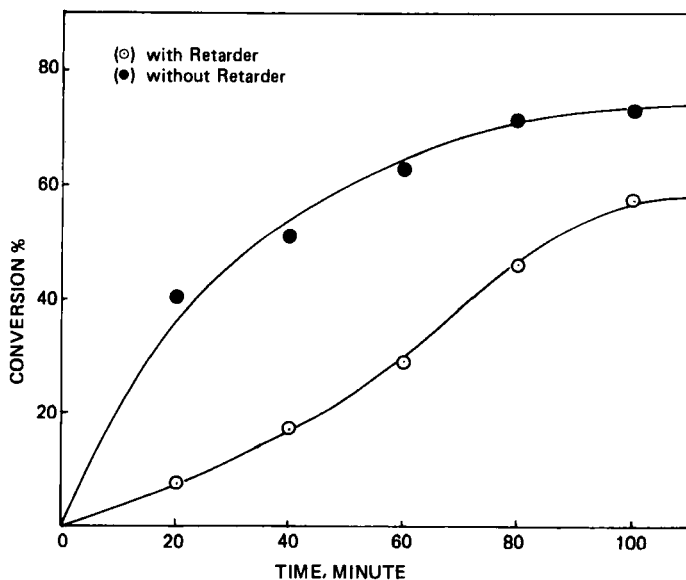


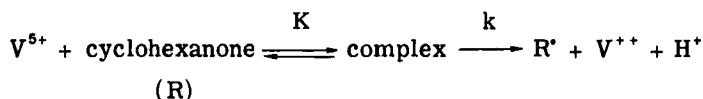
FIG. 1. Time conversion curves.  $[V^{5+}] = 0.02 \underline{M}$ ,  $[CH] = 0.096 \underline{M}$ ,  $[H_2SO_4] = 0.6 \underline{M}$ ,  $[AN] = 0.754 \underline{M}$ ,  $[Ph] = 0.015 \underline{M}$ .

crease considerably by the addition of phenol (0.015 M). This can be attributed to the retarding action of phenol on the rate of polymerization.

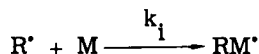
### Reaction Mechanism and Kinetic Scheme

Ce(IV) alone initiates the polymerization of acrylonitrile [8]. From this laboratory we [7] have earlier reported that permanganate also can alone initiate the polymerization of AN in aqueous sulfuric acid medium. Taking  $V^{5+}$ -cyclohexanone as the initiator and phenol as the retarder, we propose the following mechanism to explain our experimental results.

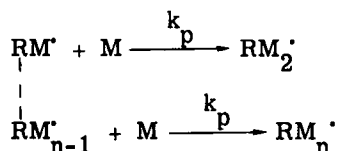
Radical Formation:



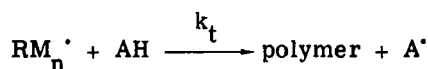
Initiation:



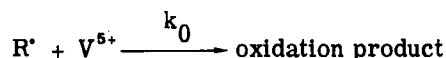
Propagation:



Termination:



Oxidation:



Applying the steady-state principle for the concentration of the free radicals, we have

$$\frac{d[R^*]}{dt} = kK[V^{5+}][R] - k_i[R^*][M] - k_0[R^*][V^{5+}] = 0$$

$$[R^*] = \frac{kK[V^{5+}][R]}{k_i[M] + k_0[V^{5+}]} \quad (1)$$

Again,

$$\frac{d[RM_n^*]}{dt} = k_i[R^*][M] - k_t[RM_n^*][AH] = 0$$

$$[RM_n^*] = \frac{k_i[R^*][M]}{k_t[AH]} \quad (2)$$

Using Eq. (1) in Eq. (2), we have

$$[RM_n^*] = \frac{k_i[M]}{k_t[AH]} \frac{kK[V^{5+}][R]}{k_i[M] + k_0[V^{5+}]}$$

or

$$[RM_n^*] = \frac{k_i kK[V^{5+}][R][M]}{k_t[AH](k_i[M] + k_0[V^{5+}])}$$

The rate of polymerization ( $R_p$ ) is given by

$$R_p = k_p[RM_n^*][M]$$

$$= \frac{k_p k_i kK[V^{5+}][R][M]^2}{k_t[AH](k_i[M] + k_0[V^{5+}])} \quad (3)$$

$$\frac{[M]}{R_p} = \frac{k_t[AH](k_i[M] + k_0[V^{5+}])}{k_i k k_p K[V^{5+}][R][M]}$$

or

$$\frac{[M]}{R_p} = \frac{k_t[AH]}{k k_p k [V^{5+}][R]} + \frac{k_0 k_t[AH]}{k_i k k_p K[R][M]} \quad (4)$$

Plots of  $[M]/R_p$  vs  $1/[M]$  are shown in Fig. 2. We observe that no negative intercept is obtained, which is a very interesting observation in this investigation. Rout et al. [2] have reported that in the retardation of Ce(IV)-initiated polymerization of acrylonitrile by chalcone, the plot of  $[M]/R_p$  versus  $1/[M]$  gives a negative intercept which they have reported to be a general phenomenon for all inhibiting substrates. We [7] have already reported the retardation of the permanganate-initiated polymerization of AN by phenol in which we observed the same phenomenon. But the results obtained in the retardation of  $V^{5+}$ -cyclohexanone initiated polymerization of AN by phenol do not conform to this general phenomenon. Unlike Ce(IV) and permanganate,  $V^{5+}$  cannot alone initiate polymerization. In the presence of cyclohexanone, however, the free radical obtained from the decomposition of the  $V^{5+}$ -cyclohexanone complex initiates polymerization, leading to growing polymer radicals. Since phenol is a proven retarder, the growing polymer radical is probably terminated by phenol through hydrogen

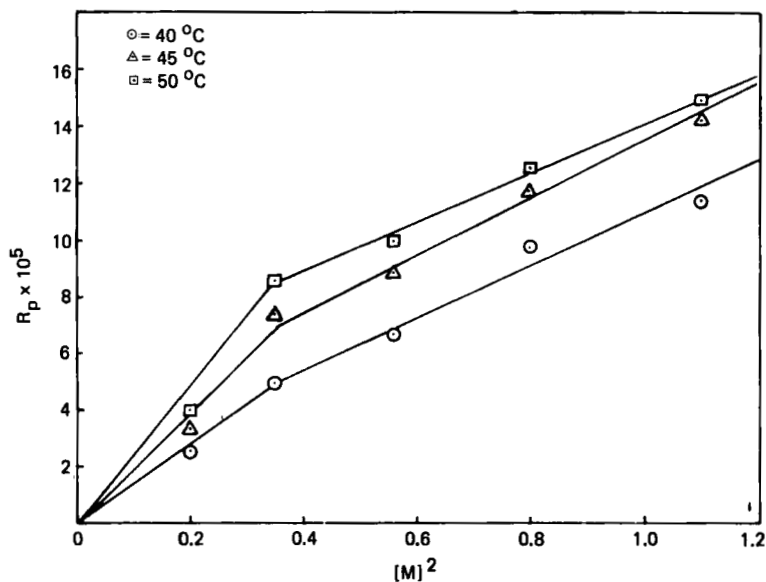


FIG. 2.  $R_p$  vs  $[M]^2$  plots.  $[V^{5+}] = 0.02 \text{ M}$ ,  $[CH] = 0.096 \text{ M}$ ,  $[H_2SO_4] = 0.6 \text{ M}$ ,  $[Ph] = 0.01 \text{ M}$ .

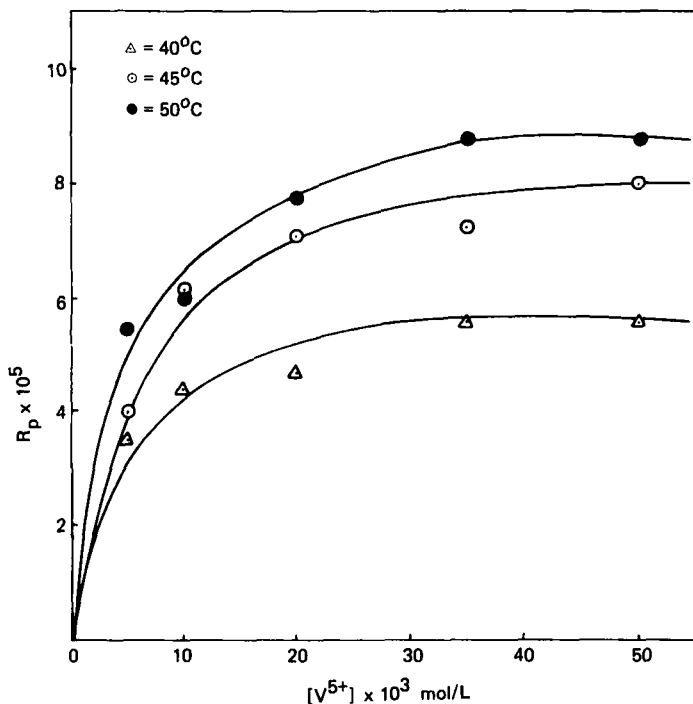


FIG. 3.  $R_p$  vs  $[V^{5+}]$  plots.  $[CH] = 0.096 \text{ M}$ ,  $[H_2SO_4] = 0.6 \text{ M}$ ,  $[AN] = 0.754 \text{ M}$ ,  $[Ph] = 0.01 \text{ M}$ .

abstraction and, in the final step, the initiating free radical ( $R'$ ) is oxidized by  $V^{5+}$  to give the oxidation products.

#### Effect of $V^{5+}$ on the Rate

The rate of polymerization increases with an increase in the value of  $[V^{5+}]$  up to a certain limit and then levels off, as shown in Fig. 3. In the increasing portion of the curve the termination is probably by the retarder. At higher concentrations of the metal ion, termination by the metal ion becomes more prominent. Under the present experimental condition, however, termination is assumed to be exclusively by phenol.

#### Effect of Monomer on the Rate

The rate of polymerization increases with an increase of monomer concentration. Plots of  $R_p$  vs  $[M]^2$  are shown in Fig. 2. It is clear



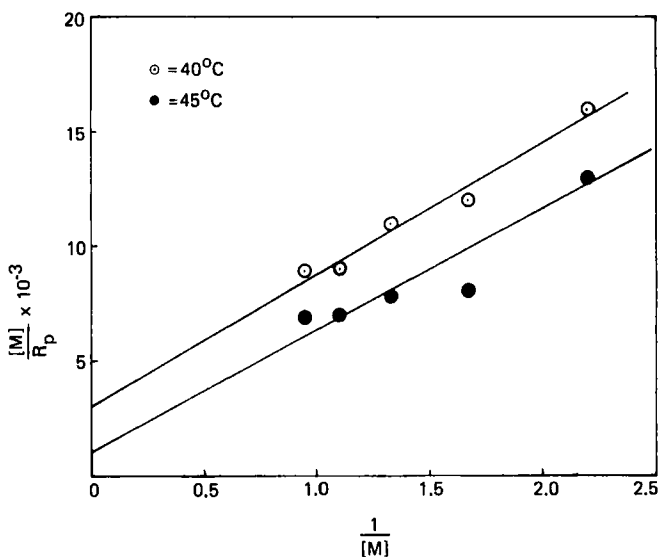


FIG. 4.  $[M]/R_p$  vs  $1/[M]$  plots.  $[V^{5+}] = 0.02 \text{ M}$ ,  $[CH] = 0.096 \text{ M}$ ,  $[H_2SO_4] = 0.6 \text{ M}$ ,  $[Ph] = 0.01 \text{ M}$ .

from Fig. 2 that up to a certain concentration of monomer (0.6 M), plots of  $R_p$  vs  $[M]^2$  are straight lines but at higher concentrations of monomer there is no proportionate increase in the rate of polymerization, which is in good agreement with the kinetic equation

$$R_p = \frac{k_i k_p K [V^{5+}] [R] [M]^2}{k_t [AH] (k_i [M] + k_0 [V^{5+}])}$$

$R_p$  vs  $[M]^2$  plots cannot strictly be straight lines passing through the origin because there is an  $[M]$  term in the denominator. However, plots of  $[M]/R_p$  vs  $1/[M]$  give positive intercepts as shown in Fig. 4, and this fits our derived equation:

$$\frac{[M]}{R_p} = \frac{k_t [AH]}{k_i k_p K [V^{5+}] [R]} + \frac{k_0 k_t}{k_i k_p K} \frac{[AH]}{[R] [M]}$$

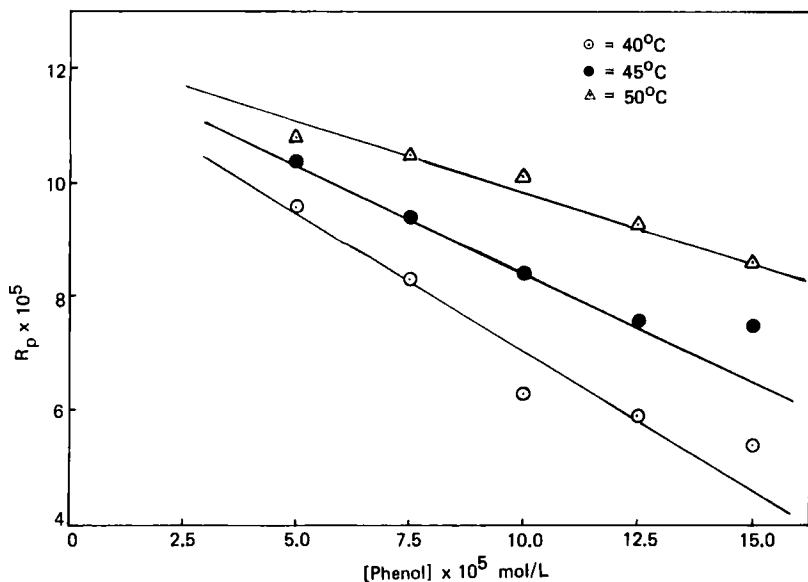


FIG. 5.  $R_p$  vs [phenol] plots.  $[V^{5+}] = 0.02 \text{ M}$ ,  $[CH] = 0.096 \text{ M}$ ,  $[H_2SO_4] = 0.6 \text{ M}$ ,  $[AN] = 0.754 \text{ M}$ .

This result is quite remarkable and contrasts with the previous generalization that for all inhibiting substrates, a plot of  $[M]/R_p$  vs  $1/[M]$  gives a negative intercept. From this we conclude that even if negative intercepts have been obtained in many cases of retarded polymerization, positive intercepts are to be expected in cases where metal ions do not initiate polymerization and the termination step involves hydrogen abstraction leading to the polymer and resonance stabilized free radicals ( $A^*$ ).

#### Effect of Phenol on the Rate

The rate of polymerization decreases with increasing concentrations of phenol (Fig. 5). Similar observations have been made by Simonye et al. [5] and Bird et al. [6] in the study of the effect of phenol on the polymerization of vinyl acetates. The propagating polymer chain undergoes termination by the retarder (AH) by hydrogen abstraction, and this leads to the formation of polymer and resonance stabilized free radicals ( $A^*$ ).

The concentration of  $H_2SO_4$  was raised from 0.3 to 0.7 M. It was observed that the rate of polymerization increased consistently in this range.

### Effect of Organic Solvents

The polymerization was carried out in aqueous sulfuric acid medium. The effect of some organic solvents when added in equal proportions (5% v/v) has been studied, and the rate of polymerization was found to follow the order DMF > MeOH > control > dioxane.

### Effect of Some Inorganic Salts

The effect of some inorganic salts (such as  $K_2SO_4$ ,  $MnSO_4$ ,  $NaCl$ , and  $CuSO_4$ ) on the rate of polymerization has been studied. All the salts except  $CuSO_4$  increase the rate of polymerization. This is contrary to what was observed in the polymerization of AN by the permanganate-glucose redox system in this laboratory. This seems to be a general feature for all retarding substrates. The explanation given by Bamford et al. [9] that ions capable of existing in more than one valance state may behave as retarders under certain conditions by entering into an oxidation-reduction type of mechanism seems to be true.

### Effect of Temperature

The polymerization of AN was studied in the temperature range 40–50°C. The rate of polymerization increased with an increase of temperature in this range. In retarded polymerization of AN by phenol with  $KMnO_4$  as the initiator, the rate of polymerization was found to decrease with increasing temperature as reported earlier [7].

The overall energy of activation as calculated from an Arrhenius plot is found to be 8.06 kcal/mol. The composite rate constant  $k_0 k_t / k_1 k_p K$  as calculated from a plot of  $[M]/R_p$  vs  $1/[M]$  is found to be  $5.04 \times 10^4$ .

### ACKNOWLEDGMENT

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