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Redox-Initiated Polymerization of Vinyl Monomers with Cu(II)-Cyclohexanone System in Acetonitrile Medium. A Kinetic Study

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ABSTRACT

The kinetics of the oxidation of cyclohexanone (CHN) by hydrated copper(II) perchlorate (HCP) in an acetonitrile medium has been studied. The orders with respect to [CHN] and [HCP] were found to be one each. This HCP + CHN redox system has been used for the polymerization of acrylonitrile, methyl methacrylate, and methyl acrylate. The rate of polymerization was proportional to $[\mathrm{CHN}]^{0.5}$, $[\mathrm{HCP}]^{0.5}$, and $[\mathrm{M}]^{1.8}$. Based on the above results, a probable mechanism for oxidation and polymerization is proposed.

INTRODUCTION

The redox-initiated polymerization of vinyl monomers with various metal ions such as Ce(IV) [1, 2], Mn(III) [3], Cr(VI) [4], and Co(III) [5], alone or in combination with reducing agents, has proved to be

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very useful. In all cases the polymerization studies were carried out in aqueous medium. But reports on redox-initiated polymerization of vinyl monomers in pure organic solvents are sporadic. Pure organic solvents allow homogeneous polymerization besides being capable of dissolving many monomers unlike aqueous medium. Therefore it was thought worthwhile to search for new redox couples which are capable of initiating vinyl polymerization in nonaqueous media. From a literature survey it is known that the redox potential [6] of the Cu(II)/Cu(I) couple in acetonitrile medium is 0.76 V, high enough to oxidize some organic compounds. Hydrated copper(II) perchlorate (HCP) in acetonitrile medium has been used as an analytical reagent for the estimation of various organic compounds such as ascorbic acid [7] and hydroquinone. Preliminary studies have been shown that HCP oxidized cyclohexanone (CHN) via a radical pathway. This prompted us to undertake a systematic study of the oxidation of CHN by HCP in acetonitrile medium and the polymerization of vinyl monomers with the above redox system to obtain insight into the mechanistic aspects of oxidation as well as polymerization reactions.

EXPERIMENTAL

All the chemicals used were of the BDH AnalaR grade. The monomers methyl methacrylate (MMA), methyl acrylate (MA), and acrylonitrile (AN) were purified by distillation at a low pressure under an N_2 atmosphere after washing with 5% NaOH, and in case of AN with 3% H_3PO_4 followed by 5% NaOH. The acetonitrile was refluxed with P_2O_5 (5 g/L) for 3 h and distilled twice before use. The polymerization experiments were conducted in the dark under an N_2 atmosphere to prevent any photochemical reaction and inhibition by atmospheric oxygen. Time-average kinetics were followed and assumed to be steady-state kinetics. The rate of monomer disappearance was followed by a gravimetric procedure. The polymers which are soluble in acetonitrile were precipitated by the addition of methanol. The oxidation was studied under pseudo-first-order conditions. The rate of reaction was followed by estimating the unreacted Cu^{2+} iodometrically at regular intervals. The detailed experimental procedure is given elsewhere [8].

RESULTS AND DISCUSSION

The kinetics of oxidation of CHN by HCP in acetonitrile medium showed the following features. Under the condition $[HCP] \ll [CHN]$, a plot of log [HCP] vs time was linear, indicating a first-order dependence of the rate on [HCP] (Fig. 1A). From the slopes of these plots the pseudo-first-order rate constants (k') were calculated. The plot of log k' vs log [CHN] was also linear (Fig. 1B) with unit slope, indi-

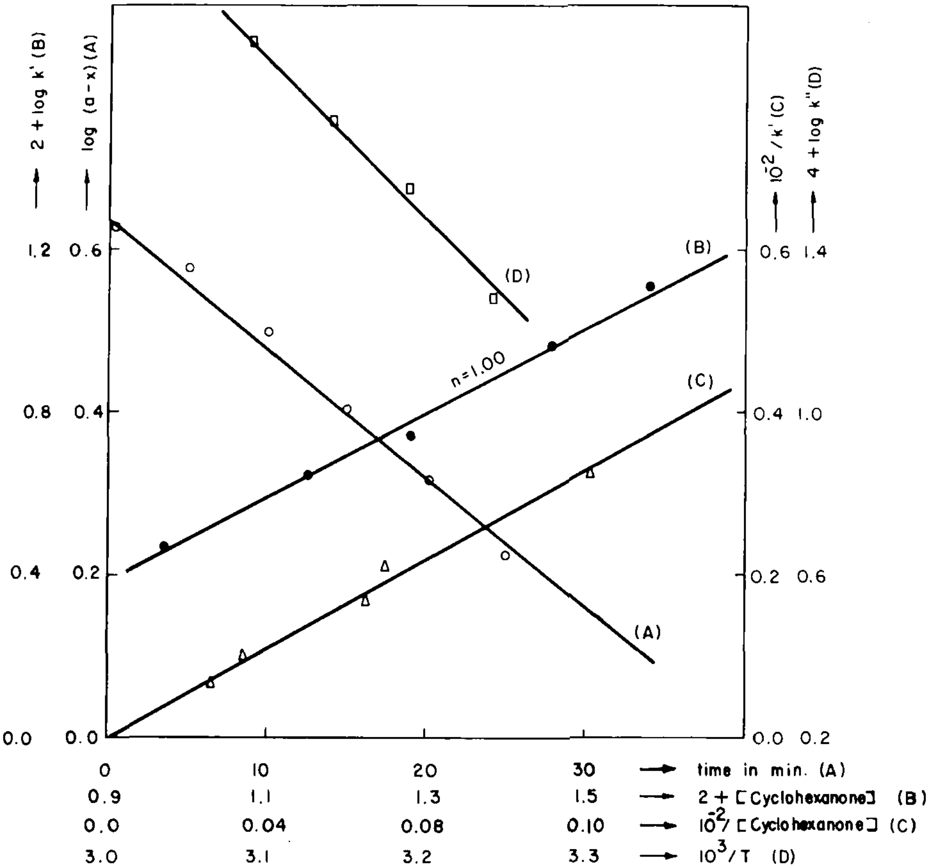

FIG. 1. (A) Plot of log (a - x) vs time: [CHN] = 9.50×10^{-2} $\underline{M}$, [HCP] = 6.75×10^{-3} $\underline{M}$, 45°C. (B) Plot of 2 + log k' vs 2 + log [CHN]: [HCP] = 7.05×10^{-3} $\underline{M}$, 45°C. (C) Plot of 1/k' vs 1/[CHN]: Conditions same as in B. (D) Plot of 4 + log k' vs 10^3/T: Conditions same as in A.

cating the order in CHN to be unity. Under the conditions employed, the product of oxidation was identified as cyclohexane-1,2-dione. Stoichiometric studies revealed that 1 mol of CHN consumed 4 mol of HCP. Induced polymerization was observed by the addition of acrylonitrile to the reaction mixture. The effect of added $NaClO_4$ on the rate of oxidation was negligible, suggesting that the reaction is of the ion-dipole type. Since the reaction was carried out in acetonitrile medium, the possibility of CHN existing in the enol form is discounted. The plot of $1/k'$ vs $1/[CHN]$ was linear and passed through the origin (Fig. 1C), indicating the absence of any complex formation between the oxidant and the substrate. In the light of the above information, a plausible mechanism for the oxidation of CHN may be written as follows:

$$C_6H_{10}O + HCP \xrightarrow{k} \dot{C}_6H_9O + H^+$$

$$\dot{C}_6H_9O + HCP \xrightarrow[\text{fast}]{H_2O} C_6H_9(OH)O + Cu^+$$

$$C_6H_9(OH)O + 2HCP \xrightarrow[\text{fast}]{} C_6H_7O_2 + 2Cu^+$$

From the above mechanism the rate law comes out to be

$$-d[HCP]/dt = k[HCP][CHN]$$

An examination of the IR spectrum of the polyacrylonitrile formed by the addition of acrylonitrile to the HCP and CHN system gave the typical carbonyl frequency at 1670 cm^{-1}, indicating the ketonic function to be intact in the radical. This supports the assumption of α-C–H bond fission in the slow step of the reaction.

Activation parameters were found to be 43.2 kJ/mol, 91.8 kJ/mol, and -160 J/deg • mol for activation energy, free energy of activation, and entropy of activation.

POLYMERIZATION

Polymerization of vinyl monomers (MMA, MA, and AN) was carried out with the HCP + CHN redox system in acetonitrile medium at 45°C. There was no polymerization in the absence of CHN, even after 24 h. The polymerization of MA and MMA is homogeneous but that of AN is heterogeneous.

Effect of [HCP] on R_p. It is known that Cu(II) is a good radical trapper [9] and a linear terminator [10] of vinyl polymerization in aqueous medium. But in the present case, in acetonitrile medium with an increase in [HCP], the rate of polymerization increased and the order in [Cu(II)] was found to be 0.5 from the slope of a double logarithmic plot of R_p and [HCP] (Fig. 2A). This clearly suggests HCP is not participating in the termination steps unlike in aqueous medium. If HCP were participating in the termination step, the rate of polymerization should have been independent or decreased with an increase in [HCP], which was not observed.

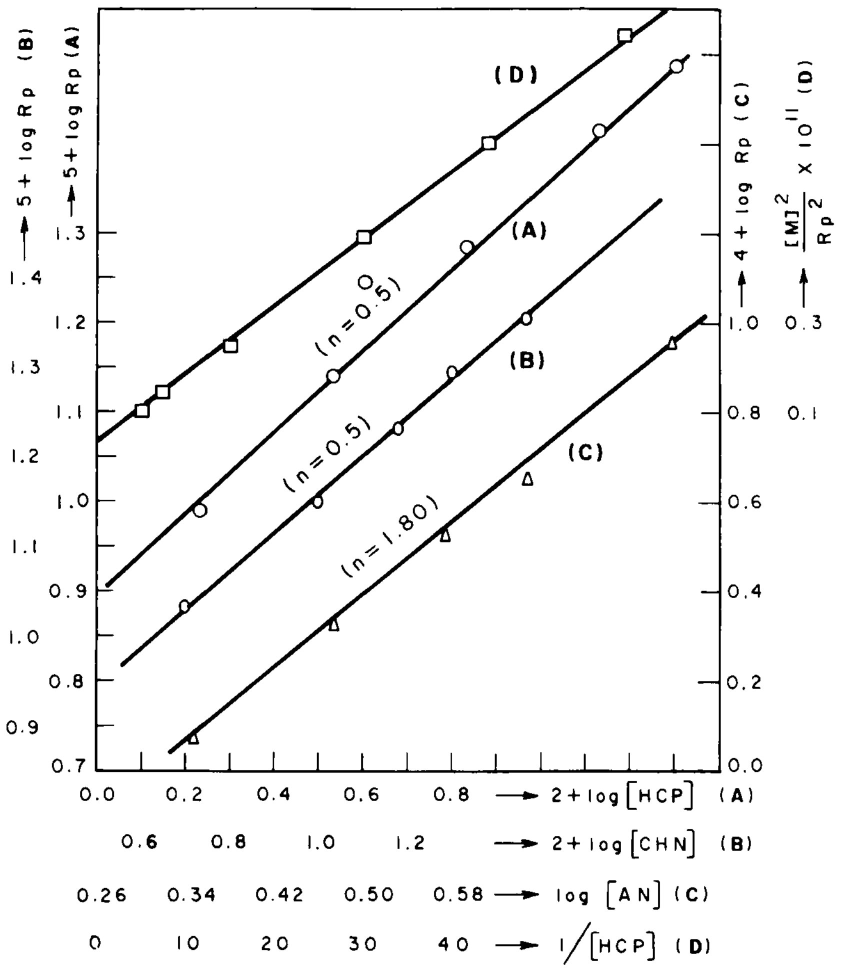

FIG. 2. (A) Plot of 5 + log R_p vs 2 + log [HCP]: [CHN] = 0.20 M, [AN] = 3.00 M, 45°C. (B) Plot of 5 + log R_p vs 2 + log [CHN]: [HCP] = 6.75 × 10^{-2} M, [AN] = 3.00 M, 45°C. (C) Plot of 4 + log R_p vs log [AN]: [HCP] = 6.75 × 10^{-2} M, [CHN] = 0.20 M, 45°C. (D) Plot of $[M]^2/R_p^2$ vs 1/[HCP]: [HCP] = 0.20 M, [AN] = 3.00 M, 45°C.

Effect of [CHN] on R_p. With an increase in [CHN] the rate of polymerization also increased and the order in [CHN] was found to be 0.4 as is evident from the slope of the double logarithmic plot of R_p vs [CHN] (Fig. 2B). This strongly suggests that the polymerization is initiated by primary radicals produced from the oxidation of CHN by HCP and that neither the primary radicals nor HCP are participating in the termination steps. This also indirectly suggests that the mutual termination of two growing polymer radicals is the most likely termination step.

Effect of [Monomer] on R_p. It is now known that the addition of organic solvents reduces the rate of polymerization in aqueous medium [11]. To carry out the polymerization in nonaqueous medium, we have to use a high concentration of the monomer. While the concentration of the monomer increases, the concentration of the solvent decreases, and this can be sufficient to cause an increase in the rate of polymerization. This suggests that the experimentally determined order is greater than expected, as in aqueous medium, if the concentration of acetonitrile is not kept constant. Since this is not possible, the order in the monomer is expected to be high.

The rate of polymerization increased significantly with an increase in [M], and the order with respect to [M] was found to be 1.80 (Fig. 2C). It is now well known that an order of 1.5 in M is either due to linear [12] or mixed [13] (mutual as well as linear) termination. In the present case the linear or mixed terminations are ruled out on the basis of the 0.5 order in [HCP] and [CHN]. The high order in M (i.e., >1.5) in this case is attributed to a solvent effect and therefore the termination is presumed to be of the mutual type.

The HCP + CHN redox system is useful to polymerize methyl acrylate (MA), methyl methacrylate (MMA), acrylonitrile, etc. (Table 1). This redox system is not useful for the polymerization of acrylamide and methacrylamide. This is probably because of the reduction in oxidation potential of the Cu(II)/Cu(I) couple in the presence of the amide group, which makes it ineffective insofar as oxidizing CHN to produce the initiating radicals is concerned.

On the basis of the above results and discussion, the following mechanism is proposed.

Production of initiating radicals (HCP is written as Cu^{2+}):

$$Cu^{2+} + CHN \xrightarrow{k_1} R^{\bullet} + H^{+} + Cu^{+}$$

$$R^{\bullet} + Cu^{2+} \xrightarrow{k_o} \text{products}$$

TABLE 1. Effect of [MA] and [MMA] on the Rate of Polymerization: [HCP] = 0.050 $\underline{M}$, [CHN] = 0.200 $\underline{M}$, 310 K

[MMA]	$R_p \times 10^4$	[MA]	$R_p \times 10^4$
0.940	0.363	1.10	1.99
1.41	0.741	1.65	3.98
1.88	1.13	2.20	6.30
2.31	1.18	2.75	9.55
2.82	1.25	3.30	12.6

Initiation of polymerization:

$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet}$$

Propagation:

$$RM^{\bullet} + M \xrightarrow{k_p} RM_2{}^{\bullet}$$

. . . .

. . . .

$$M^{\bullet}_{n-1} + M \longrightarrow M_2^{\bullet}$$

Termination of polymerization:

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_t} M_{n+m}$$

Applying the steady-state principle to reactive intermediates, the rate law comes out to be

$$R_p = \frac{k_p}{k_t^{1/2}} \left\{ \frac{k_1 k_i [HCP][CHN]}{k_i[M] + k_o[HCP]} \right\}^{1/2} [M]^{3/2}$$

which clearly explains all the experimental results obtained. Squaring and taking the reciprocal of the above equation for R_p, we get

$$\frac{[M]^2}{R_p{}^2} = \frac{k_t k_o}{k_1 k_i k_p{}^2 [M][CHN]} + \frac{k_t}{k_1 k_p{}^2 [HCP][CHN]}$$

According to the above expression, a plot of $[M]^2/R_p^2$ vs $1/[HCP]$ should give a straight line with a positive slope and intercept which, in fact, was obtained in the present study (Fig. 2D), thereby supporting the mechanism proposed and the derived rate law for polymerization. The value of the composite rate constant i.e., $k_1k_p^2/k_t$, and k_o/k_i values have been evaluated from the slope and intercept values of the plot in Fig. 2D and were found to be 2.5×10^{-7} and 2.25, respectively.

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