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Kinetics of Polymerization of Methyl Methacrylate Initiated by the Potassium Peroxodisulfate-Malonic Acid Redox System Catalyzed by Ag(I)

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ABSTRACT

The kinetics of polymerization of methyl methacrylate (MMA) initiated by the potassium peroxodisulfate ($K_2S_2O_8$)-malonic acid (MA) redox system catalyzed by Ag(I) was studied in aqueous solution at 35°C. The rate of polymerization (R_p) was proportional to $[MMA]^{1.4}$, $[K_2S_2O_8]^{0.27}$, $[MA]^{0.23}$, and $[Ag^+]^{0.5}$. The overall energy of activation was calculated to be $13.5 \text{ kcal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ between 20 and 45°C.

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INTRODUCTION

The oxidizing power of peroxosalts was first investigated by Bayer et al. [1] in 1901. However, their ability to initiate vinyl polymerization was first reported by Bacon [2] in 1946. Since then, potassium peroxodisulfate has been widely used as an initiator of vinyl polymerization [3-7]. The polymerization of MMA using $K_2S_2O_8$ as initiator in combination with ascorbic acid [8], citric acid [9], thioglycolic acid [10], and thiomalic acid [11] has been studied. The same reaction initiated by the Mn^{3+} -malonic acid [12] and Ce^{4+} -malonic acid [13] redox systems has also been reported. Mehrotra et al. [14] studied the catalyzed oxidation of malonic acid by peroxodisulfate. For the first time, we have now studied the polymerization of MMA initiated by the $K_2S_2O_8$ -MA redox system catalyzed by the Ag(I) ion at 35°C. The kinetic results of our investigation and the mechanism proposed are presented here.

EXPERIMENTAL

Materials

Peroxodisulfate was E. Merck (GR) grade. It was used without further purification. Fresh solution was prepared for each day's experiments. Malonic acid was a Riedel sample. MMA (BDH) was washed with 5% sodium hydroxide solution, followed by washing with deionized water to free it from alkali, and dried over anhydrous calcium chloride. The middle fraction of the monomer was collected by vacuum distillation. Silver nitrate was BDH (AnalaR) grade. All other reagents used were also of AnalaR grade. Water, doubly distilled and deionized, was used for the preparation of all solutions. The nitrogen used for deaeration was purified by passing it through Fieser's solution, saturated lead acetate solution, distilled water, and finally through a wash bottle containing the monomer solution.

Technique

The desired quantities of water, monomer, malonic acid, and silver nitrate were placed in the reaction vessel of ~100 mL capacity, deaerated, and then thermostatted. Polymerization was initiated by adding a known amount of $K_2S_2O_8$ solution. The polymer obtained was filtered through a G.3 sintered crucible and dried to constant weight at 70°C. The rates of polymerization were then calculated from the weights of polymer formed. The experiments were conducted in the dark.

RESULTS AND DISCUSSION

Rate Dependence on Initiator Concentration

The rate of polymerization R_p increased with increasing peroxydisulfate concentration in the range from 2.5 to 5.0×10^{-2} mol/L. The order of the reaction with respect to initiator concentration, calculated from the slope of the double logarithmic plot (Fig. 1) of R_p versus initiator concentration, was found to be 0.27 . Shukla et al. [11] have also reported a 0.27 order dependence of the rate on $[S_2O_8^{2-}]$ in

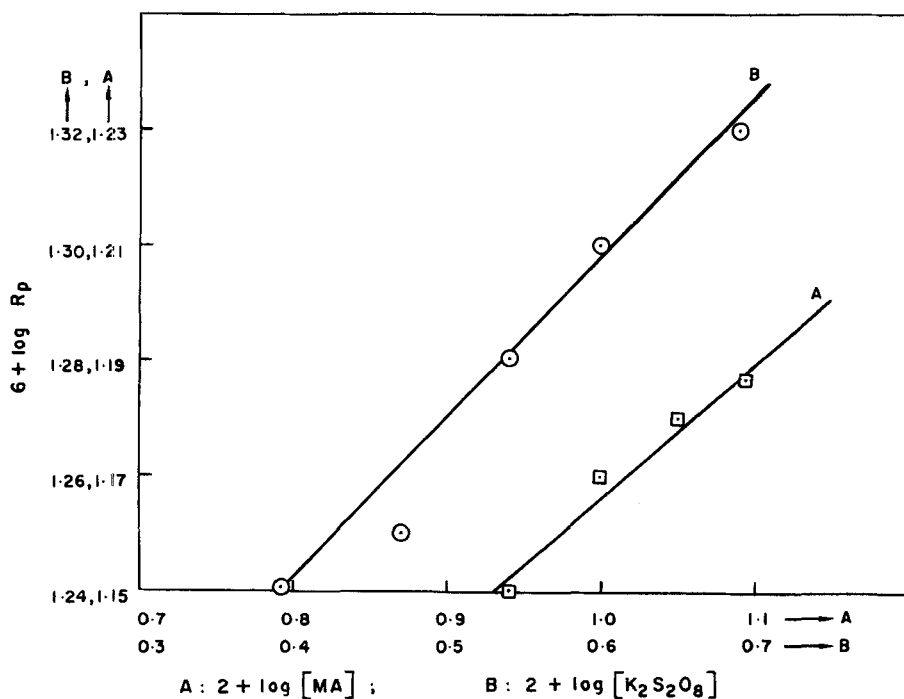


FIG. 1. Dependence of R_p on malonic acid and $K_2S_2O_8$ concentrations. (A) Plot of $\log R_p$ vs $\log [MA]$, slope = 0.23 , $[K_2S_2O_8] = 2.5 \times 10^{-2}$ mol/L, $[MMA] = 7.04 \times 10^{-2}$ mol/L, $[Ag^+] = 1 \times 10^{-4}$ mol/L, $35^\circ C$. (B) Plot of $\log R_p$ vs $\log [K_2S_2O_8]$, slope = 0.27 , $[MMA] = 7.04 \times 10^{-2}$ mol/L, $[MA] = 6.25 \times 10^{-2}$ mol/L, $[Ag^+] = 1 \times 10^{-4}$ mol/L, $35^\circ C$.

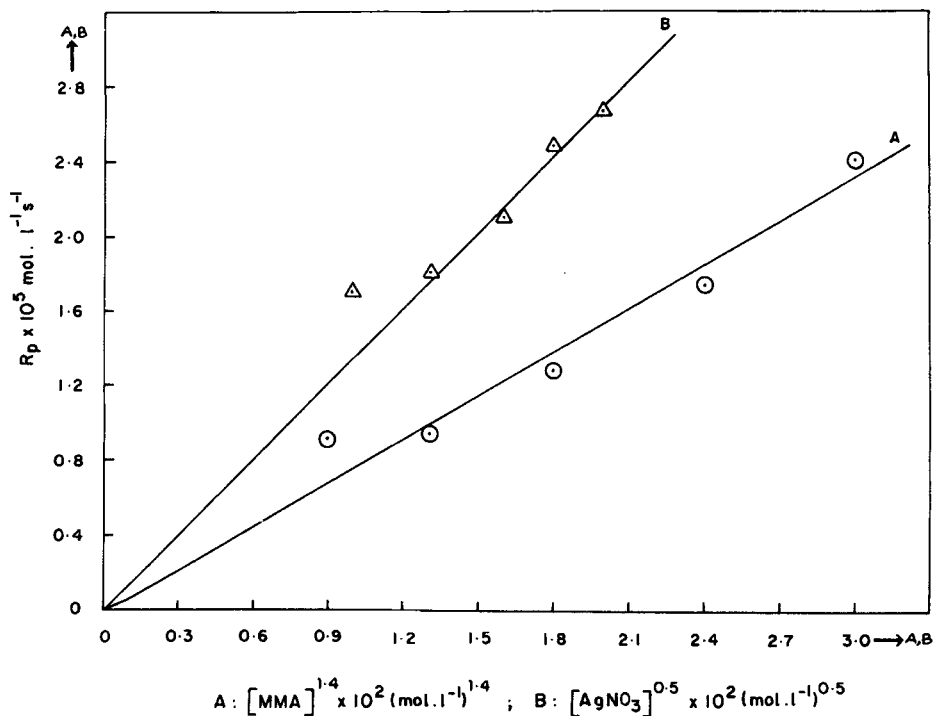


FIG. 2. Dependence of R_p on monomer and Ag(I) concentrations.

(A) Plot of R_p vs $[\text{MMA}]^{1.4}$, $[\text{K}_2\text{S}_2\text{O}_8] = 2.5 \times 10^{-2}$ mol/L, $[\text{MA}] = 6.25 \times 10^{-2}$ mol/L, $[\text{Ag}^+] = 1 \times 10^{-4}$ mol/L, 35°C . (B) Plot of R_p vs $[\text{AgNO}_3]^{0.5}$, $[\text{K}_2\text{S}_2\text{O}_8] = 2.5 \times 10^{-2}$ mol/L, $[\text{MMA}] = 7.04 \times 10^{-2}$ mol/L, $[\text{MA}] = 6.25 \times 10^{-2}$ mol/L, 35°C .

the polymerization of MMA by the $\text{K}_2\text{S}_2\text{O}_8$ -thiomalic acid redox pair with $[\text{S}_2\text{O}_8^{2-}] > 10$ mmol/L.

Rate Dependence on Activator Concentration

The rate of the reaction increased with increasing concentration of activator (malonic acid) from 0.06 to 0.13 mol/L. The slope of the double logarithmic plot (Fig. 1) of R_p vs $[\text{MA}]$ was found to be 0.23.

Rate Dependence on Monomer Concentration

R_p was found to increase with increasing concentration of monomer from 2.35 to 8.22×10^{-2} mol/L (Fig. 2). The order with respect to monomer concentration was found to be 1.4. A similar order had been observed in the Mn^{3+} -malonic acid [12] and Ce^{4+} -malonic acid systems [13].

Rate Dependence on Temperature

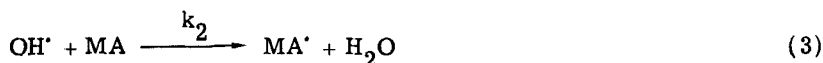
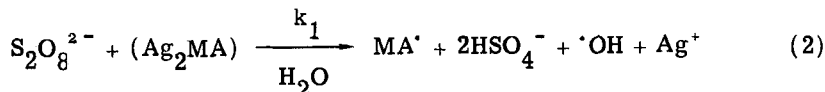
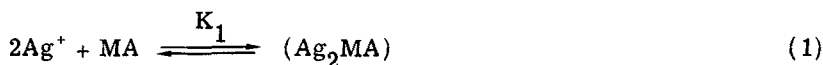
The rate increased regularly with increasing temperature from 20 to 45°C. The overall activation energy calculated from the Arrhenius plot was found to be $13.5 \text{ kcal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. In the polymerization of MMA by $K_2S_2O_8$ -thiomalic acid, Shukla et al. [11] reported an activation energy of $11.8 \text{ kcal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, which is close to our experimental result.

Effect of Ag(I) Ion

The effect of the concentration of Ag(I) on R_p was studied from 2 to 5×10^{-4} mol/L (Fig. 2). R_p was found to depend on $[Ag^+]^{0.5}$. The plot of R_p vs $[AgNO_3]^{0.5}$ was linear and passed through the origin, indicating that there is no contribution of uncatalyzed polymerization to R_p under our experimental conditions [15].

REACTION MECHANISM

The following mechanism was found to explain our results.





It is assumed that $k_4 [\text{MA}]^2 \gg k_3 [\text{MA}^\cdot][\text{M}]$.

By applying the steady-state principle to the above reaction scheme, the following kinetic expression is obtained for $[\text{R}_n^\cdot]$

$$[\text{R}_n^\cdot] = \left(\frac{k_3[\text{M}]}{k_t} \right)^{1/2} \left(\frac{2k_1K_1[\text{Ag}^+]^2[\text{S}_2\text{O}_8^{2-}][\text{MA}]}{k_4} \right)^{1/4} \quad (8)$$

From this, R_p was calculated to be

$$R_p = \frac{k_p k_3^{1/2}}{k_t^{1/2}} \left(\frac{2k_1K_1}{k_4} \right)^{1/4} [\text{Ag}^+]^{1/2} [\text{S}_2\text{O}_8^{2-}]^{1/4} [\text{MA}]^{1/4} [\text{M}]^{3/2} \quad (9)$$

where M = monomer. Equation (9) explains the orders obtained.

The formation of a 2:1 complex between Ag^+ and malonic acid was assumed, since Ag^+ ions are known to form complexes with carboxylic acids. The dependence of R_p on $[\text{M}]^{3/2}$ confirmed the involvement of monomer in the radical production step and also the incidence of mutual termination. However, the normal dependence of R_p on $[\text{Ag}^+]^{1/2}$ and the lower (0.25) orders on $[\text{MA}]$ and $[\text{PS}]$ pointed toward the possibility of bimolecular decay of primary radicals, which controls the concentration of initiating primary radicals. The kinetics of this polymerization closely resembles the results of the polymerization of methyl methacrylate by the glycine-peroxodisulfate- Ag^+ system [16]. Further studies using other substituted organic acids as reducing agents in the Ag^+ - $\text{K}_2\text{S}_2\text{O}_8$ system are in progress.

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