

Kinetic Study on Peroxidation of Benzaldehyde by Polymer-Immobilized Cobalt-EDTA Complex

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ABSTRACT: Polymer-immobilized cobalt-EDTA complex was prepared by grafted copolymerization of methacrylic acid (MAA) and acrylonitrile (AN) initiated by redox initiation of EDTA-2Na (Ethylenediamine tetraacetic acid disodium salt) with ceric ion (Ce^{2+}). High yield and selectivity for peroxidation of benzaldehyde were obtained when using the polymer-immobilized cobalt-EDTA complex as a catalyst. With the concentration of benzaldehyde increasing, the concentration of perbenzoic acid was increased from 0.38M to 0.98M, but yield of perbenzoic acid decreased from 0.76M to 0.65M. With the amount of the polymer support increased, the yield of perbenzoic acid increased from 70% to 82%. The selectivity remained about 82% in the various amounts of the polymer support. The activation energy of peroxidation of benzaldehyde was 43.4 KJ/mole. The expression of the reaction rate was: $r_i = k[RCHO]_0^{1.0}[\text{polymer support}]^{0.5}$. A mechanism for peroxidation of benzaldehyde catalysed by polymer-immobilized cobalt-EDTA complex was proposed in this investigation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3248–3257, 2001

Key words: metal immobilized; chelated polymer; peroxidation; kinetic

INTRODUCTION

The liquid phase oxidation of hydrocarbon is an important process in the chemical industry with catalysis as a key factor.^{1,2} It has been reported that a chelate polymer usually has a strong interaction between the chelate group and metal ion.^{3–6} The functional groups of P, S, As, imino-diacetic acid, hydroxamic acid, dithiocarbamate, aniline, sulfur, imine, thiol and phenyl have been introduced to form the chelated polymer. The chelated polymer, whose properties depended on the

chelating properties of the ligand, has been employed for analysis, concentration, food extraction, separation and recycle of the noble metal in wastewater and seawater. When metal-chelated polymer was used as a heterogeneous polymer support,^{7–14} it had high activity, high selectivity and recoverability. Simplifying the process of separation and purification and quality of the product would be better.

Polymers supported with EDTA chelate groups were synthesized, and the peroxidation of benzaldehyde by this polymer-immobilized cobalt-EDTA complex was also studied earlier.¹⁵ The polymer-immobilized cobalt-EDTA complex had good activity in the peroxidation of benzaldehyde due to the linking of EDTA and metal ion. That led to a

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change of the oxidation potential of the metal ions¹⁶ and improved the oxidation performance. Features of the liquid phase peroxidation of benzaldehyde with polymer-immobilized cobalt-EDTA complex include the co-active effect of water, high yield, high selectivity and no inductive period. The mechanism is possibly different from the mechanism of the oxidation with homogeneous catalyst and ion exchange resin catalyst. Consequently, the mechanism and the kinetic of peroxidation of benzaldehyde catalyzed by cobalt-immobilized polymer support were studied in this investigation.

EXPERIMENTAL

Preparation of Polymer Support

The acrylonitrile (AN) and methacrylic acid (MAA) (Merck Co.) were purified by distillation. Reagent-grade ethylenediamine tetraacetic acid disodium salt (EDTA-2Na; Merck Co.) and ammonium cerium nitrate ($\text{Ce}^{+}(\text{IV})$; Merck Co.) were used without further purification. Distilled water was obtained by using a Waters Millipore purifying system. Aqueous copolymerization of AN (75 g) with MAA (4 wt %, 5 wt %, 6 wt % and 7 wt %) initiated with 30 g of EDTA/Ce(IV) (1 : 1 mole ratio) were conducted in a 1 L, five-necked pyrex kettle equipped with a stirrer, condenser, nitrogen inlet and thermistor. The stirring rate was maintained at 500 rpm. The reaction temperature was controlled by a good thermostat controlled water bath. A Soxhlet system was used to purify copolymer via methanol as a solvent. The chelated polymer support was immersed in 0.5M $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ aqueous solution and oscillated for 24 hr at 50°C. Then, the purple color of polymer support was washed with distilled water several times until the cobalt ions in the washing water weren't detected by an ultraviolet/visible spectrophotometer (UV). The polymer support was dried in a vacuum oven and stored in a drying box.

The Oxidation of Benzaldehyde with Polymer-Immobilized Cobalt-EDTA Complex

The oxidation of benzaldehyde was conducted in a 250 ml, four-necked Pyrex kettle equipped with a stirrer, condenser, oxygen inlet and thermistor. The flow rate of oxygen was maintained at 100 ml/min. After the oxygen had purged the kettle

for 20 mins, benzaldehyde was added to the reactor, which contained cobalt chelated polymer in acetone solvent, to begin oxidation. At appropriate intervals, two samples (about 1 ml) were taken for measuring the concentrations of peracid and total acid, respectively. The iodimetry method, with starch reagent as indicator, and the sodium hydroxide titration method were used to determine the concentration of peracid and total acid, respectively. The concentration of benzoic acid was calculated by subtracting the concentration of perbenzoic acid from the concentration of total acid.

RESULTS AND DISCUSSION

The Effect of Concentration of Compounds

The oxidation of benzaldehyde was conducted under 100 ml/min flow rate of oxygen and 0.1 g of polymer-immobilized cobalt-EDTA complex (0.51 meq/g) at 20°C reaction temperature. The initial concentration of benzaldehyde was 0.5M, 1.0M and 1.5M, respectively. Figure 1 shows the generation rate of the perbenzoic acid against reaction time. The generation rate became mild after 3 hrs. With the increase in the initial concentration of benzaldehyde, the concentration of perbenzoic acid increased from 0.38M to 0.98M, but yield of perbenzoic acid decreased from 0.76M to 0.65M. The relation of selectivity of perbenzoic acid to reaction time is shown in Figure 2, which illustrates that the selectivity decreases with increasing initial concentration of benzaldehyde. The result was attributed to the fact that perbenzoic acid would be further decomposed into benzoic acid by benzaldehyde at high initial concentrations. All initial reaction rates for various initial concentrations of benzaldehyde were calculated and are shown in Table I. With increasing initial benzaldehyde concentration, the initial reaction rate increased from $5.4 \times 10^{-3}\text{M}/\text{min}$ to $1.64 \times 10^{-2}\text{M}/\text{min}$. The logarithmic curve for the initial reaction rate vs. concentration of benzaldehyde is illustrated in Figure 3. The slope of reaction curves is approximately 1.0. This indicates that the initial rate is directly proportional to the concentration of benzaldehyde. The expression is as follows:

$$r_i \propto k[\text{RCHO}]^{1.0}$$

The Effect of the Amount of Polymer Support

The curves of yield of perbenzoic acid vs. reaction time at various weights of catalyst (0.1 g, 0.2 g

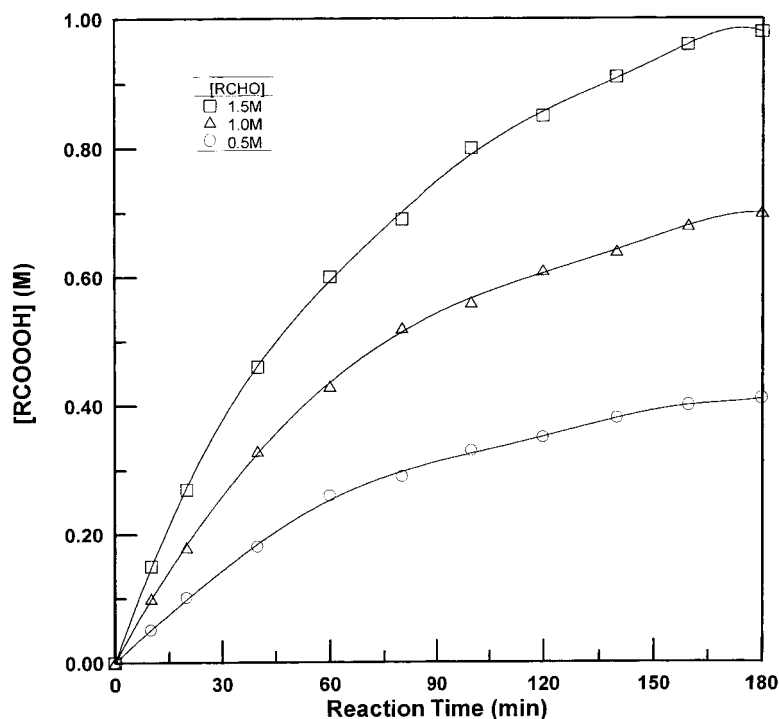


Figure 1 The reaction vs. time curves of peroxidation of benzaldehyde at various concentrations of benzaldehyde.

and 0.3 g) are shown in Figure 4. With increasing amount of the polymer-supported catalyst, the yield of perbenzoic acid increased from 70% to 82%. The relation of selectivity of perbenzoic acid to reaction time is presented in Figure 5, which shows that the selectivity almost remained at about 82% with various amounts of the polymer support. In addition, the initial reaction rates were calculated from the results of Figure 4, and are shown in Table II. With increasing amount of the polymer support, the initial reaction rate increased from $1.06 \times 10^{-2} M/\text{min}$ to $1.81 \times 10^{-2} M/\text{min}$. The logarithmic curve of the initial reaction rate vs. the amount of polymer support is shown in Figure 3. The gradient is 0.5, indicating that the rate is proportional to the square root of the amount of polymer support. The expression is as follows:

$$r_i \propto k'[\text{Co(II)} - \text{P}]^{0.5}$$

Where: P was polymer support.

The Effect of Reaction Temperature

The reaction was conducted at various reaction temperatures, 15°C, 20°C and 25°C, to study the

effect of temperature on the oxidation of benzaldehyde. The generation reaction curves of perbenzoic acid at different time are shown in Figure 6. With increasing temperature, the yield of perbenzoic acid increased in the range of reaction temperature at a rate of 10% for 5°C. Meanwhile, the selectivity of perbenzoic acid remained at about 81% at different reaction temperatures, as shown in Figure 7. The initial reaction rates were calculated from the above results and are shown in Table III. With the increase of the reaction temperature, the initial reaction rate increased from $7.9 \times 10^{-3} M/\text{min}$ to $1.47 \times 10^{-2} M/\text{min}$. The logarithmic curve of the initial reaction rate vs. the reciprocal of temperature is shown in Figure 3, which illustrates the relation of reaction rate to temperature following the Arrhenius law. Thus, the activation energy (E_a) of the peroxidation reaction was calculated to be 43.4 KJ/mole from the value of $-E_a/RT$, which was obtained from the slope of the curve: that value is in the range of the activation energy of the radical reaction.

Peroxidation Mechanism of Benzaldehyde

Some metal ions have the function of catching and carrying oxygen, for example, ferrous ions or

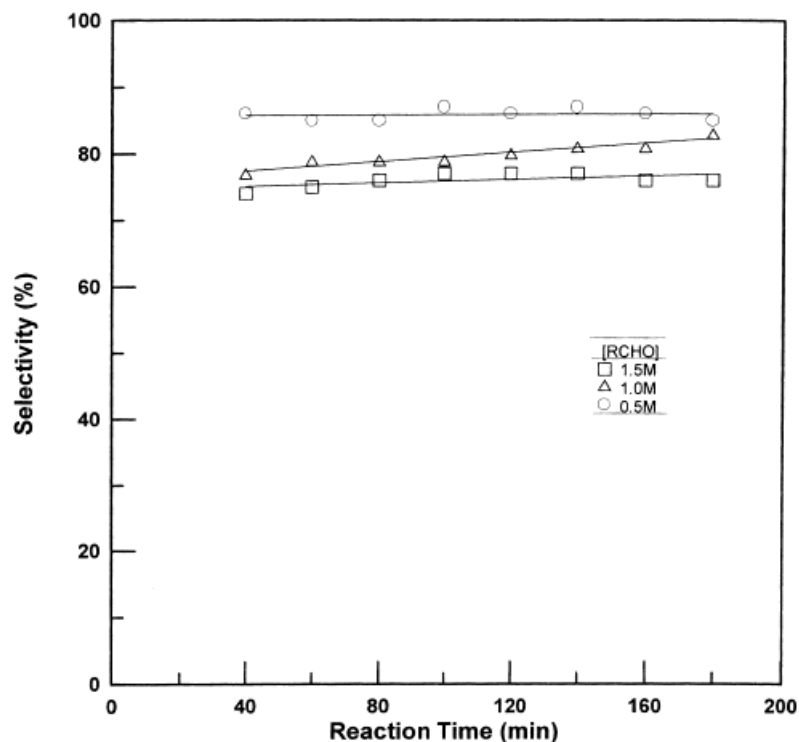
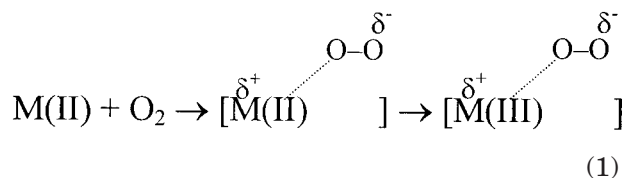


Figure 2 The selectivity of peroxidation of benzaldehyde at various concentrations of benzaldehyde.

cobalt ions can be chelated and oxidized by oxygen to form complexes.^{17,18}



M: Co, Fe ions. It is interesting that the oxidation potential of metal ions can be promoted when the metal ions are chelated with EDTA, from a literature report.¹⁶ Thus, the oxidation potential of the polymer-immobilized cobalt-EDTA complex

would increase and it would accelerate the reaction of the metal ion with oxygen. The metal ions in the chelated state containing oxygen with high valence have high catalytic activity, as shown in the following reaction expression,

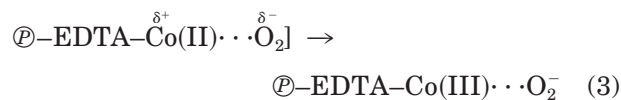
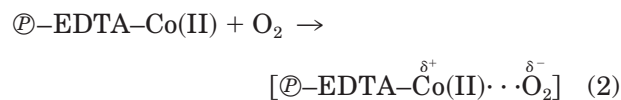


Table I Effect of $[C_6H_5CHO]_0$ on Oxidation of Benzaldehyde with Chelated Catalyst

$[RCHO]_0^a$ (M)	$[RCOOH]^a$ (M)	$[RCOOH]^a$ (M)	Initial Reaction Rate (M/min)	Conversion (%)	Yield (%)	Selectivity (%)
0.5	0.38	0.069	5.40×10^{-3}	90	0.76	84.6
1.0	0.70	0.180	1.06×10^{-2}	88	0.70	79.6
1.5	0.98	0.320	1.64×10^{-2}	87	0.65	75.4

^a R: C_6H_5- .

^b Catalyst = 1.0 g; O_2 flow rate = 100 mL/min; at 20°C.

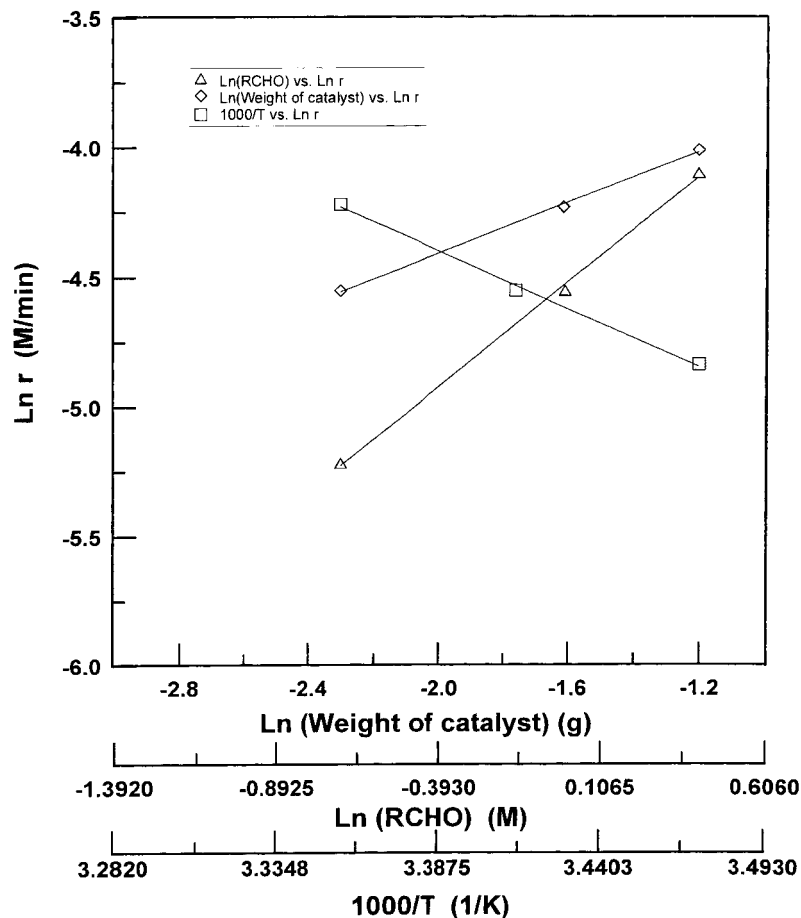
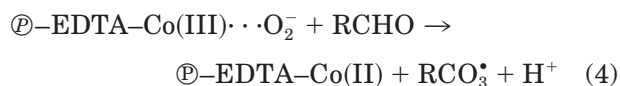


Figure 3 The logarithm plot of reaction rate vs. concentration of compounds in the peroxidation of benzaldehyde catalyzed by polymer-immobilized cobalt-EDTA complex.

Then, the metal ion complexes can further catalyze reaction of benzaldehyde to generate perbenzoic acid radical RCO_3^\bullet ,



Therefore, a possible mechanism of the liquid phase peroxidation of benzaldehyde, with polymer-immobilized cobalt-EDTA complex as a catalyst, is given as follows:

- (1) Benzaldehyde is absorbed by polymer support particles:



Where subscript (b) and (p) represent the solution phase and polymer support particle, respec-

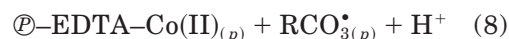
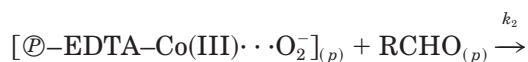
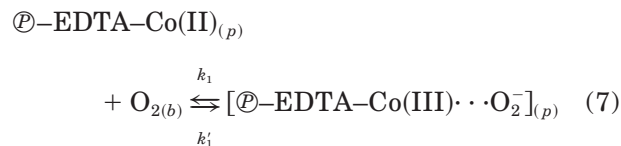
tively, and K_1 is absorption constant of benzaldehyde.

- (2) Oxygen is dissolved in the solution:



Where subscript (g) represents the gas phase and K_2 is dissolution constant of oxygen.

- (3) Initiation



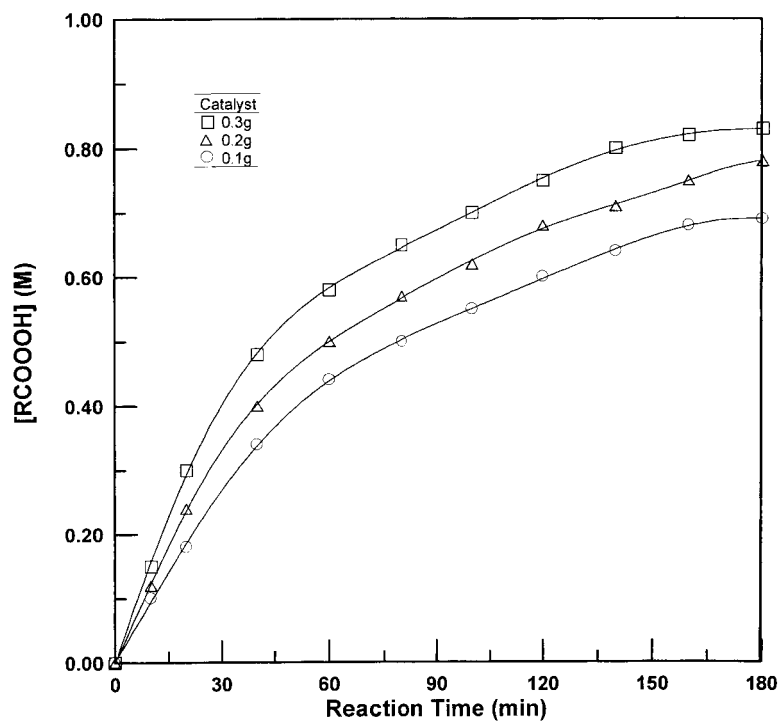


Figure 4 The reaction vs. time curves of peroxidation of benzaldehyde with various amounts of polymer support.

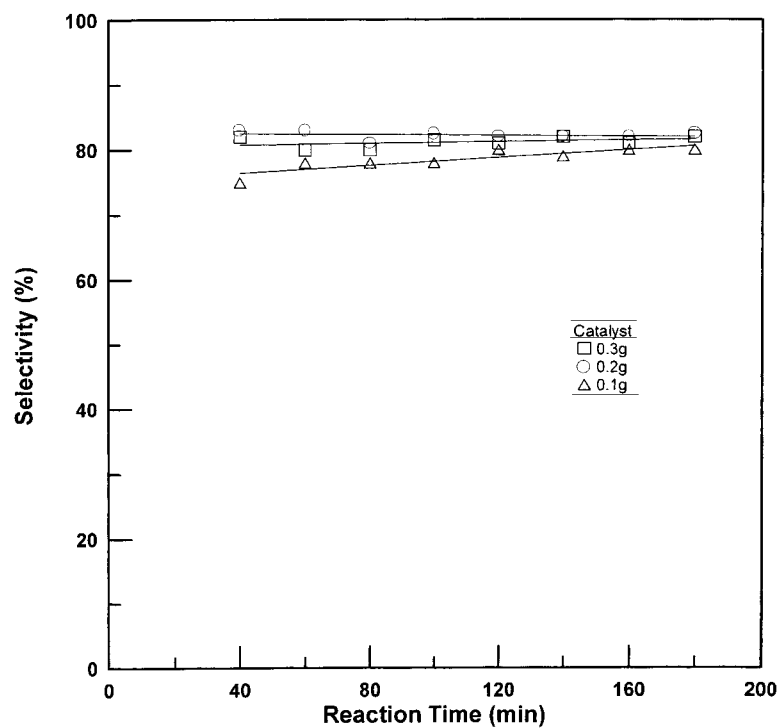


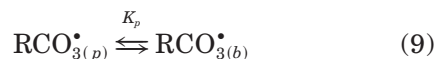
Figure 5 The selectivity of peroxidation of benzaldehyde with various amounts of polymer support.

Table II Effect of Weight of Catalyst on Oxidation of Benzaldehyde with Chelated Catalyst

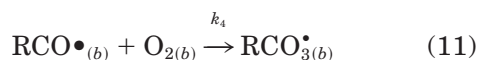
Catalyst (g)	[RCOOOH] ^a (M)	[RCOOH] ^a (M)	Initial Reaction Rate (M/min)	Conversion (%)	Yield (%)	Selectivity (%)
0.1	0.70	0.180	1.06×10^{-2}	88	0.70	79.6
0.2	0.77	0.165	1.46×10^{-2}	94	0.77	82.4
0.3	0.82	0.170	1.81×10^{-2}	99	0.82	82.8

^a R : C₆H₅-.^b [RCHO] = 1.0M; O₂ flow rate = 100 mL/min; at 20°C.

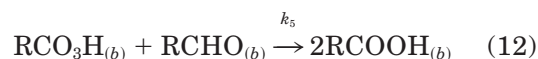
Where ⊕ represents polymer support

Where K_p is the distribution coefficient of RCO_3^{\bullet} in the solution phase and polymer support.

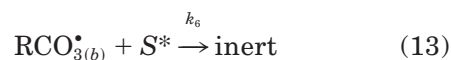
(4) Propagation



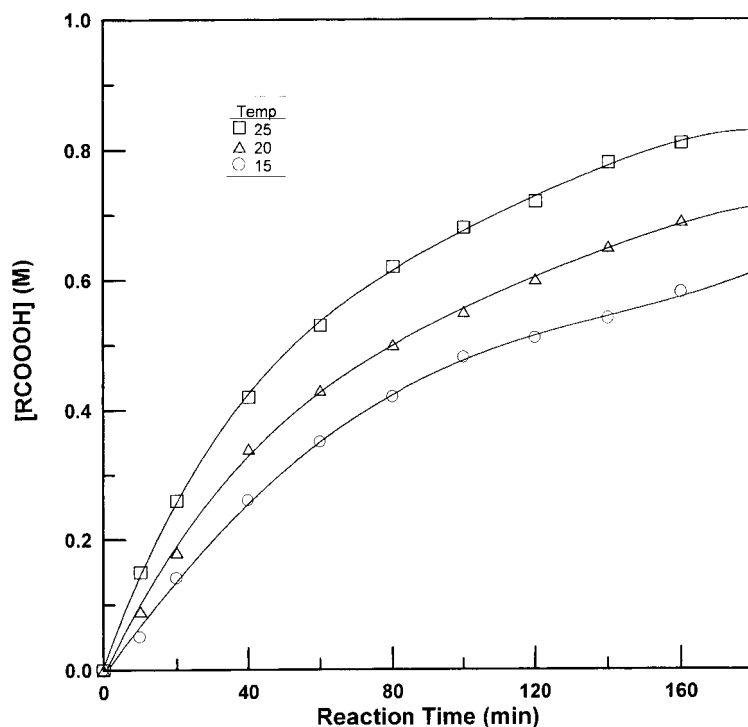
(5) Decomposition (Baeyer-Villger)



(6) Termination



The scheme of the overall reaction mechanism is shown in Figure 8. Firstly, oxygen is adsorbed by

**Figure 6** The reaction vs. time curves of peroxidation of benzaldehyde at different reaction temperatures.

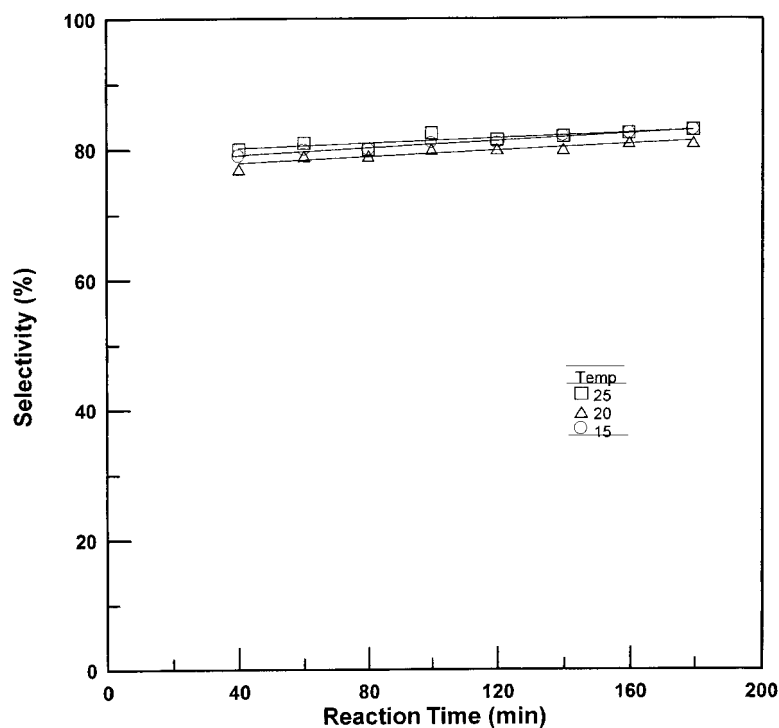


Figure 7 The selectivity of peroxidation of benzaldehyde at different reaction temperatures.

cobalt(II)-chelated polymer, and the cobalt(II) in chelated polymer is oxidized into cobalt(III). Then, benzaldehyde is adsorbed and oxidized to perbenzoic acid radicals by cobalt(III)-O₂⁻-chelated polymer support. The cobalt(III)-O₂⁻-chelated polymer would be returned to cobalt(II)-O₂⁻-chelated polymer. The perbenzoic acid and RCO[•] is formed by radical initiation peroxidation. RCO[•] could be reacted with oxygen into perbenzoic acid radicals, which could initiate benzaldehyde reaction again. Finally, perbenzoic acid could be further oxidized to benzoic acid or other compounds in side reactions.

The Kinetics of Peroxidation of Benzaldehyde

The active radicals were mainly RCO₃[•] for peroxidizing of benzaldehyde from the above mecha-

nism, consistent with the literature report.¹⁹ The mass transfer resistance of the components can be ignored for reaction with good mechanical mixing. Thus, the concentrations of the radical RCO₃[•] in solution phase and particle could conform to a linear relationship, that is:

$$[\text{RCO}_3^{\bullet}]_{(b)} = K_p [\text{RCO}_3^{\bullet}]_{(p)}$$

and

$$\frac{[\text{P-EDTA-Co(III)} \cdot \cdot \text{O}_2^-]_{(p)}}{[\text{P-EDTA-Co(II)}]_{(p)}[\text{O}_2]} = \frac{k_1}{k_1'} = K \quad (15)$$

The expression of the perbenzoic acid generation rate is:

Table III Effect of Temperature on Oxidation of Benzaldehyde with Chelated Catalyst

Temperature (°C)	[RCOOH] ^a <i>M</i>	[RCOOH] ^a <i>M</i>	Initial Reaction Rate (<i>M</i> /min)	Conversion (%)	Yield (%)	Selectivity (%)
15	0.62	0.137	7.90×10^{-3}	75	0.62	81.9
20	0.70	0.180	1.06×10^{-2}	88	0.70	79.6
25	0.81	0.182	1.47×10^{-2}	99	0.81	81.7

^a R : C₆H₅-.

^b [RCHO] = 1.0*M*; catalyst = 1.0 g; O₂ flow rate = 100 mL/min; at 20°C.

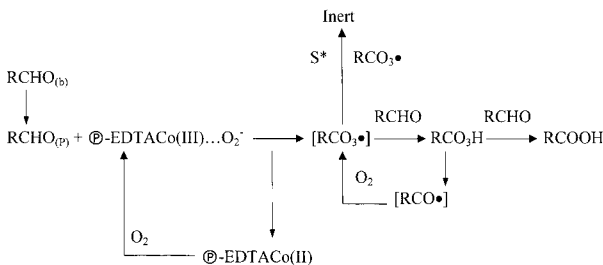


Figure 8 The scheme for reaction mechanism of peroxidation of benzaldehyde catalyzed by polymer-immobilized cobalt-EDTA complex.

$$\begin{aligned} \frac{d[\text{RCO}_3^*]_{(b)}}{dt} &= K_p k_2 [\text{Ⓟ-EDTA-Co(III)} \cdot \cdot \text{O}_2^-]_{(p)} \\ &\quad \times [\text{RCHO}]_{(p)} - k_3 [\text{RCO}_3^*]_{(b)} \\ &\quad \times [\text{RCHO}]_{(b)} + k_4 [\text{RCO}^*]_{(b)} [\text{O}_2] \\ &\quad - 2k_7 [\text{RCO}_3^*]_{(b)}^2 - k_6 [\text{S}^*] [\text{RCO}_3^*] \end{aligned} \quad (16)$$

$$\begin{aligned} \frac{d[\text{RCO}^*]_{(b)}}{dt} &= k_3 [\text{RCO}_3^*]_{(b)} [\text{RCHO}]_{(b)} \\ &\quad - k_4 [\text{RCO}^*]_{(b)} [\text{O}_2] \end{aligned} \quad (17)$$

$$\begin{aligned} \frac{d[\text{RCO}_3\text{H}]_{(b)}}{dt} &= k_3 [\text{RCO}_3^*]_{(b)} [\text{RCHO}]_{(b)} \\ &\quad - k_5 [\text{RCO}_3\text{H}]_{(b)} [\text{RCHO}]_{(b)} \end{aligned} \quad (18)$$

$$\frac{d[\text{RCO}_2\text{H}]_{(b)}}{dt} = 2k_5 [\text{RCO}_3\text{H}]_{(b)} [\text{RCHO}]_{(b)} \quad (19)$$

Hypothesizing for the quasi-stationary state, then

$$\frac{d[\text{RCO}_3^*]_{(b)}}{dt} = 0 \quad (20)$$

$$\frac{d[\text{RCO}^*]_{(b)}}{dt} = 0 \quad (21)$$

Substituting (20) and (21) into (16) and (17), respectively, and combining two expressions, then:

$$\begin{aligned} 2k_7 [\text{RCO}_3^*]_{(b)}^2 + k_6 [\text{S}^*] [\text{RCO}_3^*]_{(b)} - K_p k_2 K \\ \times [\text{Ⓟ-EDTACo(II)}]_{(p)} [\text{O}_2] [\text{RCHO}]_{(p)} = 0 \end{aligned} \quad (22)$$

$$\begin{aligned} \therefore [\text{RCO}_3^*]_{(b)} &= \frac{1}{4k_7} [-k_6 [\text{S}^*] + (k_6^2 [\text{S}^*]^2 + 8k_7 K_p k_2 K \\ &\quad \times [\text{Ⓟ-EDTACo(II)}]_{(p)} [\text{O}_2] [\text{RCHO}]_{(p)})^{1/2}] \end{aligned} \quad (23)$$

The generation rate (r_i) of perbenzoic acid is:

$$\begin{aligned} r_i &= \frac{d[\text{RCO}_3\text{H}]_{(b)}}{dt} \\ &= -k_5 [\text{RCO}_3\text{H}]_{(b)} [\text{RCHO}]_{(b)} \\ &\quad + \frac{k_3}{4k_7} [\text{RCHO}]_{(b)} [-k_6 [\text{S}^*] + (k_6^2 [\text{S}^*]^2 \\ &\quad + 8k_7 K_p k_2 K [\text{Ⓟ-EDTACo(II)}]_{(p)} [\text{O}_2] \\ &\quad \times [\text{RCHO}]_{(p)})^{1/2}] \end{aligned} \quad (24)$$

Since, $[\text{RCHO}]_o = [\text{RCHO}]_{(b)} + [\text{RCHO}]_{(p)}$

Hypothesizing, $[\text{RCHO}]_{(p)} = C_1^* \ll [\text{RCHO}]_{(b)}$ at initial peroxidation.

Then, $[\text{RCHO}]_o \approx [\text{RCHO}]_{(b)}$

The volume of the reaction system remained constant ($V = \text{constant}$),

Therefore, $[\text{RCHO}]_{(p)} = C_1^*/V = C_1$

In the initial period, $t = 0$ and $[\text{RCO}_3\text{H}] = 0$

In addition, when the oxygen supply was adequate, $[\text{O}_2]_{(b)} = C_2$

Hypothesizing, the termination reaction could be mainly self-collision of radical RCO_3^* , that is, $K_6 \rightarrow 0$, thus the expression of the initial generation rate of perbenzoic acid is:

$$r_i = k [\text{RCHO}]_o [\text{Ⓟ-EDTACo(II)}]_{(p)}^{(1/2)} \quad (25)$$

where

$$k = k_3 \frac{(8k_7 K_p k_2 K C_1 C_2)^{1/2}}{4k_7}$$

From the above mechanism, the reaction orders of concentration of benzaldehyde and polymer-immobilized cobalt-EDTA complex are 1 and 0.5, respectively, which is consistent with the above experiment results.

CONCLUSION

The peroxidation of benzaldehyde with the polymer-immobilized cobalt-EDTA complex as a catalyst was obtained at high yield and selectivity of perbenzoic acid. With increasing benzaldehyde concentration, the amount of perbenzoic acid in-

creased from 0.38M to 0.98M, but yield of perbenzoic acid decreased from 0.76M to 0.65M. The selectivity of perbenzoic acid remained at about 82% with various amounts of the polymer support. The activation energy of peroxidation of benzaldehyde was 43.4 KJ/mole. A possible reaction mechanism was proposed and the expression of initial generation rate of perbenzoic acid was given. The expression of the reaction rate is: $r_i = k[\text{RCHO}]_o^{1.0}[\text{polymer support}]^{0.5}$.

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