*Studies on Organic Peroxides. IV. Polymerization of Vinyl Acetate in Benzoyl Peroxide-Fe(II)-Benzoin Redox System**

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Polymerization of vinyl monomers in the redox systems of non-aqueous solution has been widely studied by W. Kern et al.[1]. According to them, in the redox system which consists of ferrous ion, benzoin and benzoyl peroxide, the following reactions take place by the Haber-Weiss one-electron transfer mechanism[2], in which the ferric ion is reduced to the ferrous by benzoin acting as reductant:

$$\mathrm{P+Fe^{2+} \xrightarrow{k_1} RCOO\cdot + RCOO^- + Fe^{3+}} \quad (1)$$

$$\mathrm{BzH_2+2Fe^{3+} \xrightarrow{k_2} 2Fe^{2+} + Bz + 2H^+} \quad (2)$$

where P, $\mathrm{BzH_2}$, Bz and $\mathrm{RCOO\cdot}$ represent benzoyl peroxide, benzoin, benzil and benzoate radical, respectively; k_1 and k_2 are the rate constants of the reactions 1 and 2, respectively.

Ukida[3] has ascertained the reaction 2 polarographically, and has also found that the rate of polymerization of vinyl acetate in this redox system was appreciably affected by the amount of ferrous salt added. The reaction 2 may reasonably be assumed to take place in two steps as follows:

$$\mathrm{BzH_2+Fe^{3+} \xrightarrow{k_2} Fe^{2+} + BzH\cdot + H^+}$$

$$\mathrm{BzH\cdot+Fe^{3+} \xrightarrow{rapid} Fe^{2+} + Bz + H^+} \quad (2')$$

No kinetic considerations seem, however, to have been proposed about the redox polymerization in this system.

In this paper, the dependence of the rate and the extent of polymerization of vinyl acetate on the initial concentration of the ferrous ion which was added was studied by following the course of the rate of polymerization dilatometrically, to make clear the mechanism of the ferrous-ion catalysed decomposition of benzoyl peroxide in ethanol.

Experimental

Reagents. — In order to remove aldehydes, commercial vinyl acetate was washed with 5% sodium bisulfite solution, followed by washing with water, then the monomer was dried with calcium chloride, and stored in the dark after distillation. Just before use, the monomer was distilled once more and the fraction at 71.5∼73°C was used. Ferrous chloride ($\mathrm{FeCl_2\cdot 4H_2O}$) was crystallized from iron powder and hydrochloric acid, and stored in carbon dioxide atomosphere to prevent oxidation. Ethanol was repeatedly distilled with calcium oxide to remove water. Benzoyl peroxide and benzoin were prepared and recrystallized in the usual manner.

Procedure. — Ethanolic solution of ferrous chloride and vinyl acetate solution containing benzoyl peroxide and benzoin were mixed, and then introduced into a cylindrical glass dilatometer which consists of a reaction vessel, 1.3 cm. in diameter and 15 cm. in length with a capillary tube of 25 cm. After removing the gas dissolved in the solution under reduced pressure and below -50°C, the dilatometer was sealed off and held in a thermostat at 50°C.

The initial concentration of benzoyl peroxide and benzoin was 10^{-2} mol. both per liter. The decrease in volume of the solution was followed by a travelling microscope. As the extent of conversion is directly proportional to the extent of decrease in volume of the solution, the former can be calculated by measuring the latter. In order to find the ratio of the extent of conversion to that of decrease in volume, five dilatometers containing polymerized solution were taken at random and each polymer was dried under reduced pressure and weighed. The mean value of the ratio was found to be 3.63 which is very close to the value, 3.65, reported by Starckweather et al.[4].

The temperature in the dilatometer increases somewhat owing to the inefficient dissipation of the heat of reaction; however, as the increment was at most 0.5°C, the temperature might be taken as constant during the polymerization.

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[1] W. Kern, *Makromol. Chem.*, **1**, 209, 246 (1947); W. Kern, R. Schulz and J. Stallmann, ibid., **6**, 216 (1951); W. Kern and R. Schulz, ibid., **13**, 210 (1954).

[2] F. Haber and P. Weiss, *Proc. Roy. Soc. London*, **A 147**, 332 (1934).

[3] J. Ukida, *Chem. High Polymers* (*Kobunshi Kagaku*), **10**, 358 (1953).

[4] H. G. Starckweather and G. B. Taylor, *J. Am. Chem. Soc.*, **52**, 4708(1930).

Results and Discussion

The extent of conversion, y, can be defined as a fraction of monomer converted into polymer, i. e. $1-[M]/[M]_0$, where $[M]$ and $[M]_0$ are the concentrations of the monomer at $t=t$ and $t=0$, respectively. The plots of y against t for various initial concentrations of the ferrous ion, x, in the case of the polymerizations of vinyl acetate containing 20% ethanol are shown in Fig. 1.

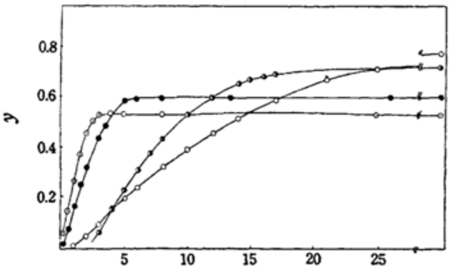

Fig. 1. Polymerization of vinyl acetate in 20% ethanol at 50°C.
$x\cdot 10^4$ (mol./l.):
○ 0, ◑ 1.0, ● 5.0, ⊙ 10.0

As seen in Fig. 1, the rate of conversion depends on the amount of ferrous salt added. In the case of rapid polymerization, the increasing viscosity of the solution at high conversion causes distortion of the meniscus and makes accurate reading difficult. Considerably sharp curvatures shown in Fig. 1 would be due to this reason.

TABLE I

DEPENDENCE OF MOLE RATIO AND FERROUS ION CONCENTRATION ON THE INITIAL RATE OF CONVERSION, THE EXTENT OF CONVERSION AND INDUCTION PERIOD

r	$x\cdot 10^4$ (mol./l.)	$(\mathrm{d}y/\mathrm{d}t)_0^2\cdot 10^2$ (hr.$^{-2}$)	y_∞	Z	ind. period (hr.)
0.63	0.0	0.14	0.740	0.55	—
	2.5	0.16	0.649	0.91	4.0
	5.0	0.20	0.649	0.91	1.5
	10.0	0.25	0.597	1.20	1.5
1.89	0.0	0.12	0.791	0.41	7.5
	1.0	0.42	0.709	0.66	1.5
	5.0	1.00	0.600	1.18	1.5
	10.0	1.96	0.547	1.61	1.0
2.52	0.0	0.25	0.773	0.45	1.0
	1.0	0.96	0.715	0.63	2.5
	5.0	2.90	0.595	1.23	0.2
	10.0	6.76	0.523	1.82	—
5.67	0.0	0.25	0.825	0.33	1.0
	1.0	0.80	0.792	0.41	—
	5.0	4.00	0.737	0.56	—
	10.0	9.00	0.655	0.94	—

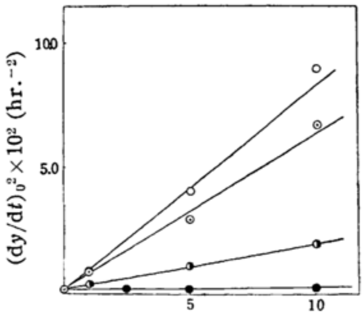

Fig. 2. Dependence of the rate of conversion on x for various values of mole ratio r.
r: ● 0.63, ◑ 1.89, ⊙ 2.52, ○ 5.67

The square of the initial rate of conversion, $(\mathrm{d}y/\mathrm{d}t)_0^2$, the extent of conversion when no more polymerization proceeds, y_∞, and the value of induction period are listed in Table I. For each value of mole ratio, r, of the initial concentration of the monomer to that of ethanol, the plot of the square of $(\mathrm{d}t/\mathrm{d}y)_0$ against x, gives a straight line shown in Fig. 2. This relation may be derived kinetically in the following manner.

The polymerization of vinyl acetate is initiated by the radicals produced from the decomposition of benzoyl peroxide. Assuming a stationary state with benzoate radicals, the rate of polymerization can be expressed as follows:

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t=(k_p/k_t^{1/2}) \times (k_d+k_1[\mathrm{Fe}^{2+}])^{1/2}[\mathrm{P}]^{1/2}[\mathrm{M}] \qquad (3)$$

where $[\mathrm{M}]$ and $[\mathrm{Fe}^{2+}]$ are the concentrations of the monomer and the ferrous ion, respectively, and k_p, k_t and k_d are the rate constants of chain growth, chain termination and apparent spontaneous decomposition of benzoyl peroxide, respectively.

The thermal decomposition of benzoyl peroxide in ethanol is of the first order with respect to the concentration of benzoyl peroxide and the rate of decomposition is the sum of a spontaneous cleavage and a radical induced chain reaction[5]. The following expression for the ferrous ion concentration may be derived from reactions 1 and 2:

$$k_1[\mathrm{P}][\mathrm{Fe}^{2+}]=2k_2[\mathrm{BzH}_2][\mathrm{Fe}^{3+}] \qquad (4)$$

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[5] S. Kato and F. Mashio, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kôgyô Kagaku Zassi)*, **59**, 380 (1956).

The rate of reaction 2 may be appreciably slower than that of 1[3], therefore, the rate determining step of this redox system may be involved in 2. As mentioned above, the initial concentrations of benzoyl peroxide and benzoin have been chosen as the same and they are much greater than that of the ferrous ion. In this case, the ferrous-ion concentration can be expressed as

$$[\mathrm{Fe}^{2+}]=(2k_2/k_1)x \qquad (5)$$

Therefore, the concentration of ferrous ion in the polymerizing solution may be directly proportional to that of ferrous ion added. From Eqs. 3 and 5, the following expression for the initial rate of conversion can be derived:

$$(\mathrm{d}y/\mathrm{d}t)_0{}^2=(k_p{}^2/k_t)[\mathrm{P}]_0(k_d+2k_2x) \qquad (6)$$

This equation corresponds to the curves in Fig. 2.

The initial rate of polymerization is, however, greatly affected by the mole ratio, r, as shown in Table I. In deriving Eq. 6, ethanol was assumed to be an ideal solvent which would not affect $(\mathrm{d}y/\mathrm{d}t)_0$; however, if a new radical which is produced from a molecule of ethanol attacked by a growing radical, is not so active as to initiate a new chain, ethanol will act as inhibitor or retarder. However, this reason may be invalidated by the fact that $(\mathrm{d}y/\mathrm{d}t)_0$ was approximately constant and independent of the ratio, r, in the absence of ferrous ion. The dependence of the rate of conversion on the ratio r, therefore, would be ascribed to the changes of the rate constants k_1 and k_2, which would be affected by the composition of the solution.

From the curves in Fig. 2, the ratio k_2/k_d can be calculated; for example, k_2/k_d is about 12,000 for $r=2.52$, showing that a small amount of ferrous chloride accelerates efficiently the rate of polymerization in this redox system.

The concentration of benzoyl peroxide at time t may be expressed as

$$[\mathrm{P}]=[\mathrm{P}]_0\exp\{-(k_d+2k_2x)t\} \qquad (7)$$

in the early stage of polymerization.

Substituting Eq. 7 into Eq. 3, and integrating from $t=0$ to $t=t$, it follows:

$$\ln(1-y)=(2k_p/k_t{}^{1/2})[\mathrm{P}]_0{}^{1/2}(k_d+2k_2x)^{-1/2} \times[\exp\{-(k_d+2k_2x)t/2\}-1] \qquad (8)$$

The concentration of benzoyl peroxide, however, will be reduced more rapidly than that of benzoin, for the former decomposes not only in the reaction 1, but it will also decompose thermally. The concentration of ferrous ion, therefore, will be increased gradually. But assuming the concentration of ferrous ion to be constant, the extent of conversion at sufficient time of duration, y_∞, can be expressed as:

$$Z\equiv\{1/\ln(1-y_\infty)\}^2=(k_t/4k_p{}^2[\mathrm{P}]_0)(k_d+2k_2x) \qquad (9)$$

The values of Z are listed in Table I. From Eq. 9, it is expected that a plot of Z against x would give a straight line. Fig. 3 shows the relation between Z and x, and it is seen that the extent of conversion decreases with increasing ferrous ion concentration for each value of r. The abnormal decrease of Z with monomer concentration 90%, may be ascribed to the decrease of k_t due to the increased viscosity at a high conversion[6].

Eq. 9 has been introduced on the assumption that none of the velocity constants nor the ferrous ion concentration vary through the polymerization processes. But, these would actually vary with the change in the composition of the solution. However, it is possible, in principle, to calculate the value of x that makes the extent of conversion at any time t maximum.

If the right-hand side of Eq. 8 is differentiated with respect to x and the result equated to zero, the condition for the minimum of $\ln(1-y)$ and hence the maximum of y may be obtained. The relationship found is

$$\exp(k_d+2k_2x)t/2=1+(k_d+2k_2x)t \qquad (10)$$

Two solutions of this equation may be obtained graphically, i. e.,

$$(k_d+k_2x)t/2=0 \qquad (11)$$

$$k_d+2k_2x\cong 2.5/t \qquad (12)$$

Since neither k_d nor k_2 is zero, Eq. 11 has no physical meaning. It may be said that Eq. 12 is the relation between x and the time t when the extent of conversion y with the initial ferrous ion concentration x becomes of greater value than any other one.

The rate constants k_d and k_2 can be calculated from Figs. 2 and 3 which correspond to Eqs. 6 and 9, respectively, though it is very doubtful whether each rate constant in Eq. 9 has kept up its original meaning.

The values of k_d and k_2 thus obtained

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[6] G. V. Schulz and G. Harborth, *Makromol. Chem.*, **1**, 106 (1947).

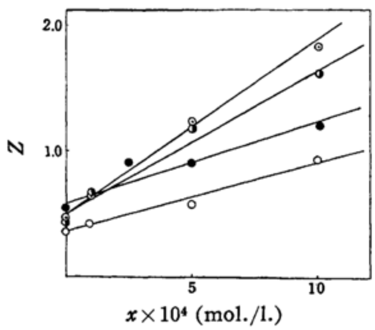

Fig. 3. Relation between Z and x for each value of r.
r: ● 0.63, ◑ 1.89, ⊙ 2.52, ○ 5.67

were $0.07\,\mathrm{hr.}^{-1}$ and $300\,\mathrm{l.\,mol.}^{-1}\,\mathrm{hr.}^{-1}$, respectively, and the ratio k_2/k_d was about 4,300 which was much less than that obtained only from Eq. 6. The cause of this discrepancy may be ascribed to the reason mentioned above.

It is of interest, however, to test Eq. 11. Substitution of those numerical values into Eq. 12 leads to Eq. 13, i. e.,

$$0.07+600x \cong 2.5/t \tag{13}$$

For a series of x, the corresponding time was calculated from Eq. 13 and compared with one obtained experimentally from Fig. 1.

It is noted, as seen in Table II, that the values of t calculated are in fairly good agreement with those obtained experimentally.

TABLE II
COMPARISON OF CALCULATED VALUES OF t WITH THOSE OBSERVED

$x \cdot 10^4$ (mol. 1^{-1})	t (calcd.) (hr.)	t (obsd.) (hr.)
10	4	～4
5	7	4～12
1	18	12～25
0	36	25～

Summary

Polymerization of vinyl acetate in the benzoyl peroxide-iron-(II)-benzoin redox-system was studied in ethanol. From the extent of decrease in volume, the rate of conversion was calculated. It was found that the square of the initial rate of conversion was proportional to the initial concentration of ferrous ion and that the extent of conversion at the time when the polymerization was finished, decreased with increasing amount of ferrous ion which was added.

The initial rate of conversion in this redox system was found to depend also on the mole ratio of the monomer to ethanol. The reason might be ascribed to the change in the rate constant.

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