*Studies on Organic Peroxides. V. Decomposition of Benzoyl Peroxide by Iron(II)**

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It has been found that the rate of the decomposition of peroxides was greatly accelerated by ferrous ion[1]. In the presence of the latter, the decomposition is supposed to take place according to the Haber-Weiss one-electron transfer mechanism as follows[2]:

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

where P and R denote benzoyl peroxide and phenyl group respectively. It is noted that this decomposition is not homolytic but semi-ionic. Therefore, it would be expected that the physical properties of solvents play an important role apart from the discussions about the induced decomposition of benzoyl peroxide. In the previous paper[3], this mechanism was postulated in order to explain the dependence of the initial rate of polymerization of vinyl acetate in the benzoyl peroxide-Fe(II)-benzoin redox system on the initial concentration of ferrous ion. In this paper, the analytical method was applied to the ferrous ion catalysed decomposition of peroxide in order to verify this mechanism.

Experimental

Reagents used were of reagent grade or prepared by the method reported previously[3]. A definite amount of ferrous chloride crystals ($\mathrm{FeCl_2 \cdot 4H_2O}$) was dissolved in ethanol (50 ml.) in a three-necked flask provided by a condenser. The reaction was initiated by the addition of ethanolic solution (50 ml.) of benzoyl peroxide. Oxygen-free carbon dioxide gas was bubbled through the reaction mixture for the purpose of stirring the solution and preventing the ferrous ions from being oxidized by air. Reactions were carried out at temperatures between 15 and 32°C. The analytical procedures of benzoyl peroxide was a modification of the method recommended by Nozaki[4]. At specified times after

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[1] M. S. Kharasch, A. Funo and W. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950).

[2] F. Haber and P. Weiss, *Proc. Roy. Soc. London*, **A147**, 332 (1934).

[3] S. Hasegawa et al., This Bulletin, **31**, 696 (1958).

[4] K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **19**, 872 (1947).

the beginning of the reaction, aliquots of the reaction mixture were pipetted out from the flask into an Erlenmeyer flask containing 1 ml. of saturated sodium hydrogen phosphate to eliminate ferric ions, which would, otherwise, disturb the correct analysis of benzoyl peroxide. Five milliliters of acetic anhydride in which 0.3 g. of sodium iodide had been dissolved was added and then allowed to stand about half an hour at room temperature. Iodine liberated was titrated with 0.01 N sodium thiosulfate solution adding 1% starch solution towards the last. This method of analysis is favored by the fact that the atmosphere above the solution to be analysed need not be replaced by inert gas.

Ferrous ion is known to react with $\alpha\alpha'$-bipyridyl forming a very stable red complex which has the maximum absorbance at 510 mμ. Colorimetric measurement was, therefore, applied to determine the concentration of the ferrous ion in the reaction mixture. One milliliter of an aqueous solution of 1% $\alpha\alpha'$-bipyridyl was buffered at pH of 4.75 by acetic acid~sodium acetate solution. Ten milliliters of the reaction mixture was added to the solution followed by dilution with water. When it was allowed to stand at room temperature, colloidal particles of benzoyl peroxide appeared which grew up to precipitate after standing for 2~3 hr. This precipitate was filtered off and the absorbance of the solution at 470 mμ was measured by a photoelectric colorimeter. A plot of the absorbance against the ferrous ion concentration in a series of blank experiments showed a straight line relationship up to about 1.5×10^{-4} mol./l. of ferrous ion, in accordance with Beer's law.

The initial concentration of benzoyl peroxide was 5×10^{-3} mol./l. in each run.

Results and Discussion

The extent of the decomposition of benzoyl peroxide induced by ferrous ions was plotted against time as shown in Fig. 1. As is seen from the figure, this reaction takes place with considerable rate even at room temperature.

According to the reaction 1, the rate of the ferrous ion induced decomposition of benzoyl peroxide should be expressed as follows:

$$-\mathrm{d}[P]/\mathrm{d}t=k_1[P][\mathrm{Fe}^{2+}] \qquad (2)$$

or rearranging Eq. 2,

$$-\mathrm{d}\ln[P]/\mathrm{d}t=k_1[\mathrm{Fe}^{2+}] \qquad (3)$$

Instead of the extent of the decomposition, the logarithm of the corresponding volume v of sodium thiosulfate consumed in titration, was plotted against time t; this is shown in Fig. 2 for various initial ferrous ion concentrations at 25°C. Extrapolated values of each curve evidently correspond to the initial concentration of benzoyl peroxide. It is to be noted from Fig. 2 that the slope of the curves, i. e., $\mathrm{d}\log[P]/\mathrm{d}t$ has not suffered a marked change during the reaction. This means that the apparent decomposition rate of benzoyl peroxide is nearly of the first order with respect to benzoyl peroxide. Another evidence for the first order reaction lies in the fact that the slope of the curves in Fig. 3 in which $\log v$ was plotted against t, seems to be independent of the initial concentration of benzoxyl peroxide.

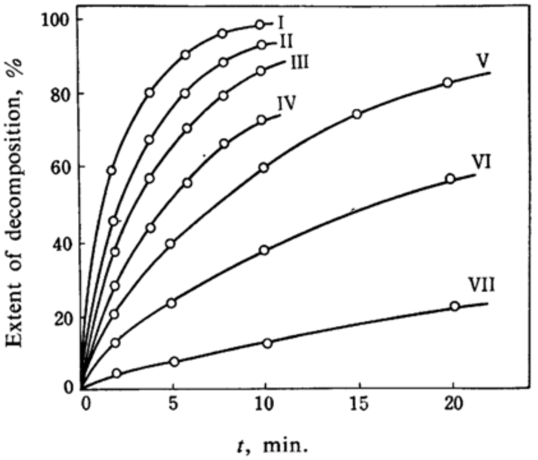

Fig. 1. Extent of decomposition of benzoyl peroxide in ethanol at 25°C. $[\mathrm{FeCl}_2]_0\times10^4$: I, 25.1; II, 16.5; III, 13.6; IV, 10.6; 6.8; VI, 5.4; VII, 2.5 mol./l., respectively; $[\mathrm{BPO}]_0$: 5×10^{-3} mol./l.

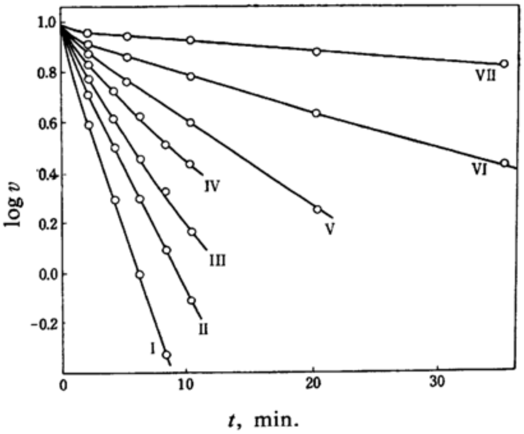

Fig. 2. Relation between $\log v$ and t. Numbers are identical with those in Fig. 1.

The slopes of the curves in Fig. 2 seem to be linearly proportional to the initial concentration of ferrous ion. Although care was taken to remove oxygen, the trace of oxygen in the solution might oxidize the ferrous ions. In addition, ferrous ions are oxidized by reaction 1. Therefore, it is necessary to determine the true concentration of ferrous ions in solution.

The ferrous ion concentration in the reaction mixture at any time was determined by the colorimetric method. The slope $-\mathrm{d}\log$

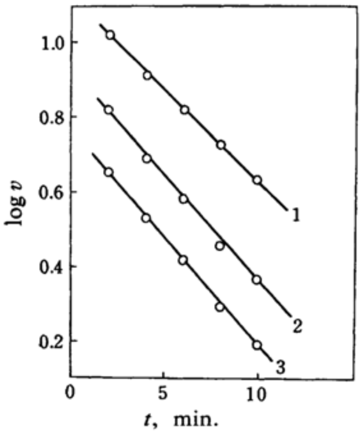

Fig. 3. Relation between $\log v$ and t at 25°C; $[\mathrm{BPO}]_0 \times 10^3$: 1, 7.5; 2, 5.0; 3, 3.3 mol./l., respectively; $[\mathrm{FeCl_2}]_0$: 10.1×10^{-4} mol./l.

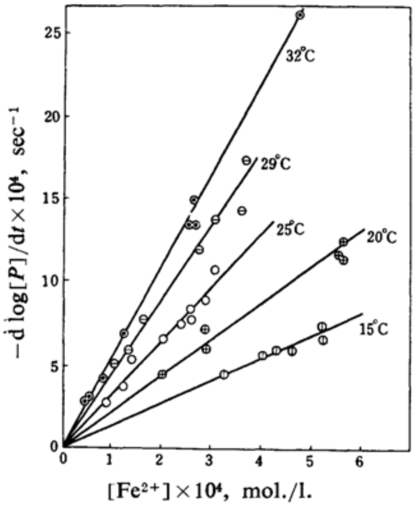

Fig. 4. Plots of $-\mathrm{d}\log[P]/\mathrm{d}t$ against actual ferrous ion concentration in ethanol at various temperatures.

$[P]/\mathrm{d}t$ was plotted against the ferrous ion concentration as shown in Fig. 4. The plots gave straight lines, all of which converged to the origin of the coordinate at each temperature.

Thus it could be said that equation 2 is the complete expression for the reaction rate in accordance with the mechanism postulated above.

Table I shows the numerical values for $[\mathrm{Fe^{2+}}]$, $-\mathrm{d}\log[P]/\mathrm{d}t$ and k_1 at various temperatures. Fig. 5 shows the Arrhenius plot which gives a straight line. The Arrhenius equation for the decomposition reaction was calculated to be $k_1 = 2.2 \times 10^{11} \exp(-14.21 \times 10^3/\boldsymbol{RT})$ mol^{-1} l. sec^{-1} with a standard deviation of 0.40 for $\log A$ and 0.55 kcal. mol.$^{-1}$ for E, where A and E represent the frequency factor and the activation energy, respectively.

TABLE I. RATE CONSTANTS FOR BENZOYL PEROXIDE-IRON(II) REACTION

t °C	$[\mathrm{Fe^{2+}}]$ $\times 10^4$ mol. l^{-1}	$-\mathrm{d}\log[P]/\mathrm{d}t$ $\times 10^4$ sec^{-1}	k_1 mol.$^{-1}$ l. sec^{-1}	k_1 av.
32	4.65	29.0	14.4	14.4±0.2
	2.65	15.0	13.0	
	2.60	16.7	14.8	
	2.50	15.0	13.8	
	1.20	7.67	14.7	
	0.80	4.67	13.4	
	0.50	3.33	15.3	
	0.43	3.00	16.1	
29	3.65	19.3	12.2	11.8±0.2
	3.55	16.0	10.4	
	3.05	15.3	11.6	
	2.70	13.3	11.3	
	1.60	8.67	12.5	
	1.30	6.67	11.8	
	1.00	5.67	13.1	
25	3.00	12.0	9.21	8.44±0.14
	2.85	10.0	8.08	
	2.55	9.33	8.43	
	2.55	8.67	7.83	
	2.35	8.33	8.16	
	2.00	7.33	8.44	
	1.35	5.67	9.67	
	1.20	4.17	8.00	
	0.85	3.00	8.13	
20	5.55	14.0	5.84	5.71±0.12
	5.55	12.7	5.27	
	5.45	13.0	5.49	
	2.85	8.00	6.46	
	2.85	6.67	5.39	
	1.98	5.00	5.82	
15	5.15	8.33	3.73	3.56±0.05
	5.15	7.33	3.28	
	4.55	6.67	3.38	
	4.20	6.67	3.66	
	3.95	6.33	3.69	
	3.20	5.00	3.60	

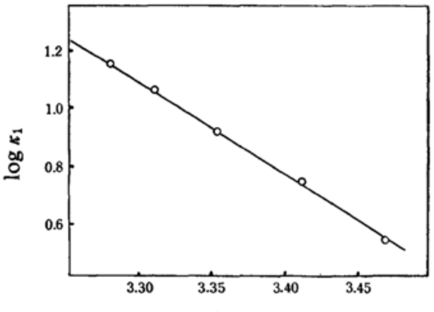

Fig. 5. Arrhenius plot of $\log k_1$ against $1/T$.

As is seen above, the reaction proceeds bimolecularly in accordance with the Haber-Weiss mechanism, and hence the reaction should be of the second order. However, as shown in Fig. 2, the apparent decomposition was approximately of the first order. In order for the reaction to be of the first order, the ferrous ion concentration in Eq. 2 must be kept constant during the reaction. Ferrous ion concentration was decreased rapidly at first, but became nearly contant within 2~3 min. It could be said therefore, that ferrous ion concentration was roughly kept constant during the stationary state.

It is well known that the thermal decomposition rate of peroxides in various solvents can be expressed as5)

$$-\mathrm{d}[P]/\mathrm{d}t = k_d[P] + k_i[P]^x \qquad (4)$$

where k_d represents the specific rate of spontaneous cleavage, k_i the specific rate constant of induced decomposition and x the order of the induced reaction which may vary between 0.5 and 2.0. In ethanol solution, x was reported to be unity6), and the apparent decomposition rate was of the first order. In this case, the essential reactions were considered to take place as follows:

$$\mathrm{P} \xrightarrow{k_d} \mathrm{2RCOO\cdot} \qquad (5)$$

$$\mathrm{RCOO\cdot + CH_3CH_2OH} \xrightarrow{k_2} \mathrm{RCOOH + CH_3\underset{\cdot}{C}HOH} \qquad (6)$$

$$\mathrm{CH_3\underset{\cdot}{C}HOH + P} \xrightarrow{k_3} \mathrm{CH_3CHO + RCOO\cdot + RCOOH} \qquad (7)$$

$$\mathrm{CH_3\underset{\cdot}{C}HOH + RCOO\cdot} \xrightarrow{k_4} \mathrm{RCOOH + CH_3CHO} \qquad (8)$$

and the apparent decomposition rate was given by

$$-\mathrm{d}[P]/\mathrm{d}t = k'[P] \qquad (9)$$

where k' is a constant including some specific rate constants in the equations given above. The specific rate constant for the spontaneous decomposition k_d may be negligible at room temperature. Hence, in the presence of ferrous ion, reaction 7 will take part in the decomposition of benzoyl peroxide together with reaction 1. The overall rate of the decomposition reaction may be expressed as

$$-\mathrm{d}[P]\,\mathrm{d}t = k_1[P]\,[\mathrm{Fe^{2+}}] + k'[P] \qquad (10)$$

If the reaction 7 occurs predominantly, the mole ratio of benzoyl peroxide decomposed to ferrous ion consumed will be greater than unity. In fact as is seen from Fig. 2, the amount of the peroxide decomposed in each case was much greater than those expected from reaction 1. However, comparing Eq. 10 with Eq. 2 which was confirmed experimentally, the second term of the right hand side in Eq. 10 could be neglected. This indicates that radical-induced decomposition of benzoyl peroxide may be suppressed by the presence of ferrous ions, as in the case of the decomposition of benzoyl peroxide by dimethyl aniline7).

In order to explain both the first order decomposition and the suppression of reaction 7, reduction of ferric to ferrous ion may be postulated. Since ethanol radical is considered as an electron donor, this reduction would take place through reaction 11:

$$\mathrm{CH_3\underset{\cdot}{C}HOH + Fe^{3+}} \xrightarrow{k_5} \mathrm{CH_3CHO + Fe^{2+} + H^+} \qquad (11)$$

Thus it may be assumed that the reactions 1, 6, 8 and 11 are predominant. If the stationary state conditions for radicals are applied, then for RCOO·,

$$k_1[P]\,]\,\mathrm{Fe^{2+}}] = k_2[\mathrm{RCOO\cdot}]\,[\mathrm{CH_3CH_2OH}] + k_4[\mathrm{RCOO\cdot}]\,[\mathrm{CH_3\underset{\cdot}{C}HOH}] \qquad (12)$$

and for $\mathrm{CH_3\underset{\cdot}{C}HOH}$,

$$k_2[\mathrm{RCOO\cdot}]\,[\mathrm{CH_3CH_2OH}] = k_4[\mathrm{RCOO\cdot}]\,[\mathrm{CH_3\underset{\cdot}{C}HOH}] + k_5[\mathrm{CH_3\underset{\cdot}{C}HOH}]\,[\mathrm{Fe^{3+}}] \qquad (13)$$

Therefore, from these equations, it follows

$$k_1[P]\,[\mathrm{Fe^{2+}}] = k_5[\mathrm{CH_3\underset{\cdot}{C}HOH}]\,[\mathrm{Fe^{3+}}] + 2k_4[\mathrm{RCOO\cdot}]\,[\mathrm{CH_3\underset{\cdot}{C}HOH}] \qquad (14)$$

The left hand side in Eq. 14 represents the rate of the oxidation of ferrous ion and the first term of the right hand side is that of reduction of ferric ion. As mentioned earlier, the ferrous ion concentration did not suffer a marked change during the reaction after a stationary state was attained. Hence, the second term of the right hand side in Eq. 14 may be neglected. The main reactions in this study may, therefore, be reduced to reactions 1, 6 and 11. Among these reactions, iron may be considered to serve as electron transferer.

Swain et al.8) believe that two benzoxy groups

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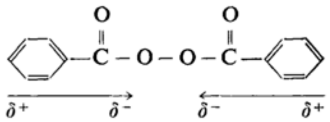
5) P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **68**, 1686 (1946); ibid., **69**, 2299 (1947); W. E. Cass, ibid., **68**, 1976 (1946).

6) S. Kato and F. Mashio, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **59**, 380 (1956).

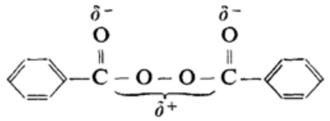
7) M. Imoto and C. Suckon, *Chem. High Polymers* (*Kobunshi Kagaku*) **11**, 396 (1954).

8) C. G. Swain, W. T. Stockmayer and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950); ibid., **68**, 1686 (1946).

in benzoyl peroxide are dipoles attached to one another in such a way as to repel each other:



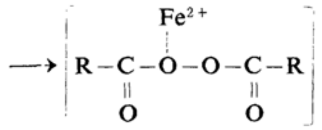
and they ascribed the driving force of the decomposition of the peroxide to the electrostatic repulsion between two benzoxy groups. Whereas, Imoto et al.[7] proposed that the driving force was due to the repulsion between oxygen atoms on carbonyl groups,



and successfully explained the effect of substituents on phenyl rings of benzoyl peroxide upon the rate of decomposition in the presence of dimethyl aniline.

In the reaction of benzoyl peroxide with ferrous ion, as is the case for the reaction between benzoyl peroxide and dimethyl aniline, the two species, when they approach, will interact with each other forming an activated complex:

$$\mathrm{RCOO-OOCR+Fe^{2+}}$$



$$\longrightarrow \left[\mathrm{R-\underset{\underset{O}{\|}}{C}-\overset{\overset{Fe^{2+}}{\vdots}}{O}-O-\underset{\underset{O}{\|}}{C}-R}\right]$$

$$\longrightarrow \mathrm{RCOO^{-}+RCOO\cdot+Fe^{3+}} \qquad (15)$$

An electron jump from ferrous ion to either of the oxygen atoms bonded to each other will easily take place. Orr and Williams[9] suggested the formation of the activated complex by coördination of the ferrous ion and hydroperoxide.

The spontaneous decomposition of benzoyl peroxide in various solvents has been widely studied by many authors[10] and they found that the activation energy was 28∼30 kcal./mol., which is slightly lower than the O−O bond energy, 34 kcal./mol., calculated by Pitzer[11].

A short discussion of activation entropy may be relevant to the present problem. It is noted that the frequency factor of the thermal decomposition of benzoyl peroxide in various solvents is of the order of $10^{13}\sim10^{15}\ \mathrm{mol^{-1}\ l.\ sec^{-1}}$, the value for which is abnormally large owing, probably, to the chain process. But, as already stated, in the present case, the factor A was found to be 2.2×10^{11}. This will also suggest the fundamental difference in the reaction mechanisms in two cases. Rollefson[12] considers that the activation entropy is a measure of the bond strength of activated complex. The frequency factor of 2.2×10^{11} corresponds to the entropy loss of about 11.2 e. u. provided the transmission coefficient is unity. The value may be compared with $\Delta S^{\ddagger}$ of −10 e. u. which is accompanied by the loss of only one degree of translational freedom[9]. Accordingly, it seems that ferrous ion forms a weakly combined complex with benzoyl peroxide molecule. From the standpoint of the entropy factor, the decomposition mechanism proposed above could again be considered to be reasonable.

Summary

An investigation of the rate of decomposition of benzoyl peroxide by ferrous ion in ethanol has been made. The rate of the reaction was linearly proportional to the concentrations of benzoyl peroxide and ferrous ion, in accordance with Haber-Weiss one electron transfer mechanism. But the apparent decomposition rate was of the first order. The Arrhenius equation was $k_1=2.2\times10^{11}\exp(-14{,}210/\boldsymbol{RT})\ \mathrm{mol^{-1}\ l.\ sec^{-1}}$.

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[9] R. J. Orr and H. L. Williams, *J. Phys. Chem.*, **57**, 925 (1953).

[10] K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946); P. F. Hartman, H. G. Sellers and D. Turnbull, ibid., **69**, 2416 (1947); A. T. Blomquist and A. J. Buselli, ibid., **73**, 3883 (1951).

[11] K. S. Pitzer, ibid., **70**, 2140 (1948).

[12] G. K. Rollefson, *J. Phys. Chem.* **56**, 976 (1952).