# *Decomposition of Peroxybenzoic Acid in Solution.*
## *III. Decomposition in Ethers*

By Katsumi TOKUMARU and Osamu SIMAMURA

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In previous papers[1,2], an account has been given of the decomposition of peroxybenzoic acid in alcohols and hydrocarbons and a radical chain mechanism has been proposed for the decomposition. This part deals with the decomposition of peroxybenzoic acid in diethyl, diisopropyl, and di-*n*-butyl ether.

### Experimental

**Materials.**—Peroxybenzoic acid was prepared as previously described[1].

Diethyl ether was shaken with cold 50% sulphuric acid, followed by aqueous sodium hydroxide, dried with calcium chloride and then with sodium metal, and distilled under an atmosphere of nitrogen. Diisopropyl ether and di-*n*-butyl ether were similarly purified. Dioxan was refluxed with sodium metal in a stream of nitrogen and distilled.

**Kinetic Measurements.**—Rate of decomposition of peroxybenzoic acid was measured under an atmosphere of nitrogen by the same method as in Part I[1].

**Product Study.** — The general procedure was essentially the same as that described in Part II[2].

*1) Decomposition in Diisopropyl Ether.* — Peroxybenzoic acid (5.0 g., 36 mmol.) was decomposed in diisopropyl ether (150 ml.), in a stream of nitrogen at 65°C for 6 hr. Carbon dioxide (4 mmol.) was caught by absorption in a potash bulb. The reaction mixture was distilled, with occasional addition of fresh diisopropyl ether to the distilling flask to remove volatile matter completely. The distillate and the condensate in a trap cooled with solid carbon dioxide were combined and shown to contain isopropyl alcohol and acetone by gas chromatography. This mixture was extracted repeatedly with water, and the aqueous extract, on treatment with 2, 4-dinitrophenylhydrazine, gave 2, 4-dinitrophenylhydrazone of acetone (24 mmol.), melting point and mixed melting point with an authentic sample, 126°C. The residue from the distillation was extracted with water, and the aqueous extract, on treatment with 2, 4-dinitrophenylhydrazine, gave no appreciable precipitate; the organic layer was extracted with aqueous sodium hydrogen carbonate, and the extract gave benzoic acid (3.8 g., 31 mmol.), m. p. 121°C, on acidification.

In an experiment intended to investigate gaseous products, peroxybenzoic acid (2.8 g., 20 mmol.) was decomposed in diisopropyl ether (50 ml.) at 65°C in a closed system. Analysis of the gaseous products by absorption method showed formation of carbon dioxide (2 mmol.) and oxygen (3 mmol.).

*2) Decomposition in Diethyl Ether.*—Peroxybenzoic acid (2.8 g., 20 mmol.) was decomposed in boiling diethyl ether under an atmosphere of nitrogen. The reaction mixture was distilled. The distillate and the condensate in a trap chilled with solid carbon dioxide were combined and the mixture shown by gas chromatography to contain ethyl alcohol and acetaldehyde, on treatment with 2, 4-dinitrophenylhydrazine, gave 2, 4-dinitrophenylhydrazone of acetaldehyde (7 mmol.), melting point and mixed melting point with an authentic sample, 168°C. The distillation of the remaining reaction mixture at reduced pressure gave acetic acid (trace), which was identified by the infrared spectrum. The residue from the distillation consisted of almost pure benzoic acid (2.2 g., 18 mmol.), m. p. 121°C.

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[1] K. Tokumaru, O. Simamura and M. Fukuyama, This Bulletin, 35, 1673 (1962).

[2] K. Tokumaru and O. Simamura, ibid., 35, 1678 (1962).

*3) Decomposition in Di-n-butyl Ether.* — Peroxybenzoic acid (2.1 g., 15 mmol.) was decomposed in di-*n*-butyl ether at 60°C in a stream of nitrogen. The reaction mixture was distilled, and the distillate, treated with 2, 4-dinitrophenylhydrazine, gave 2, 4-dinitrophenylhydrazone of *n*-butyraldehyde (3 mmol.), melting point (from ethyl alcohol) and mixed melting point with an authentic sample, 122°C. Gas chromatographic analysis of the distillate showed the presence of *n*-butyraldehyde and *n*-butyl alcohol. Benzoic acid (1.7 g., 14 mmol.), m. p. 121°C, was obtained from the residue of the distillation.

## Results and Discussion

Peroxybenzoic acid decomposed rapidly in ethers. The initial rapid decomposition often was followed by decomposition with decreasing speed as shown in Fig. 1, and the rate of decomposition did not conform to a simple first-order kinetics. Therefore, only percentage decomposition of peroxybenzoic acid is shown in Table I. The results of the product study are summarized in Table II.

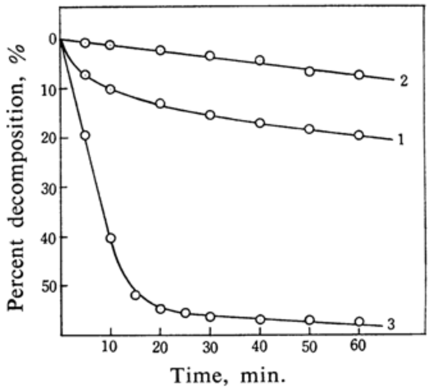

Fig. 1. Decomposition of peroxybenzoic acid in ethers at 50°C (initial concentration of peroxybenzoic acid, 0.1 mol./l.).

1 Diisopropyl ether
2 Di-*n*-butyl ether
3 Dioxan

If peroxybenzoic acid decomposes in ethers by the radical chain mechanism postulated previously[1,2], the reaction paths in ethers will be represented as follows.

$$\mathrm{PhCO_3H} \rightarrow \mathrm{PhCO_2}\cdot + \mathrm{HO}\cdot \qquad (1)$$

$$\mathrm{PhCO_2}\cdot \rightarrow \mathrm{Ph}\cdot + \mathrm{CO_2} \qquad (1')$$

$$\mathrm{ROCHR'R''} + \mathrm{Radical} \rightarrow \mathrm{RO\dot{C}R'R''} + \text{Stable molecule} \qquad (2)$$

$$\mathrm{PhCO_3H} + \mathrm{RO\dot{C}R'R''} \rightarrow \mathrm{ROCR'R''OH} + \mathrm{PhCO_2}\cdot \qquad (3)$$

$$\mathrm{RO\dot{C}R'R''} \rightarrow \mathrm{R}\cdot + \mathrm{R'R''CO} \qquad (4)$$

$$\mathrm{ROCR'R''OH} \rightarrow \mathrm{ROH} + \mathrm{R'R''CO} \qquad (5)$$

In the above mechanism, the radicals formed from peroxybenzoic acid abstract a hydrogen atom $\alpha$ to the oxygen of ether (reaction 2). Solvent radicals thus formed, that is, 1-alkoxyalkyl radicals, attack peroxybenzoic acid, producing 1-hydroxyalkyl ether and the benzoyloxy radical (reaction 3), which in turn abstracts a hydrogen atom from ether, propagating the chain. 1-Hydroxyalkyl ether will be unstable, decomposing to an alcohol and a carbonyl compound (reaction 5). There exists the alternative possibility of thermal decomposition of the solvent radical (reaction 4), but it does not seem important, since, in the first place, in the decomposition of benzoyl peroxide in ethers, its induced decomposition by 1-alkoxyalkyl radicals is reported to take place to an appreciable extent[3-5], and, secondly, peroxybenzoic acid is more readily attacked by radicals than benzoyl peroxide is, as will be shown in a subsequent paper. The alcohols formed by reaction 5 may suffer further oxidation by peroxybenzoic acid as described in Part I of this series. In fact, the production of acetone and isopropyl alcohol from diisopropyl ether can be explained on the basis of the above reaction scheme, and some part of the acetone may have been formed by further oxidation of isopropyl alcohol. The products from diethyl and di-*n*-butyl ether listed in Table II are explained similarly.

TABLE I. DECOMPOSITION OF PEROXYBENZOIC ACID IN ETHERS AT 50°C

| Solvent | Percent decomposition in<br>10 min. | <br>30 min. | <br>1 hr. |
|---|---|---|---|
| Diisopropyl ether | 10.3 | 15.6 | 19.6 |
| Di-*n*-butyl ether | 1.2 | 3.4 | 7.4 |
| Dioxan | 40.5 | 56.5 | 57.5 |
| Isopropyl alcohol* | 17.8 | 44.5 | 62.1 |
| Cumene** | 4.1 | 7.5 | 13.9 |

*$k_1$ at 50°C: $3.4 \times 10^{-4}$ sec$^{-1}$ [1]

**$k_1$ at 60°C: $3.8 \times 10^{-5}$ sec$^{-1}$ [2]

The isolation of benzoic acid in a yield ranging from 80 to 93% indicates that the benzoyloxy radical underwent only a slight thermal decomposition and mainly abstracted an $\alpha$-hydrogen of ethers. This conclusion is well in accord with the behaviour of the benzoyloxy radical in the decomposition of benzoyl peroxide in ethers [3-5].

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3) W. E. Cass, *J. Am. Chem. Soc.*, **69**, 500 (1947).

4) E. H. Drew and J. C. Martin, *Chem. and Ind.*, **1959**, 925.

5) D. B. Denny and G. Feig, *J. Am. Chem. Soc.*, **81**, 5322 (1959).

TABLE II. PRODUCTS FORMED IN DECOMPOSITION OF PEROXYBENZOIC ACID IN ETHERS

| Ether | Temp. | Product and yield (% based on peroxybenzoic acid) | | | |
|---|---|---|---|---|---|
| | | Products from ether | Benzoic acid | Carbon dioxide | Oxygen |
| Diethyl | under reflux | Acetaldehyde, 35;<br>Ethyl alcohol,<br>Acetic acid | 90 | | |
| Diisopropyl | 65°C | Acetone, 67;<br>Isopropyl alcohol | 80 | 11 | |
| Diisopropyl | 65°C | | | 10 | 15 |
| Di-*n*-butyl | 60°C | *n*-Butyraldehyde, 20;<br>*n*-Butyl alcohol | 93 | | |

Peroxybenzoic acid has been thought[6,7] to exist in a monomeric form with an intramolecular hydrogen bond in a non-polar solvent, but in polar solvents like alcohols and ethers, it can form an intermolecular hydrogen bond with an oxygen atom of the solvent molecule. This view has been supported by a spectroscopic study of peroxybenzoic acid made in this laboratory[7]. Thus it is reasonable to suppose that the acidic dissociation of peroxybenzoic acid will be favoured in polar solvents like alcohols and ethers with a basic oxygen atom, producing peroxybenzoate anions. These anions will attack peroxybenzoic acid with electron transfer, giving radicals according to the mechanism suggested by Kirmse and Horner[8] as follows:

$$PhCO_3^- + PhCO_3H \rightarrow PhCO_3\cdot + PhCO_2^- + HO\cdot$$

This process will contribute, as an initial radical forming process, to the rapid decomposition of peroxybenzoic acid in ethers and alcohols. Some part of the benzoylperoxy radicals thus formed may give rise to molecular oxygen by some mechanism such as:

$$2PhCO_3\cdot \rightarrow 2PhCO_2\cdot + O_2$$

For the production of oxygen an alternative mechanism similar to that postulated by Kharasch and coworkers[9] in the case of $\alpha$-cumyl hydroperoxide cannot be excluded, thus:

$$RO_2^- + ROOH \rightarrow RO^- + ROH + O_2$$

## Summary

Decomposition of peroxybenzoic acid was studied in diethyl, diisopropyl and di-*n*-butyl ether and explained in terms of the same radical mechanism that was postulated previously. Besides ready induced decomposition of peroxybenzoic acid by solvent radicals and facile abstraction of a hydrogen atom from ether by radicals, attack of peroxybenzoate anions on peroxybenzoic acid was pointed out to be an important contributing factor for the relatively rapid decomposition in ethers.

*Department of Chemistry*
*Faculty of Science*
*The University of Tokyo*
*Hongo, Tokyo*

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[6] W. H. T. Davison, *J. Chem. Soc.*, **1951**, 2456.

[7] T. Mitsuhashi, O. Simamura and K. Tokumaru, unpublished observation.

[8] W. Kirmse and L. Horner, *Chem. Ber.*, **89**, 836 (1956).

[9] M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **16**, 113 (1951); M. S. Kharasch, A. Fono, W. Nudenberg and B. Bischof, ibid., **17**, 207 (1952).