Decomposition of Peroxybenzoic Acid in Solution.
I. Decomposition in Alcohols

By Katsumi TOKUMARU, Osamu SIMAMURA and Masaru FUKUYAMA

(Received June 25, 1962)

In the course of an investigation of epoxidation of olefins with peroxybenzoic acid in this Laboratory, peroxybenzoic acid was found to decompose appreciably in ethyl alcohol at room temperature(1). Search of the literature revealed that, concerning the decomposition of organic peroxyacids in alcohols, only Swern and coworkers' report(2) was available, which stated that long chain aliphatic peroxyacids such as peroxylauric acid decomposed appreciably in methyl alcohol at 25°C. We then undertook investigation on the decomposition of peroxybenzoic acid in alcohols and some other solvents. During our research, Swern and coworkers(3) again reported the decomposition of peroxylauric acid in solvents and offered a non-radical, concerted mechanism.

After our work had been completed, Lefort, Paquot, and Sorba(4) proposed a radical mechanism for the decomposition of peroxylauric acid in petroleum ether. More recently Lefort, Sorba, and Rouillard(5) published a study on the decomposition of the same acid mainly in cyclohexane, and Heywood, Phillips, and Stansbury(6) presented a radical mechanism for the decomposition of peroxyacetic acid in hydrocarbon solutions. Further, Cohen and Edwards(7) made a kinetic study of decomposition of peroxybenzoic acid in benzene and 1-butanol in the presence of 2, 2-diphenyl-1-picrylhydrazyl and concluded a free radical cleavage of peroxybenzoic acid. We now report our results and propose a radical chain mechanism for the decomposition of peroxybenzoic acid in alcohols.

Experimental

Materials. — Peroxybenzoic acid was prepared from benzoyl peroxide according to Braun's procedure(8) as modified by Kolthoff et al.(9) Methylene chloride was used for extraction of peroxybenzoic acid. The extract was dried with sodium sulphate, the solvent removed by suction with a water-jet aspirator, and the remaining peroxybenzoic acid sublimed(10) several times under reduced pressure of a rotary vacuum pump to give samples of 96~99% purity (determined by iodometric titration(11)).

Methyl alcohol was refluxed with silver nitrate and potassium hydroxide and distilled. The distillate was refluxed with magnesium methoxide and distilled before use. Ethyl alcohol was similarly purified. Isopropyl alcohol was refluxed with 2, 4-dinitrophenylhydrazine and distilled. The distillate

---

1) M. Fukuyama, Thesis (Tokyo University), 1958.

2) W. E. Parker, C. Riccuiti, C. L. Ogg and D. Swern, *J. Am. Chem. Soc.*, **77**, 4037 (1955).

3) W. E. Parker, L. P. Witnauer and D. Swern, ibid., **80**, 323 (1958).

4) D. Lefort, C. Paquot and J. Sorba, *Bull. soc. chim. France*, **1959**, 1385.

5) D. Lefort, J. Sorba and D. Rouillard, ibid., **1961**, 2219.

6) D. L. Heywood, B. Phillips and H. A. Stansbury, Jr., *J. Org. Chem.*, **26**, 281 (1961).

7) S. R. Cohen and J. O. Edwards, *J. Phys. Chem.*, **64**, 1086 (1960).

8) G. Braun, "Organic Syntheses", Coll. Vol. I (1946), p. 431.

9) I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Polymer Sci.*, **2**, 199 (1947).

10) C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75**, 4250 (1953).

11) D. Swern, "Organic Reactions", Vol. VII, John Wiley and Sons, Inc., New York (1953), p. 378.

was refluxed with aluminium isopropoxide and distilled. *tert*-Butyl alcohol was purified by repeated partial freezing and finally distilled.

Nitrogen was freed from oxygen according to Fieser's directions[12]. Oxygen was passed through aqueous potassium permanganate acidified with sulphuric acid and dried with sulphuric acid.

Product Study.—A typical experiment for each alcohol is described.

Decomposition in Ethyl Alcohol. — Peroxybenzoic acid (9.7 g., 70 mmol.) was dissolved in 100 ml. of ethyl alcohol and left to stand in the dark for two months at room temperature until peroxybenzoic acid had been decomposed completely. The solvent was distilled, and fresh alcohol added to the residue and distilled to remove low boiling volatile matter. The combined distillates, on treatment with 2,4-dinitrophenylhydrazine, gave 2,4-dinitrophenylhydrazone of acetaldehyde (11 mmol.), m. p. (from ethyl alcohol) and mixed m. p. with an authentic sample, 168°C. Subsequent distillation of the residue under reduced pressure gave acetic acid, which was characterized as the *p*-toluidide (16 mmol.), m. p. and mixed m. p. with an authentic sample, 147°C. The residue from the distillation consisted of almost pure benzoic acid, (8.2 g., 67 mmol.), m. p. 121°C.

Decomposition in Isopropyl Alcohol.—Peroxybenzoic acid (10.3 g., 75 mmol.) was dissolved in 80 ml. of isopropyl alcohol and allowed to stand in the dark until peroxybenzoic acid had completely disappeared. The reaction mixture was distilled, and the distillate, treated with 2,4-dinitrophenylhydrazine, yielded 2,4-dinitrophenylhydrazone of acetone (42 mmol.), m. p. 126°C. The solid residue was benzoic acid (9.1 g., 75 mmol.), m. p. 121°C. When peroxybenzoic acid (0.5 g., 3.6 mmol.) was allowed to decompose in isopropyl alcohol (50 ml.) at 60°C for 4 hr., the reaction mixture, worked up as above, gave acetone, identified as 2,4-dinirophenylhydrazone (2.2 mmol.), m. p. 126°C, and benzoic acid (0.4 g., 3.3 mmol.).

Decomposition in Methyl Alcohol. — Peroxybenzoic acid (0.5 g., 3.6 mmol.) was decomposed in boiling methyl alcohol (50 ml.) for 10 hr., under a stream of nitrogen. Distillation of the reaction mixture gave formaldehyde, identified as 2,4-dinitrophenylhydrazone (1.5 mmol.), m. p. 165°C and benzoic acid (0.4 g., 3.3 mmol.).

Analysis of Gaseous Products.—A solution of peroxybenzoic acid was placed in a reaction flask. The flask was cooled with dry ice-ethyl alcohol, evacuated to remove oxygen, and let stand to warm up, and after introduction of nitrogen and chilling with the cooling mixture the system was evacuated again. After the cycle of these operations was repeated three times, the reaction was started by immersing the flask in a thermostat and gas was collected, as it evolved from the reaction mixture, on mercury in a gas burette connected to the reaction flask. When the reaction was complete, the gas was analyzed for carbon dioxide and oxygen by absorption in potassium hydroxide solution and in alkaline pyrogallol solution, respectively.

In one run, decomposition of 3.2 g. (23 mmol.) of peroxybenzoic acid in 40 ml. of isopropyl alcohol at 58°C gave 0.5 mmol. of carbon dioxide and 0.3 mmol. of oxygen.

Kinetic Measurements. — In a 200 ml. round bottomed flask equipped with a gas inlet tube and a spiral condenser carrying a calcium chloride tube at the top was placed a measured amount of an alcohol and the flask was immersed in a thermostat kept at a specified temperature. Nitrogen was passed through the alcohol to exclude oxygen, a weighed amount of peroxybenzoic acid was added, and after dissolution the concentration of the acid was determined iodometrically (normally about 0.1 mol./l.) The time of the sampling was taken as time zero for the kinetic run. Aliquots (2.00 ml.) were withdrawn at intervals and titrated in the usual manner.

At first kinetic results were not reproducible. We then found that the following treatment of reaction vessels gave tolerably reproducible results. A reaction vessel was first washed with concentrated methyl alcoholic solution of potassium hydroxide followed by water, and with concentrated nitric acid followed by water; then dilute solution of peroxybenzoic acid in the organic solvent in which the reaction was to be run was placed in the vessel and kept at 60°C for 3 hr.; and finally the vessel was thoroughly washed with this solvent and dried.

When the effect of light was investigated, a quartz flask or a glass flask coated with black enamel was used. In usual runs no special precaution was taken to exclude diffuse room light; control experiments established that this had no detectable effect upon the reaction rate.

Normally, at 30°C, an induction period ranging from ten to sixty minutes was observed, and sometimes it continued as long as three hours, but it

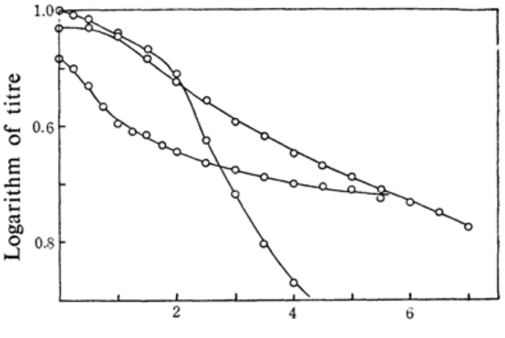

Fig. 1. Rate of decomposition of peroxybenzoic acid in isopropyl alcohol at 30°C (initial concentration of peroxybenzoic acid, ca. 0.1 mol./l.). A plot against time of logarithm of the concentration of peroxybenzoic acid expressed in titre (in ml.) of standard thiosulphate solution (0.04 N) consumed for an aliquot (2 ml.) of peroxybenzoic acid solution.

---

[12] L. F. Fieser, "Experiments in Organic Chemistry", D. C. Heath and Co., Boston, 3rd Ed. (1955), p. 299.

seldom was observed above 50°C. The induction period was followed by a rapid and steady decomposition, but after a few hours the rate began to decrease gradually; some typical runs are shown in Fig. 1. The first-order rate constant for the decomposition was obtained from the slope of the straight part of the curve drawn through plots against time of logarithm of the concentration of peroxybenzoic acid. The mean values of the rate constants from several determinations with standard deviations are shown in Table II.

Results and Discussion

The results of the product study are shown in Table I.

The results of kinetic runs are summarized in Table II, which shows that the apparent decomposition rate in alcohols decreases in the order: isopropyl > ethyl > methyl alcohol. The rate in *tert*-butyl alcohol was nil at 30°C.

The rate of decomposition was larger in an atmosphere of nitrogen than in an atmosphere of oxygen or air for the respective alcohols. In the presence of *p*-benzoquinone in isopropyl alcohol in an atmospherere of nitrogen the decomposition took place much slower, as shown in Fig. 2. When solution of peroxybenzoic acid in isopropyl alcohol was irradiated with ultraviolet light in a quartz flask, a very rapid decomposition occurred. Acceleration by ultraviolet light was also observed in benzene solution, although it took place to a much smaller extent than in isopropyl alcohol.

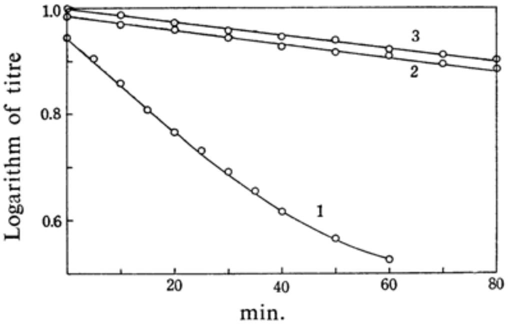

Fig. 2. Rate of decomposition of peroxybenzoic acid in isopropyl alcohol at 55°C (initial concentration of peroxybenzoic acid, ca. 0.1 mol./l.). A plot against time of logarithm of the concentration of peroxybenzoic acid expressed in titre (in ml.) of standard sodium thiosulphate solution (0.04 N) consumed for an aliquot (2 ml.) of peroxybenzoic acid solution.

1, Reaction in a stream of nitrogen
2, In the presence of *p*-benzoquinone (7×10^{-3} mol./l.) in a stream of nitrogen
3, Reaction in an atmosphere of oxygen

These findings suggest that radicals are involved in the decomposition of peroxybenzoic acid in alcohols. It is quite natural and reasonable to assume homolytic rupture of the oxygen-oxygen bond of peroxybenzoic acid as a radical initiation process, giving a benzoyloxy and a hydroxyl radical:

$$C_6H_5C(=O)OOH \rightarrow C_6H_5C(=O)O\cdot + HO\cdot$$

The radicals thus formed attack a molecule of

TABLE I. PRODUCTS FORMED IN DECOMPOSITION OF PEROXYBENZOIC ACID IN ALCOHOLS

		Products (yield, %)				
Alcohol	Temp.	Products from alcohol		Benzoic acid	Carbon dioxide	Oxygen
Methyl	Under reflux	Formaldehyde	42	92		
Ethyl	Room temp.	Acetaldehyde	15	96		
		Acetic acid	22			
Isopropyl	Room temp.	Acetone	56	100		
Isopropyl	60°C	Acetone	61	92		
Isopropyl	58°C				1.2	2

TABLE II. APPARENT PSEUDO-FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION OF PEROXYBENZOIC ACID IN SEVERAL ALCOHOLS AT 30°C

	in Air	in Nitrogen		
Alcohol	$k_1\times10^5$ sec^{-1}	$k_1\times10^5$ sec^{-1}	Relative rate	Relative rate per α-hydrogen
Methyl	0.23 ± 0.04	0.32 ± 0.10	0.3	0.2
Ethyl	0.34 ± 0.07	1.1 ± 0.3	1	1
Isopropyl	0.52 ± 0.05 (0.42 ± 0.04)*	2.7 ± 0.8	2.5	5
tert-Butyl	0	0	0	

* This value is for the decomposition in an atmosphere of oxygen.

TABLE III. RELATIVE RATE CONSTANTS FOR SOME PROCESSES IN THE REACTIONS OF BENZOYL PEROXIDE AND FENTON'S REAGENT WITH ALCOHOLS

Alcohol	Benzoyl peroxide[13]		Fenton's reagent[14]	
	Apparent first-order constant at 60°C (relative value)	k_2 for reaction 2 at 60°C	k_{3B}/k_4 at 60°C	$k_{2'}$ for reaction 2' at room temp.
Methyl	0.20			0.42
Ethyl	1.00	1.00	1.00	1.00
Isopropyl	3.58	3.08	11.36	1.58
tert-Butyl	0.004			

solvent alcohol, abstracting a hydrogen atom α to the hydroxyl group and giving a 1-hydroxyalkyl radical, which will hereafter in this report be briefly called "solvent radical".

Since the apparent decomposition rates were different in various alcohols and the effects of oxygen and *p*-benzoquinone were observed, it is concluded that the induced decomposition of peroxybenzoic acid by solvent radicals must have occurred. If the induced decomposition had not occurred, the apparent decomposition rate of peroxybenzoic acid would have been larger in ethyl alcohol than in isopropyl alcohol, since acetaldehyde primarily formed in the former is more easily oxidized by peroxybenzoic acid than acetone formed in the latter as shown by a separate experiments.

These results suggest a mechanism comprising the following series of reactions.

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

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

$$PhCO_2\cdot + RR'CHOH \rightarrow PhCO_2H + RR'\dot{C}OH \qquad (2)$$

$$HO\cdot + RR'CHOH \rightarrow H_2O + RR'\dot{C}OH \qquad (2')$$

$$PhCO_3H + RR'\dot{C}OH \rightarrow PhCO_2\cdot + RR'C(OH)_2 \qquad (3)$$

$$PhCO_3H + RR'\dot{C}OH \rightarrow HO\cdot + PhCO_2CRR'OH \qquad (3')$$

$$PhCO_2\cdot + RR'\dot{C}OH \rightarrow PhCO_2CRR'OH \qquad (4)$$

$$HO\cdot + RR'\dot{C}OH \rightarrow RR'C(OH)_2 \qquad (4')$$

$$PhCO_2CRR'OH \rightarrow PhCO_2H + RR'CO$$

$$RR'C(OH)_2 \rightarrow H_2O + RR'CO$$

Reaction 1' represents the well known decomposition of the benzoyloxy radical. It turned out, however, that this reaction did not take place to an appreciable extent in alcohols, since, the yield of benzoic acid was invariably nearly quantitative.

Reactions 2 and 2' are abstraction by radicals of a hydrogen atom from a molecule of alcohol; the former has already been proposed by Mashio and Kato[13] for the decomposition of benzoyl peroxide in alcohols, and the latter by Merz and Waters[14] for the reaction of the Fenton reagent with alcohols. They estimated the relative rate constants for reactions 2 and 2', which are shown in Table III. The relative rates decrease in the order: isopropyl > ethyl > methyl alcohol. This order can be interpreted as indicating that a larger rate constant corresponds to a larger resonance stabilization of the solvent radical formed.

Reactions 3 and 3' represent the induced decomposition of peroxybenzoic acid by solvent radicals. Although which of reactions 3 or 3' is the more important could not be determined, the results with hydrocarbons to be subsequently reported suggest that it probably is reaction 3 that took place predominantly. Similar reactions have been also proposed for the induced decomposition of benzoyl peroxide[13,15,16], acetyl peroxide[17], and persulphate[18] by 1-hydroxyalkyl radicals. It has been reported that the induced decomposition of benzoyl peroxide is readily caused by 1-hydroxyalkyl radicals or 1-alkoxyalkyl radicals among various radicals[15,16].

Mashio and Kato[13] has estimated the rate constant k_{3B} for the following reaction relative to the rate constant for reaction 4.

$$PhCO_2OCOPh + RR'\dot{C}OH \rightarrow PhCO_2CRR'OH + PhCO_2\cdot \qquad (3B)$$

Since k_4's can be assumed to be nearly equal for various alcohols, the magnitude of k_{3B}/k_4 is regarded as a measure for k_{3B}. As seen from Table III, k_{3B}/k_4 is larger for isopropyl alcohol than for ethyl alcohol. It therefore

---

[13] S. Kato and F. Mashio, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **59**, 380 (1956); F. Mashio and S. Kato, *Science and Technology* (*Kyoto Techn. Univ.*), **5**, 51 (1956).

[14] J. H. Merz and W. A. Waters, *Discussions Faraday Soc.*, **2**, 179 (1947).

[15] W. E. Cass, *J. Am. Chem. Soc.*, **68**, 1976 (1946).

[16] K. Nozaki and P. D. Bartlett, ibid., **69**, 2299 (1947).

[17] M. S. Kharasch, J. L. Rowe and W. H. Urry, *J. Org. Chem.*, **16**, 905 (1951).

[18] K. B. Wiberg, *J. Am. Chem. Soc.*, **81**, 252 (1959).

seems that k_{3B} is larger for the more electron-donating 1-hydroxyalkyl radical, since the electron-donating property decreases in the order: 1-hydroxy-1-methylethyl > 1-hydroxyethyl > hydroxymethyl radical.

Reactions 4 and 4′ are written as termination reactions; the former has also been suggested for the decomposition of benzoyl peroxide[13].

Evidently, rapid decomposition of peroxybenzoic acid requires the presence of a hydrogen at the α-carbon atom in alcohol; indeed the decomposition was not noticeable in *tert*-butyl alcohol at room temperature. Table II indicates that the rate constant depends upon the nature of the α-hydrogen atom. Moreover, it is interesting to note that there seems to be a parallelism in the apparent decomposition rate between peroxybenzoic acid and benzoyl peroxide as shown by comparison of the values in Table II with those in Table III.

In the present mechanism, the induced decomposition of peroxybenzoic acid by solvent radicals is the major process which distinguishes solvents in the decomposition rate. This process is controlled, in the first place, by the stationary concentration of solvent radicals and, secondly, by their reactivity towards peroxybenzoic acid. The stationary concentration of solvent radicals would tend to increase, other things being equal, according as an α-hydrogen atom of the alcohol is abstracted more readily. The resulting 1-hydroxyalkyl radicals are resonance-stabilized in the order: 1-hydroxy-1-methylethyl > 1-hydroxyethyl > hydroxymethyl. The order of the efficiency with which they are formed from the corresponding alcohols therefore falls in the order: isopropyl > ethyl > methyl alcohol. The reactivity of solvent radicals towards peroxybenzoic acid can be assumed to be parallel to that towards benzoyl peroxide, that is, to be governed by their electron-donating property. Then for this property again the same order as above is valid, as mentioned earlier. Thus alcohols will favour the induced decomposition in the order: isopropyl > ethyl > methyl alcohol, in agreement with the findings in the rate study.

The evolution of oxygen observed in the case of the decomposition in isopropyl alcohol at 58°C might suggest participation of peroxybenzoate anions, since dissociation of peroxybenzoic acid as an acid would be favoured in a polar solvent like alcohols, and the peroxybenzoate anion has been shown to react with peroxybenzoic acid giving oxygen[19]. Oxygen is also formed from α-cumyl hydroperoxide both in aqeous alkaline solution and in cumyl alcohol[20].

Summary

Decomposition of peroxybenzoic acid was studied in methyl, ethyl, isopropyl and *tert*-butyl alcohol. The primary and the secondary alcohols were oxidized to the corresponding carbonyl compounds, which were sometimes further oxidized. The apparent decomposition rate of peroxybenzoic acid in alcohols decreased in the order: isopropyl alcohol > ethyl alcohol > methyl alcohol $\gg$ *tert*-butyl alcohol. For these decompositions a radical mechanism, which involves the homolytic rupture of peroxybenzoic acid and its induced decomposition by 1-hydroxyalkyl radicals derived from the respective alcohols, was proposed. A possible participation of peroxybenzoate anions in these decompositions was suggested.

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

---

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

[20] 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).