Decomposition of Peroxybenzoic Acid in Solution. IV. Decomposition in Solvents in the Presence of Radical-Generators

By Katsumi TOKUMARU, Naoki INAMOTO and Osamu SIMAMURA

(Received September 22, 1962)

In previous parts of this series, decompositions of peroxybenzoic acid in alcohols⁽¹⁾, hydrocarbons⁽²⁾ and ethers⁽³⁾ have been reported, and a radical chain mechanism has been proposed. In this mechanism, the initial radical-forming decomposition of peroxybenzoic acid and its induced decomposition by radicals are essential features. In order to get further information about the induced decomposition, decomposition of peroxybenzoic acid in solvents has been carried out in the presence of radical-generators such as α, α'-azobisisobutyronitrile and isobutyryl peroxide, and the results are described in this part.

Experimental

Materials.—Peroxybenzoic acid was prepared and purified as described previously⁽¹⁾. α, α'-Azobisisobutyronitrile was recrystallized from ether, m. p. 105~106°C. Isobutyryl peroxide was synthesized from isobutyryl chloride prepared by the usual method⁽⁴⁾ and sodium peroxide according to the procedure of Kharasch et al.⁽⁵⁾

Kinetic Measurements.—The rate of decomposition of peroxybenzoic acid was measured by the same method as described previously⁽¹⁾. The active oxygen of peroxybenzoic acid was determined by the usual method⁽⁶⁾. This method was found not applicable to the case of isobutyryl peroxide, because this peroxide was not easily reduced with iodide under these experimental conditions. Isobutyryl peroxide therefore was assayed according to Wagner, Smith and Peter's⁽⁷⁾ procedure.

Product Study.—*Decomposition of Peroxybenzoic Acid in Benzene in the Presence of α, α'-Azobisisobutyronitrile.*—To a solution of peroxybenzoic acid (5.5 g., 40 mmol.) in benzene (20 ml.) heated on a boiling water bath α, α'-azobisisobutyronitrile (6.6 g., 40 mmol.) was added in small portions over 2 hr., and the mixture was heated for a further

---

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

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

3) K. Tokumaru and O. Simamura, ibid., 35, 1955 (1962).

4) H. C. Brown, *J. Am. Chem. Soc.*, **60**, 1325 (1938).

5) M. S. Kharasch, S. S. Kane and H. C. Brown, ibid., **63**, 526 (1941).

6) D. Swern, "Organic Reactions", Vol.7, John Wiley and Sons Inc., New York (1953), p. 378.

7) C. D. Wagner, R. H. Smith and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976 (1947).

4.5 hr. to complete the reaction. Nitrogen and hydrogen cyanide evolved during the reaction. The reaction mixture, to which sodium hydrogen carbonate was added, was subjected to steam distillation and tetramethylsuccinonitrile was separated from the distillate. On treatment with 2, 4-dinitrophenylhydrazine of the aqueous distillate, 2, 4-dinitrophenylhydrazone of acetone (3.6 mmol.) precipitated. From the residue of the steam distillation benzoic acid (4.3 g., 35 mmol.) was obtained.

In another experiment, peroxybenzoic acid (2.0 g., 14.5 mmol.) and α, α'-azobisisobutyronitrile (2.5 g., 15 mmol.) were similarly allowed to decompose in boiling benzene (20 ml.) for 6.5 hr. The reaction mixture was first distilled on a boiling water bath, chloroform was added to the distilling flask as a carrier to remove low boiling volatile matter completely, and the distillation was continued. The distillate was extracted with water; the aqueous extract, on treatment with 2, 4-dinitrophenylhydrazine, gave 2, 4-dinitrophenylhydrazone of acetone (0.6 mmol.). To the residue from the distillation sodium hydrogen carbonate was added, and the mixture was distilled with steam. The aqueous distillate, on treatment with 2, 4-dinitrophenylhydrazine, gave 2, 4-dinitrophenylhydrazone of acetone (0.6 mmol.).

Decomposition of Benzoyl Peroxide in Benzene in the Presence of α, α'-Azobisisobutyronitrile.—Benzoyl peroxide (5.0 g., 20.6 mmol.) and α, α'-azobisisobutyronitrile (6.6 g., 40 mmol.) were decomposed in boiling benzene (20 ml.) for 7 hr. During the decomposition nitrogen evolved, but hydrogen cyanide was not detected. The reaction mixture was distilled as in the second experiment above, but no acetone was detected in the aqueous extract of the distillate. The residue from the distillation was added with sodium hydrogen carbonate and subjected to steam distillation. Addition of 2, 4-dinitrophenylhydrazine to the aqueous distillate gave 2, 4-dinitrophenylhydrazone of acetone (1.5 mmol.), and the residue from the steam distillation gave benzoic acid (1.5 g., 12.3 mmol.) after the usual working up procedure.

Decomposition of Peroxybenzoic Acid in Benzene in the Presence of Isobntyryl Peroxide.—To a solution of peroxybenzoic acid (4.8 g., 34 mmol.) in benzene (50 ml.) heated at 60°C, a benzene solution of isobutyryl peroxide (17 mmol. in 30 ml.) was added gradually and the heating was continued for a total of 3 hr. The reaction mixture was distilled on a boiling water bath. The distillate was shown to contain isopropyl alcohol and acetone by gas chromatography. It was extracted with water, and the aqueous extract, on treatment with 2, 4-dinitrophenylhydrazine, gave 2, 4-dinitrophenylhydrazone of acetone (4 mmol.). Benzoic acid (3.1 g., 25 mmol.) was obtained from the residue of the distillation.

Decomposition of Peroxybenzoic Acid in Cumene in the Presence of Isobutyryl Peroxide.—A solution of isobutyryl peroxide (4 mmol.) in cumene (20 ml.) was added little by little to a cumene solution (100 ml.) of peroxybenzoic acid (3.0 g., 22 mmol.) heated at 60°C and the heating was continued for a total of 3.5 hr. The reaction mixture was extracted with water, and, on addition of 2, 4-dinitrophenylhydrazine in ethanol to the aqueous extract, 2, 4-dinitrophenylhydrazone of acetone (trace) precipitated. The cumene layer was extracted with aqueous sodium hydrogen carbonate, and the aqueous extract gave benzoic acid (1.7 g., 14 mmol.). Distillation of the cumene solution gave cumyl alcohol (1.2 g., 9 mmol.), m. p. 33°C. The needle shaped crystals (0.2 g.) in the residue from the distillation were filtered off, washed with ethyl alcohol and identified as 2, 3-dimethyl-2, 3-diphenylbutane by m. p. (from ethyl alcohol) and mixed m. p. with an authentic sample, 118~119°C, and by comparing infrared spectra.

Results and Discussion

The results of the analysis of reaction products are summarized in Table I.

The formation of acetone and hydrogen cyanide in the decomposition in the presence of α, α'-azobisisobutyronitrile indicates oxidative attack[8] on the 1-cyano-1-methylethyl radical generated from this azonitrile. The process must be the induced decomposition of peroxybenzoic acid by the 1-cyano-1-methylethyl radical (reaction 1) with formation of the benzoyloxy radical and acetone cyanhydrin, the latter subsequently decomposing to acetone and hydrogen cyanide.

$$\mathrm{PhCO_3H + (CH_3)_2\dot{C}CN} \rightarrow \mathrm{PhCO_2\cdot + (CH_3)_2C(OH)CN} \qquad (1)$$

$$\mathrm{(CH_3)_2C(OH)CN} \rightarrow \mathrm{(CH_3)_2CO + HCN} \qquad (2)$$

Distillation of the reaction mixture gave a distillate containing acetone, and subsequent steam-distillation of the residue after addition of sodium hydrogen carbonate yielded a further crop of acetone in a nearly equal amount (isolated as 2, 4-dinitrophenylhydrazone). The latter acetone must have been produced, in the course of the steam-distillation, from some precursor, probably acetone cyanhydrin benzoate produced by the following reaction:

$$\mathrm{PhCO_2\cdot + (CH_3)_2\dot{C}CN} \rightarrow \mathrm{PhCO_2C(CH_3)_2CN} \qquad (3)$$

A mechanism similar to that suggested by Suehiro[9] for the reaction of peroxybenzoic acid with the triphenylmethyl radical may not be excluded:

$$\mathrm{PhCO_3H + (CH_3)_2\dot{C}CN} \rightarrow \mathrm{PhCO_2H + (CH_3)_2C(CN)O\cdot} \qquad (4)$$

The 1-cyano-1-methylethoxy radical will give rise to acetone and hydrogen cyanide through

---

[8] N. Inamoto and O. Simamura, *J. Org. Chem.*, **23**, 408 (1958).

[9] T. Suehiro, presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

TABLE I. PRODUCTS FORMED FROM DECOMPOSITION OF PEROXYBENZOIC ACID IN THE PRESENCE OF RADICAL-GENERATORS

Both the amount of radical-generators and the yields of products are given in percent of the peroxybenzoic acid used.

Radical-Generator	Solvent	Temp. °C	Benzoic acid	Other products
α, α′-Azobisisobutyronitrile 100	Benzene	Under reflux	87	Acetone, 9 Hydrogen cyanide
Isobutyryl peroxide 50	Benzene	60	73	Acetone, 12 Isopropyl alcohol
Isobutyryl peroxide 18	Cumene	60	64	α-Cumyl alcohol, 41 Acetone, trace 2, 3-Dimethyl-2, 3-diphenylbutane, 5

similar paths to those postulated previously in the reaction of α, α′-azobisisobutyronitrile with nitro compounds[8]. If reaction 4 takes place to the complete exclusion of reaction 1, the benzoyloxy radical will not be produced for reaction 3 to occur, and consequently it would be difficult to account for the formation of acetone cyanhydrin benzoate without invoking the improbable reaction 5. It therefore seems that reaction 4 should be only of subordinate importance compared with reaction 1.

The formation of acetone cyanhydrin benzoate would suggest that the following reaction might take place:

$$\mathrm{PhCO_3H} + (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{CN} \rightarrow \mathrm{PhCO_2C(CH_3)_2CN} + \mathrm{HO}\cdot \qquad (5)$$

This possibility, however, seems to be unlikely in view of the evidence discussed previously[2,3], which favours reaction 1 as the more probable one.

In contrast to the case with peroxybenzoic acid, when benzoyl peroxide was decomposed in benzene in the presence of α, α′-azobisisobutyronitrile, no evolution of hydrogen cyanide was detected. Simple distillation of the reaction mixture gave no acetone, but steam-distillation of the residue from the distillation gave acetone, whose source is also attributable to acetone cyanhydrin benzoate.

While peroxybenzoic acid decomposed slowly in *o*-dichlorobenzene at 80°C, addition of α, α′-azobisisobutyronitrile accelerated the decomposition enormously. Thus, while the half life of decomposition of peroxybenzoic acid (the initial concentration, 0.1 mol./l.) was 10.7 hr. in the absence of α, α′-azobisisobutyronitrile, it decreased to 40 min. in its presence (the initial concentration of α, α′-azobisisobutyronitrile, 0.2 mol./l.). On the basis of the rate constant for the unimolecular decomposition of α, α′-azobisisobutyronitrile, 1.53×10^{-4} sec^{-1} at 80°C[10], it is estimated that about 30% of this initiator was decomposed in the course of 40 min., during which 50% of the peroxybenzoic acid originally present had reacted. According to Eqs. 1 and 3, this amount of the acid consumed the 1-cyano-1-methylethyl radical from just an equimolecular quantity of the initiator, that is, 25% of the original amount. This is in rather good agreement with the value of 30% deduced above, indicating that the average efficiency of the 1-cyano-1-methylethyl radical in reaction with peroxybenzoic acid is about 80%. This efficiency of 80% may be too high, because part of peroxybenzoic acid may fairly rapidly be consumed by oxidation of chemical species other than the 1-cyano-1-methylethyl radical, e. g., dimethylketenecyanoisopropylimine produced by dimerization of this radical.

Isobutyryl peroxide decomposes much more rapidly than peroxybenzoic acid in most solvents[11,12]. In the presence of the former, the latter decomposed very rapidly at 60°C. For example, the presence of isobutyryl peroxide (concentration, 0.04 mol./l.) in benzene solution of peroxybenzoic acid (0.1 mol./l.) at 60°C, reduced the half life of peroxybenzoic acid to only 270 sec. Investigation of the products showed the formation of acetone and isopropyl alcohol besides benzoic acid. It therefore was deduced that the isopropyl radical generated thermally from isobutyryl peroxide by way of the isobutyryloxy radical attacks the oxygen atom of peroxybenzoic acid, producing a molecule of isopropyl alcohol and a benzoyloxy radical, and the isopropyl alcohol is further oxidized to acetone (reactions 6 and 7).

$$\mathrm{PhCO_3H} + (\mathrm{CH_3})_2\mathrm{HC}\cdot \rightarrow (\mathrm{CH_3})_2\mathrm{CHOH} + \mathrm{PhCO_2}\cdot \qquad (6)$$

$$(\mathrm{CH_3})_2\mathrm{CHOH} \xrightarrow{\text{oxidation}} (\mathrm{CH_3})_2\mathrm{CO} \qquad (7)$$

---

[10] F. M. Lewis and M. S. Matheson, *J. Am. Chem. Soc.*, **71**, 747 (1949).

[11] J. Smid and M. Szwarc, *J. Chem. Phys.*, **29**, 432 (1958).

[12] K. Tokumaru and O. Simamura, unpublished results.

Obviously, the oxidation of isopropyl alcohol to acetone in accordance with the findings described previously[1] contributes to consumption of peroxybenzoic acid at a rate larger than that corresponding to the straightforward decomposition of isobutyryl peroxide followed by reaction 6 alone.

It was expected that if the reaction was carried out in cumene, which has a hydrogen atom reactive towards radicals, the isopropyl radical generated as well as the benzoyloxy radical from reaction 6 would abstract the hydrogen atom from cumene giving an α-cumyl radical (reactions 8 and 9). This radical then would attack peroxybenzoic acid producing α-cumyl alcohol and a benzoyloxy radical, the latter undergoing reaction 9 leading to the induced decomposition of peroxybenzoic acid as was shown previously[2].

$$(CH_3)_2HC\cdot + PhCH(CH_3)_2 \rightarrow C_3H_8 + Ph(CH_3)_2C\cdot \qquad (8)$$

$$PhCO_2\cdot + PhCH(CH_3)_2 \rightarrow PhCO_2H + Ph(CH_3)_2C\cdot \qquad (9)$$

$$Ph(CH_3)_2C\cdot + PhCO_3H \rightarrow PhC(CH_3)_2OH + PhCO_2\cdot \qquad (10)$$

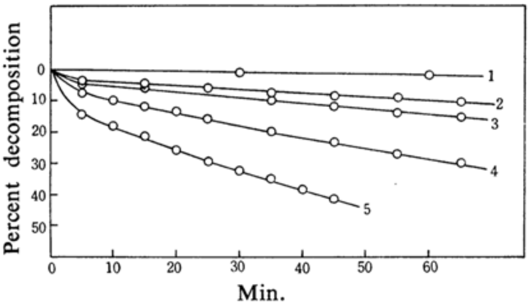

Fig. 1. Decomposition of peroxybenzoic acid in cumene in the presence of isobutyryl peroxide at 40°C. The initial concentration of peroxybenzoic acid, 0.1 mol./l. The initial concentration of isobutyryl peroxide relative to peroxybenzoic acid (in mol. %) : 1, 0% ; 2, 5.6% ; 3, 13.8% ; 4, 22.6% ; 5, 46.0%.

In fact, addition of isobutyryl peroxide to a cumene solution of peroxybenzoic acid caused a rapid decomposition of the latter as depicted in Fig. 1, and α-cumyl alcohol and 2, 3-dimethyl-2, 3-diphenylbutane were found among the products. Evidently 2, 3-dimethyl-2, 3-diphenylbutane, which was not detected in the decomposition in cumene in the absence of isobutyryl peroxide[2], was produced by dimerization of the α-cumyl radical, whose stationary concentration was higher owing to rapid supply of radicals by the decomposition of isobutyryl peroxide than that otherwise prevailing.

The rate of decomposition of peroxybenzoic acid became larger according as the initial concentration of isobutyryl peroxide was increased, but further kinetic study was not made, since this reaction was complicated.

Acetyl peroxide, which is known to decompose more slowly than isobutyryl peroxide, was added to a cumene solution of peroxybenzoic acid at 60°C, but the apparent decomposition rate of peroxybenzoic acid was not so much accelerated as when isobutyryl peroxide was added.

The present results indicate that in the presence of an efficient radical-generator a very rapid decomposition of peroxybenzoic acid takes place, and that this is due to the enhanced induced decomposition of the latter by radicals derived from the former.

Summary

The decomposition of peroxybenzoic acid in solvents was accelerated in the presence of radical-generators such as α, α'-azobisisobutyronitrile and isobutyryl peroxide. This acceleration was ascribed to the induced decomposition of peroxybenzoic acid by radicals formed directly or indirectly from these radical-generators.

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