Decomposition of Peroxybenzoic Acid in Solution. V. Decomposition of Peroxybenzoic Acid and of Benzoyl Peroxide in Binary Mixtures of Carbon Tetrachloride with Cyclohexane, Toluene, or Diethyl Ether

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In the course of investigation of the decomposition of peroxybenzoic acid in various organic solvents[1-4], it has become evident that peroxybenzoic acid suffers induced decomposition on the oxygen to oxygen bond by radicals derived from hydrocarbons, alcohols and ethers with great ease. Although a similar induced decomposition also takes place with benzoyl peroxide, the reactivity towards benzoyl peroxide differs widely from radical to radical, decreasing in the order: 1-hydroxyalkyl, 1-alkoxyalkyl>alkyl>chloroalkyl radical[5]. It therefore has seemed of interest to examine the behaviour of chloroalkyl radicals towards peroxybenzoic acid. An account is given in this paper of results of the decomposition of peroxybenzoic acid and of benzoyl peroxide in a binary mixture of carbon tetrachloride with a solvent containing hydrogen, in which the trichloromethyl radical is supposed to be produced by abstraction of a chlorine atom from carbon tetrachloride by radicals.

Experimental

Materials. — Peroxybenzoic acid was prepared according to the procedure described previously[1]. Benzoyl peroxide was purified by precipitation from a solution in chloroform by addition of methyl alcohol. The solvents used were purified as described previously[1-3].

Decomposition of Peroxybenzoic Acid in a Mixture of Cyclohexane and Carbon Tetrachloride. — Peroxybenzoic acid (2.8 g., 20 mmol.) was decomposed in a mixture of cyclohexane (50 ml.) and carbon tetrachloride (25 ml.) at 80°C under an atmosphere of nitrogen. The reaction mixture was extracted with aqueous sodium hydrogen carbonate, and the aqueous extract gave benzoic acid (1.8 g., 15 mmol.) on acidification. Distillation of the organic layer afforded a mixture of carbon tetrachloride and cyclohexane, crude cyclohexyl chloride (ca. 3 g., 25 mmol.) and cyclohexanol (0.2 g., 2 mmol.). Benzene and chloroform were detected in the recovered solvent by gas chromatography. Presence of small amount of chlorobenzene in the crude cyclohexyl chloride was confirmed by infrared spectrum and gas chromatography. Cyclohexanol was identified as 3,5-dinitrobenzoate, m. p. and mixed m. p. with an authentic sample, 112°C. In the residue from the distillation, ε-caprolactone (0.3 g., 3 mmol.) was found and identified as ε-hydroxycaproic acid hydrazide, m. p. 112°C.

Decomposition of Peroxybenzoic Acid in a Mixture of Toluene and Carbon Tetrachloride.—Peroxybenzoic acid (2.8 g., 20 mmol.) was decomposed in a mixture of toluene (50 ml.) and carbon tetrachloride (25 ml.) at 80°C in a stream of nitrogen. The reaction mixture was distilled; after the solvent was recovered, benzyl alcohol distilled over (trace, identified by infrared absorption measurement). Extraction of the residue from the distillation with aqueous sodium hydrogen carbonate gave benzoic acid (2.1 g., 17 mmol.). In the distillate benzene, chlorobenzene and chloroform were detected, but no benzyl chloride was detected by gas chromatography.

Decomposition of Peroxybenzoic Acid in a Mixture of Diethyl Ether and Carbon Tetrachloride.—Peroxybenzoic acid (2.8 g., 20 mmol.) was decomposed in a mixture of diethyl ether (50 ml.) and carbon tetrachloride (25 ml.) at 37°C under an atmosphere of nitrogen. After 30 hr. the reaction mixture was distilled. Acetaldehyde (5 mmol.) was detected in the distillate and characterized as the 2,4-dinitrophenylhydrazone, m. p. 168°C. Chloroform and ethyl alcohol were found by gas chromatography. However, no chloroether was detected in the distillate. Benzoic acid (2.1 g., 17 mmol.) was isolated from the residue from the distillation.

Decomposition of Benzoyl Peroxide in a Mixture of Cyclohexane and Carbon Tetrachloride.—Benzoyl peroxide (3.0 g., 12.4 mmol.) was decomposed in a mixture of cyclohexane (100 ml.) and carbon tetrachloride (50 ml.) at 80°C under an atmosphere of nitrogen until the peroxide was completely decomposed. Distillation of the reaction mixture gave a mixture of carbon tetrachloride and cyclohexane, crude cyclohexyl chloride (ca. 34.4 g., 290 mmol.) and a liquid boiling at higher temperatures (trace). The crude cyclohexyl chloride was shown to contain small amount of chlorobenzene by the infrared spectrum and by gas chromatography, and in the recovered solvent chloroform and benzene were detected by gas chromatography. Extraction

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

[4] K. Tokumaru, N. Inamoto and O. Simamura, ibid., 36, 72 (1963).

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

of the residue from the distillation with aqueous sodium hydrogen carbonate gave benzoic acid (1.1 g., 9 mmol.). The cyclohexyl chloride was hydrolysed to cyclohexanol and characterized as 3,5-dinitrobenzoate, m. p. 112°C.

Decomposition of Benzoyl Peroxide in a Mixture of Toluene and Carbon Tetrachloride.—Benzoyl peroxide (5.0 g., 20.6 mmol.) was decomposed in a mixture of toluene (100 ml.) and carbon tetrachloride (50 ml.) at 80°C under an atmosphere of nitrogen until the peroxide was completely decomposed. The reaction mixture was distilled, giving carbon tetrachloride, toluene, chlorobenzene (0.9 g., 8 mmol.), b. p. ca. 35°C at 20 mmHg, and benzyl chloride (0.5 g., 4 mmol.), b. p. ca. 72°C at 20 mmHg. Both chlorides were identified by infrared absorption measurement and by gas chromatography, and the benzyl chloride, on treatment with *N, N*-dimethylaniline, afforded benzyldimethylanilinium chloride, m. p. 110°C. In the recovered solvent, benzene and chloroform were detected by gas chromatography. The remaining mixture from the distillation was extracted with aqueous sodium hydrogen carbonate, and the aqueous layer gave benzoic acid (0.8 g., 6.5 mmol.) on acidification. Further distillation of the organic mixture gave a distillate (1.8 g.), b. p. 90~120°C at 2 mmHg, which on cooling, gave bibenzyl as needle shaped crystals (0.5 g.), melting point (from ethyl alcohol) and mixed m. p. with an authentic sample, 52°C.

Decomposition of Benzoyl Peroxide in a Mixture of Diethyl Ether and Carbon Tetrachloride.—Benzoyl peroxide (10.0 g., 41.2 mmol.) was allowed to decompose in a mixture of diethyl ether (200 ml.) and carbon tetrachloride (100 ml.) at 37°C for four weeks in a stream of nitrogen. During the reaction volatile product was collected in a trap cooled with dry ice and ethyl alcohol. After the reaction was over, the reaction mixture was distilled below 40°C on a water bath under reduced pressure of a water-jet aspirator. The distillate was subjected to redistillation, giving, after ether and carbon tetrachloride, a fraction (ca. 15 g.), b. p. ca. 25°C at 60 mmHg. This turned out to be 1-chloroethyl ethyl ether, since it afforded, on being allowed to stand in the air, hydrogen chloride and acetaldehyde, which was identified by conversion into the 2,4-dinitrophenylhydrazone, m. p. 168°C. The recovered solvent and the condensate in the trap were combined and extracted with water, and the aqueous extract, on treatment with 2,4-dinitrophenylhydrazine, gave 2,4-dinitrophenylhydrazone of acetaldehyde. The residue from the first distillation was extracted with aqueous sodium hydrogen carbonate, and the aqueous layer yielded benzoic acid (2.2 g., 18 mmol.) on acidification. Addition of methyl alcohol to the organic layer caused precipitation of benzoyl peroxide (0.8 g., 3 mmol.). After it was filtered off, methyl alcohol was removed and the liquid residue was shown to contain chlorobenzene by infrared measurements.

Results and Discussion

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

The formation of all the products containing no chlorine atom is readily understood on the basis of the free radical mechanism previously postulated for the decomposition of peroxybenzoic acid in solution[1-4], which involves the initial homolysis of the oxygen to oxygen bond:

$$PhCO_3H \rightarrow PhCO_2\cdot + HO\cdot$$

In a mixture of carbon tetrachloride and cyclohexane, the radicals thus generated abstract a hydrogen atom from cyclohexane giving a cyclohexyl radical and benzoic acid or water. The cyclohexyl radical causes the

Table I. Products from decomposition of peroxybenzoic acid or benzoyl peroxide in a mixture of carbon tetrachloride and a solvent (SH) (1 : 2 by volume)

Product and yield (in % based on peroxide)

Solvent	Peroxide*	Temp. °C	Benzoic acid	Product of S–Cl type	Products formed by oxidation of solvent	Other products detected
Cyclohexane	PBA	80	75	Cyclohexyl chloride, 125	Cyclohexanol, 10; ε-caprolactone, 15	Benzene, chloroform, chlorobenzene
	BPO	80	73	Cyclohexyl chloride, 2300		Benzene, chloroform, chlorobenzene, ester (trace)
Toluene	PBA	80	85	Benzyl chloride not detected	Benzyl alcohol, trace	Benzene, chloroform, chlorobenzene
	BPO	80	32	Benzyl chloride, 19		Bibenzyl (13), high boiling liquid, chlorobenzene, benzene, chloroform
Diethyl ether	PBA	37	85	1-Chloroethyl ethyl ether not detected	Acetaldehyde, 25; ethyl alcohol	Chloroform
	BPO	37	47	1-Chloroethyl ethyl ether, approximately 330		Benzoyl peroxide recovered (7), acetaldehyde, chlorobenzene

* PBA and BPO stand for peroxybenzoic acid and benzoyl peroxide, respectively.

induced decomposition of peroxybenzoic acid giving a benzoyloxy radical and cyclohexanol, the latter subsequently giving ε-caprolactone as has previously been discussed in detail(2). For the other solvent mixtures formation of the products containing no chlorine is accounted for in a similar way.

In the presence of carbon tetrachloride besides cyclohexane, the cyclohexyl radical would abstract a chlorine atom from the former yielding cyclohexyl chloride and a trichloromethyl radical. This radical gives chloroform on abstraction of a hydrogen atom from cyclohexane. Chlorobenzene is thought to be formed by attack on carbon tetrachloride by the phenyl radical generated by decomposition of the benzoyloxy radical.

Similarly, benzyl chloride and 1-chloroethyl ethyl ether found in the products from the decomposition of benzoyl peroxide in binary mixtures of carbon tetrachloride with toluene and diethyl ether are formed by abstraction of a chlorine atom from carbon tetrachloride by solvent radicals, namely, the benzyl and the 1-ethoxyethyl radical.

In the decomposition of peroxybenzoic acid in a mixture of cyclohexane and carbon tetrachloride, both cyclohexyl chloride and cyclohexanol were formed, indicating that the two following reactions took place side by side:

$$C_6H_{11}\cdot + PhCO_3H \rightarrow C_6H_{11}OH + PhCO_2\cdot \qquad (1)$$

$$C_6H_{11}\cdot + CCl_4 \rightarrow C_6H_{11}Cl + CCl_3\cdot \qquad (2)$$

However, in this solvent mixture the yield of cyclohexyl chloride was much higher in the decomposition of benzoyl peroxide than in the case of peroxybenzoic acid. The yield of as much as 23 mol. of cyclohexyl chloride for one mole of the benzoyl peroxide decomposed shows that the chain reaction that produces cyclohexyl chloride is sustained for a considerable number of cycles:

$$C_6H_{11}\cdot + CCl_4 \rightarrow C_6H_{11}Cl + CCl_3\cdot$$

$$CCl_3\cdot + C_6H_{12} \rightarrow CHCl_3 + C_6H_{11}\cdot$$

The difference between the two peroxides undoubtedly lies in greater tendency of peroxybenzoic acid to be attacked by the cyclohexyl radical.

In the decomposition of peroxybenzoic acid in a mixture of toluene and carbon tetrachloride and of diethyl ether and carbon tetrachloride no chlorides derived from the solvents, that is, benzyl chloride and 1-chloroethyl ethyl ether, were found, showing that the reactions corresponding to reaction 2 could not successfully compete with those corresponding to reaction 1 in these cases. The benzyl and the 1-ethoxyethyl radical are accepted as stabilized owing to resonance and therefore rather sluggish in reaction, so that they would abstract a chlorine atom from carbon tetrachloride only slowly, but it is quite remarkable that they attacked peroxybenzoic acid with ease.

On the other hand, the decomposition of benzoyl peroxide in these solvent mixtures gave benzyl chloride and 1-chloroethyl ethyl ether, indicating that the benzyl and the 1-ethoxyethyl radical abstracted a chlorine atom from carbon tetrachloride rather than react exclusively with benzoyl peroxide. Thus it is concluded that peroxybenzoic acid reacts with the cyclohexyl, benzyl and 1-ethoxyethyl radical much more readily than benzoyl peroxide does.

In a mixture of diethyl ether and carbon tetrachloride the decomposition of benzoyl peroxide was not finished in four weeks, whereas it was shown complete in ten days at 37°C in a separate experiment in pure diethyl ether; indeed, the 1-ethoxyethyl radical is known to be highly reactive towards benzoyl peroxide(6). It is concluded from these findings that the induced decomposition of benzoyl peroxide by the 1-ethoxyethyl radical is suppressed in the presence of carbon tetrachloride, the 1-ethoxyethyl radical readily reacting with carbon tetrachloride instead of reacting with benzoyl peroxide. The change in polarity of the solvent, that is, from pure ether to a mixture of ether and carbon tetrachloride might be another contributing factor.

The formation of bibenzyl in the decomposition of benzoyl peroxide in a mixture of toluene and carbon tetrachloride is accounted for by the comparative inefficiency of the benzyl radical in attacking benzoyl peroxide; thus its stationary concentration would be increased to such an extent that the dimerization giving bibenzyl would become noticeable. The comparative inertness of the benzyl radical towards carbon tetrachloride should be partly responsible for the increased stationary concentration.

The trichloromethyl radical formed from carbon tetrachloride would abstract a hydrogen atom from a molecule of solvent (SH) giving chloroform (reaction 3), and it could attack peroxybenzoic acid, producing phosgene and hydrogen chloride (reactions 4 and 4′).

$$CCl_3\cdot + SH \rightarrow CHCl_3 + S\cdot \qquad (3)$$

$$CCl_3\cdot + PhCO_3H \rightarrow CCl_3OH + PhCO_2\cdot \qquad (4)$$

$$CCl_3OH \rightarrow COCl_2 + HCl \qquad (4')$$

Reaction 3 is a well known reaction, and in fact extensive formation of chloroform was

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

observed in all cases examined. Reaction 4, however, does not seem important, since formation of only negligible traces of phosgene and hydrogen chloride was observed. Thus the trichloromethyl radical, in contrast with the other radicals so far examined, appears to be extremely reluctant to attack peroxybenzoic acid. The cause should be ascribed to the electron-accepting property of the trichloromethyl, as will subsequently be discussed.

Summary

Decompositions of peroxybenzoic acid and of benzoyl peroxide were carried out in binary mixtures of carbon tetrachloride with cyclohexane, toluene or diethyl ether. The results of the product study strongly support the radical mechanism established previously and show that the oxygen to oxygen bond of peroxybenzoic acid is attacked by radicals more readily than that of benzoyl peroxide, but even peroxybenzoic acid is hardly attacked by the trichloromethyl radical.

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