Decomposition of Peroxybenzoic Acid in Solution.
II. Decomposion in Hydrocarbons

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In the preceding paper[1] we have proposed a radical chain mechanism for the decomposition of peroxybenzoic acid in alcohols. In alcohols, peroxybenzoic acid decomposes not only through the initial homolytic rupture, but also through the induced decomposition due to attack by 1-hydroxyalkyl radicals formed from alcohol molecules. In the decomposition of benzoyl peroxide, it is well known that the induced decomposition of the oxygen-oxygen bond by radicals derived from solvent molecules does not occur as readily in hydrocarbons as in alcohols or ethers[2]. Therefore, by analogy with benzoyl peroxide, we first imagined that peroxybenzoic acid might decompose in hydrocarbons with a lesser extent of the induced decomposition by solvent radicals and the apparent decomposition rate might approximate the initial decomposition rate of peroxybenzoic acid. The present report deals with the decomposition of peroxybenzoic acid in several hydrocarbons; it has turned out that peroxybenzoic acid also is extensively attacked by solvent radicals in hydrocarbons.

Experimental

Materials. — Peroxybenzoic acid was prepared according to the procedure previously described[1]. *n*-Heptane was shaken with sulphuric acid, followed by aqueous sodium hydroxide solution, dried with calcium chloride and then with sodium metal, and distilled. Cyclohexane was treated with nitric acid-sulphuric acid mixture, washed with aqueous sodium hydroxide, dried with calcium chloride and then with sodium metal, and distilled. Cyclohexanol was washed with aqueous sodium hydroxide, dried with anhydrous sodium sulphate, purified with repeated freezing, and distilled. Cumene was shaken with sulphuric acid, washed with aqueous sodium hydroxide solution, dried with calcium chloride and then with sodium metal, and distilled under an atmosphere of nitrogen. Benzene and toluene were shaken with sulphuric acid, washed with sodium hydroxide solution, dried with calcium chloride and then with sodium metal and distilled; benzene was further purified with repeated freezing and finally distilled over sodium. Carbon tetrachloride was refluxed with a mixture of aqueous potassium hydroxide solution and ethyl alcohol, washed with sulphuric acid and then with aqueous sodium hydroxide, dried with calcium chloride, and distilled.

Kinetic Measurements.—In some kinetic runs the procedure was essentially the same as described in Part I[1]. In most runs aliquots (2 ml.) of a solution of peroxybenzoic acid (0.1 mol./l.) were placed in glass tubes, the tubes were evacuated thoroughly with alternate chilling and warming to remove oxygen, sealed, and immersed in a thermostat kept at 79°C, and the contents were analyzed iodometrically for peroxybenzoic acid at intervals. Typical runs are shown in Fig. 1. Under the present experimental conditions no induction period

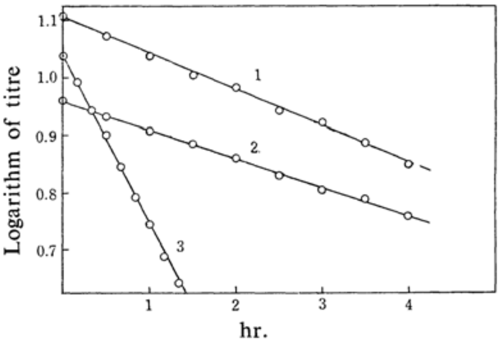

Fig. 1. Rate of decomposition of peroxybenzoic acid in hydrocarbons at 79°C (initial concentration of peroxybenzoic acid, ca. 0.1 mol./l.). A plot against time of logarithm of the concentration of peroxybenzoic acid expressed in titre (in ml.) of standard thiosulphate solution (0.04 N) consumed for an aliquot (2 ml.) of peroxybenzoic acid.
1, 2 in cyclohexane, 3 in cumene

TABLE I. APPARENT PSEUDO-FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION OF PEROXYBENZOIC ACID IN SOME SOLVENTS
at 79°C; initial concentration, ca. 0.1 mol./l.

Solvent	$k_1 \times 10^4$ sec^{-1}
Carbon Tetrachloride	0.02
Benzene	0.26±0.02
n-Heptane	0.33±0.02
Cyclohexane	0.37±0.02
Toluene	1.6 ±0.1
Cumene	1.9 ±0.1
Cyclohexanol	~40

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

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

was observed. 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 together with deviation are shown in Table I.

Product Study.—The decomposition was carried out in a three-necked round bottomed flask equipped with an inlet tube for nitrogen and a spiral condenser, to the top of which were connected, in order of mention, a trap cooled with dry-ice ethyl alcohol, a calcium chloride tube and a potash bulb. A weighed amount of peroxybenzoic acid dissolved in a solvent was placed in the flask which was immersed in a thermostat and allowed to decompose in a slow stream of nitrogen. The decomposition was carried out until no more absorption of carbon dioxide in the potash bulb was observed. Then the reaction mixture was worked up.

For analysis of gaseous products, a solution of small amount of peroxybenzoic acid was decomposed in a closed system, and the gas evolved was analysed for carbon dioxide and oxygen by absorption method as described in Part I[1].

Decomposition in n-Heptane. — Peroxybenzoic acid (9.3 g., 67 mmol.) dissolved in 250 ml. of *n*-heptane (the initial concentration of peroxybenzoic acid, 0.27 mol./l.) was heated at 90°C for 19 hr. in a stream of nitrogen. After the decomposition was over, benzoic acid, deposited in the reaction flask, was filtered off; a little water was observed to have been formed. The filtrate was extracted repeatedly with 5% aqueous sodium hydrogen carbonate. The organic layer was dried with anhydrous sodium sulphate and distilled giving heptane and two fractions, b. p. 45~50°C at 22 mmHg (0.75 g.) and b. p. ca. 68°C at 22 mmHg (0.8 g.), respectively. The former was shown to be a mixture of heptanols and heptanones and the latter a mixture of C_7 esters, such as amyl acetate, by comparison of the infrared spectra with those of authentic specimens. The aqueous extract, on acidification with hydrochloric acid and extraction with ether, afforded benzoic acid, m. p. 121°C. The total amount of this acid formed in this reaction was 5.7 g. (46.8 mmol.).

The amount of the carbon dioxide formed as estimated from the increment of the weight of the potash bulb was 0.70 g. (15.8 mmol.). No formation of oxygen was observed in the reaction in heptane.

Decomposition in Cyclohexane. — Solution of peroxybenzoic acid (10.5 g., 76 mmol.) in 250 ml. of cyclohexane (the initial concentration, 0.3 mol./l.), was heated at 79°C for 27 hr. in a stream of nitrogen. The reaction mixture was cooled and the deposited benzoic acid filtered off; a small amount of water was noticeable in the reaction mixture. The filtrate was shaken with water; the aqueous layer, on treatment with 2,4-dinitrophenylhydrazine, gave 2,4-dinitrophenylhydrazone of cyclohexanone (trace), m. p. 158°C. It was then extracted with aqueous sodium hydrogen carbonate to isolate benzoic acid. Most of the solvent was removed from the organic layer on a water bath, and in the recovered cyclohexane benzene was detected by its characteristic ultraviolet absorption at 220~270 mμ. The residue was subjected to fractionation giving cyclohexanol (0.4 g., 4 mmol.), b. p. 68°C at 20 mmHg, which was identified by infrared spectrum measurement, and characterized as 3,5-dinitrobenzoate, m. p. 112°C, and a small amount of a colourless viscous liquid, b. p. 110°C at 2 mmHg, which was identified with ε-caprolactone by converting it into ε-hydroxycaproic acid hydrazide (Found: C, 49.31; H, 9.79. Calcd. for $C_6H_{14}N_2O_2$: C, 49.30; H, 9.63%.), m. p. 114~115°C[3,4]. The residue in the distilling flask was shown to be a mixture of ε-caprolactone and its polymers by treatment with hydrazine hydrate on a boiling water-bath, ε-hydroxycaproic acid hydrazide being obtained. The total amount of ε-caprolactone in the monomeric and the polymeric form was about 2 g. (18 mmol.). In this experiment benzoic acid recovered amounted to 6.1 g. (50 mmol.) and carbon dioxide, 0.83 g. (19 mmol.). A separate small scale experiment in a closed system showed that no oxygen was formed in cyclohexane.

Decomposition in Cyclohexanol. — Peroxybenzoic acid, (1.4 g., 10 mmol.) was decomposed in cyclohexanol (40 ml.) (the initial concentration, 0.26 mol./l.) at 79°C for 1 hr. under an atmosphere of nitrogen. The reaction mixture was diluted with benzene, and extracted with water. The aqueos extract, on treatment with 2,4-dinitrophenylhydrazine, gave 2,4-dinitrophenylhydrazone of cyclohexanone (0.2 mmol.), m. p. 158°C. The organic layer was worked up as described for the experiment with cyclohexane to give benzoic acid (1.15 g., 9.5 mmol.) and ε-caprolactone (0.07 g., 0.6 mmol.), identified as ε-hydroxycaproic acid hydrazide, m. p. 114~115°C.

Decomposition in Cumene. — Peroxybenzoic acid (12.5 g., 90 mmol.) was decomposed in cumene (200 ml., the initial concentration of the acid, 0.35 mol./l.) at 79°C for 8 hr. in a stream of nitrogen. A small amount of water was detected. The reaction mixture was extracted with aqueous sodium hydrogen carbonate, and the aqueous extract gave benzoic acid (9.9 g., 81 mmol.) on acidification. The organic layer was extracted with aqueous sodium hydroxide; the aqueous extract was reddish brown, but gave no identifiable substance. Distillation of the organic layer afforded cumene and cumyl alcohol (2.1 g., 15 mmol.), b. p. 63~66°C at 2 mmHg, a considerable amount of tarry matter (ca. 0.5 g.) remaining. Cumyl alcohol was purified by repeated sublimations under reduced pressure, m. p. 33°C, (Found: C, 79.33; H, 9.05. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88%). The infrared spectrum of the crude cumyl alcohol showed the presence of acetophenone in trace amount.

In separate experiments, oxygen was not detected by the absorption method.

Decomposition in Toluene. — Peroxybenzoic acid (3.5 g., 25 mmol.) was decomposed in toluene (70 ml., the initial concentration of the acid, 0.36 mol./l.) at 79°C for 5 hr. in a stream of nitrogen.

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[3] F. J. Van Natta, J. W. Hill and W. H. Carothers, *J. Am. Chem. Soc.*, **56**, 455 (1934).

[4] S. L. Friess, ibid., **71**, 2571 (1949).

Extraction of the reaction mixture with aqueous sodium hydrogen carbonate gave benzoic acid (3.5 g., 28 mmol.). Distillation of the organic layer gave toluene, benzyl alcohol, (0.2 g., 2 mmol.), b. p. 105°C at 20 mmHg, and a tarry residue (ca. 0.2 g.). The benzyl alcohol was characterized by formation of 3,5-dinitrobenzoate, m. p. 112°C, and by the infrared spectrum.

Decomposition in Carbon Tetrachloride in the Presence of Iodine.—Peroxybenzoic acid (5.1 g., 37 mmol.) and iodine (10.0 g., 39.5 mmol.) were dissolved in carbon tetrachloride (130 ml.) and the solution was heated under reflux for 90 hr.

The precipitate formed was filtered off and washed with carbon tetrachloride and ethyl alcohol until the colour due to iodine was no longer observed in washings. After being dried, it was identified as diiodine pentoxide (0.4 g., ca. 1 mmol.), by determining both neutralization and oxidation equivalent (Found: neutralization equivalent, 165.9; oxidation equivalent, 27.4. Calcd. for I_2O_5: neutralization equivalent, 166.9; oxidation equivalent, 27.82.). The filtrate was shaken with aqueous sodium thiosulphate solution to remove iodine, and extracted with aqueous sodium hydrogen carbonate. The aqueous extract gave benzoic acid (4.0 g., 33 mmol.). Carbon tetrachloride was distilled, and the residue from the distillation was subjected to steam distillation. From the distillate hexachloroethane (0.1 g.). was obtained and identified by infrared spectrum measurement, m. p. (from ethyl alcohol) and mixed m. p. with an authentic sample measured in a sealed tube, 185°C.

Results and Discussion

The results of kinetic runs are shown in Table I. The apparent decomposition rates varied from solvent to solvent, and the tendency of variation was not always similar to that in the case of benzoyl peroxide[2].

When a small amount of *p*-benzoquinone was added in *n*-heptane solution of peroxybenzoic acid, apparent decomposition was retarded: at 90°C, with an initial concentration of 0.1 mol./l. of peroxybenzoic acid, k_1 was $1.5\times10^{-4}\,\mathrm{sec}^{-1}$ in the absence of *p*-benzoquinone, and $1.4\times10^{-5}\,\mathrm{sec}^{-1}$ in its presence ($0.6\sim1.2\times10^{-2}$ mol./l.).

The results of the product study are summarized in Table II. The sum of the amounts in which benzoic acid and carbon dioxide were formed is a measure of the amount of the CO_3H group decomposed, and it amounted nearly to 100% of the peroxybenzoic acid used, as seen from this table. However, in the reaction in toluene, the yield of benzoic acid exceeds the amount of the peroxybenzoic acid decomposed. This suggests that part of the benzoic acid probably was formed by the oxidation of toluene by way of benzyl alcohol and benzaldehyde.

As in the case of the reaction in alcohols, the radical nature of the decomposition of peroxybenzoic acid in hydrocarbons is indisputable. On the basis of the results of the kinetic and the product analysis, the following series of reactions are postulated which include the induced decomposition (reaction 3) of peroxybenzoic acid by solvent radicals (S·) generated from molecules of a hydrocarbon (SH) by abstraction of a hydrogen atom (reactions 2, 2′ and 2″).

$$\mathrm{PHCO_3H} \rightarrow \mathrm{PhCO_2\cdot} + \mathrm{HO\cdot} \tag{1}$$

$$\mathrm{PhCO_2\cdot} \rightarrow \mathrm{Ph\cdot} + \mathrm{CO_2} \tag{1'}$$

$$\mathrm{PhCO_2\cdot} + \mathrm{SH} \rightarrow \mathrm{PhCO_2H} + \mathrm{S\cdot} \tag{2}$$

$$\mathrm{HO\cdot} + \mathrm{SH} \rightarrow \mathrm{H_2O} + \mathrm{S\cdot} \tag{2'}$$

$$\mathrm{Ph\cdot} + \mathrm{SH} \rightarrow \mathrm{PhH} + \mathrm{S\cdot} \tag{2''}$$

$$\mathrm{PhCO_3H} + \mathrm{S\cdot} \rightarrow \mathrm{SOH} + \mathrm{PhCO_2\cdot} \tag{3}$$

$$\mathrm{S\cdot} + \mathrm{HO\cdot} \rightarrow \mathrm{SOH} \tag{4}$$

$$\mathrm{S\cdot} + \mathrm{PhCO_2\cdot} \rightarrow \mathrm{PhCO_2S} \tag{4'}$$

$$\mathrm{S\cdot} + \mathrm{S\cdot} \rightarrow \mathrm{S_2} \tag{4''}$$

$$\mathrm{SOH} \rightarrow \text{Oxidation products} \tag{5}$$

TABLE II. YIELDS (IN %) OF PRODUCTS FORMED IN DECOMPOSITION OF PEROXYBENZOIC ACID IN SOME SOLVENTS

Solvent	Temp. °C	Products from solvents	Benzoic acid	Carbon dioxide	Remark
n-Heptane	90	Heptanols Heptanones C_7-Ester	69	23	Water detected
Cyclohexane	79	Cyclohexanol 5 Cyclohexanone trace ε-Caprolactone 24	66	25	Water and benzene detected
Cyclohexanol	79	Cyclohexanone 2 ε-Caprolactone 6	95		
Cumene	79	α,α-Dimethylbenzyl alcohol 17 Distillation residue	89	8	Water detected
Toluene	79	Benzyl alcohol 8 Benzoic acid Distillation residue	112		

Reaction 1′ is the well known decomposition of the benzoyloxy radical. This reaction takes place to an appreciable extent in hydrocarbons, competing with the abstraction of a hydrogen atom from a solvent molecule (reaction 2). Reaction 1′ is less important in cumene and toluene, which possess a hydrogen atom at the α position available for ready abstraction by the benzoyloxy radical; in fact in these hydrocarbons the yield of benzoic acid was nearly quantitative. In contrast to this, the yield of benzoic acid was lower and that of carbon dioxide higher in cyclohexane and heptane; in these hydrocarbons hydrogen atoms are not as liable to attack as the α-hydrogen atom in cumene and toluene. However, in cumene and toluene, such possibility could not be excluded that the oxidation of the aromatic nucleus by peroxybenzoic acid through an ionic or molecular mechanism may occur in which peroxybenzoic acid transfers an atom of oxygen to the aromatic nucleus, being itself converted into benzoic acid.

Radicals generated in the reacting solution abstract a hydrogen atom from a molecule of hydrocarbon (SH) giving rise to a hydrocarbon radical (S·), which appears to react mainly by decomposing peroxybenzoic acid. The products from this induced decomposition are the corresponding alcohol (SOH) and the benzoyloxy radical. The alcohol may further be oxidized (reaction 5) to the corresponding carbonyl compound, carboxylic acid and ester according to the scheme set forth in Part I⁽¹⁾. In fact, the successive oxidation of cyclohexanol, the primary product from cyclohexane, to cyclohexanone and ε-caprolactone was borne out as described in the experimental part.

The retarding action of *p*-benzoquinone indicates that the induced decomposition is important. In the absence of the induced decomposition water ought to have been formed in much larger amount than actually found, and the benzoate ester ($PhCO_2S$) derived from the hydrocarbon would have been formed at least in an amount comparable to that of the alcohol (SOH, reactions 4 and 4′), because hydroxyl radicals would abstract a hydrogen atom from a molecule of hydrocarbon more efficiently than benzoyloxy radicals do, the stationary concentration of the latter radical thus becoming larger than that of the former. In fact no such benzoate ester was detected at all.

A similar mechanism has recently been postulated by other workers for the induced decomposition of other organic peroxyacids. Thus, Lefort, Paquot and Sorba⁽⁵⁾ have found that decomposition of peroxylauric acid in petroleum ether gave *n*-undecanol in a good yield and postulated attack of a *n*-undecyl radical generated by decomposition of a lauroyloxy radical on a molecule of peroxylauric acid giving a molecule of *n*-undecanol and a lauroyloxy radical.

$$C_{11}H_{23}\cdot + C_{11}H_{23}CO_3H \rightarrow C_{11}H_{23}OH + C_{11}H_{23}CO_2\cdot$$

More recently Heywood, Phillips and Stansbury⁽⁶⁾ have studied decomposition of peroxyacetic acid in several solvents and proposed a radical chain mechanism very similar to ours. There, the induced decomposition of peroxyacetic acid by solvent radicals (S·) has also been postulated, giving rise to a molecule of the corresponding alcohol and a acetyloxy radical, which decomposes to a methyl radical and carbon dioxide.

$$S\cdot + CH_3CO_3H \rightarrow SOH + CH_3CO_2\cdot$$

Further, Lefort, Sorba and Rouillard⁽⁷⁾ have presented a similar mechanism for the formation of cyclohexanol in the decomposition of peroxylauric acid in cyclohexane.

It is noteworthy that peroxybenzoic acid is, as shown in the present work, readily attacked at the peroxidic oxygen atom even by the radical derived from hydrocarbon, which is usually regarded as rather inefficient in causing the induced decomposition of benzoyl peroxide⁽²⁾ compared with radicals from ethers and alcohols. In this respect, peroxybenzoic acid is rather similar to hydroperoxides than to benzoyl peroxide. Thus, Fordham and Williams⁽⁸⁾ have postulated the attack of α,α-dimethylbenzyl radicals on α,α-dimethylbenzyl hydroperoxide to produce a molecule of α,α-dimethylbenzyl alcohol and an α,α-dimethylbenzyloxy radical in decomposition of α,α-dimethylbenzyl hydroperoxide in cumene. Further, Bateman and Hughes⁽⁹⁾ have assumed induced decomposition of cyclohexenyl hydroperoxide by cyclohexenyl radicals giving cyclohexenol and a cyclohexenoxy radical, whereas in the decomposition of benzoyl peroxide in cyclohexane⁽¹⁰,¹¹⁾, such a mode of decomposition does not seem to be significant.

As regards the initiation process in alcohols and hydrocarbons, we have proposed a unimolecular homolysis of the oxygen to oxygen

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

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

7) D. Lefort, J. Sorba and D. Rouillard, *Bull. soc. chim. France*, **1961**, 2219.

8) J. W. R. Fordham and H. L. Williams, *Can. J. Research*, **B27**, 943 (1949).

9) L. Bateman and H. Hughes, *J. Chem. Soc.*, **1952**, 4594.

10) P. H. Hermans and J. Van Eyk, *J. Polymer Sci.*, **1**, 407 (1946).

11) C. Walling and E. S. Savas, *J. Am. Chem. Soc.*, **82**, 1738 (1960).

bond of peroxybenzoic acid producing a benzoyloxy radical and a hydroxyl radical (reaction 1). Since peroxybenzoic acid was found to be consumed very slowly in carbon tetrachloride, it was at first thought that the rate of the homolysis of the oxygen to oxygen bond had been measured, the induced decomposition by the solvent radical, the trichloromethyl radical, having hardly occurred. If peroxybenzoic acid decompose by a similar reaction scheme in carbon tetrachloride to that in alcohols and hydrocarbons, the benzoyloxy radical initially formed will predominatly decompose to carbon dioxide and a phenyl radical, which abstracts a chlorine atom from carbon tetrachloride and yields chlorobenzene and a trichloromethyl radical; the latter will then give hexachloroethane by dimerization or phosgene and hydrogen chloride through its attack on peroxybenzoic acid or its combination with a hydroxyl radical. In fact the decomposition products in carbon tetrachloride contained only negligible traces of chlorobenzene, hexachloroethane and phosgene[12]. These findings therefore lead us to conclude that the decomposition rate of peroxybenzoic acid observed in carbon tetrachloride cannot be regarded as representing the unimolecular homolysis of peroxybenzoic acid.

If peroxybenzoic acid decomposed in benzene predominantly by the radical path, biphenyl and phenol ought to have been obtained. Actually, among the decomposition products in benzene neither biphenyl nor phenol was detected and only a trace of carbon dioxide was formed[12], indicating that the benzoyloxy radical was produced only to a limited extent. It is true that any phenol produced might have been further oxidized by peroxybenzoic acid[13], but the above findings strongly suggest that most part of peroxybenzoic acid reacted by oxidizing the benzene nucleus through a mechanism other than homolytic.

In order to get a deeper insight into the initiation process, decomposition of peroxybenzoic acid in carbon tetrachloride in the presence of iodine was carried out with the intention of catching benzoyloxy radicals according to Hammond's[14] procedure used in his study on benzoyl peroxide. However, in the present experiment, unexpectedly, diiodine pentoxide was obtained, showing that peroxybenzoic acid oxidized iodine to diiodine pentoxide, and that this method was not suitable for the study of the unimolecular homolytic decomposition of peroxybenzoic acid.

Meanwhile in this laboratory peroxybenzoic acid has been shown to initiate a radical polymerization of methyl methacrylate[15] and kinetic measurements of this polymerization have yielded the following expression for the rate constant of the initiation, the initiation efficiency of unity being assumed:

$$2.11\times10^4 \exp(-15400/\boldsymbol{RT})\,\mathrm{sec}^{-1}$$

This rate constant may well be taken to be that for the initial homolytic rupture of the oxygen to oxygen bond in peroxybenzoic acid. Indeed it is extremely striking that both activation energy and frequency factor are so small as compared with the corresponding values for other organic peroxides. Thus, for example, with benzoyl peroxide, the following value[16] is reported.

$$3.0\times10^{13} \exp(-29600/\boldsymbol{RT})\,\mathrm{sec}^{-1}$$

Recently Cohen and Edwards[17] have carried out kinetic study of decomposition of peroxybenzoic acid in the presence of 2, 2-diphenyl-1-picrylhydrazyl in benzene or in *n*-butyl alcohol at 60 and 65°C, estimated the rate constant of the free-radical cleavage of peroxybenzoic acid and calculated the activation energy to be about 30 kcal./mol. in benzene. Since there is no cogent reason for assuming that there exists no interaction at all between peroxybenzoic acid and 2, 2-diphenyl-1-picrylhydrazyl other than the latter is consumed by being attacked by radicals generated from the former, the values obtained by the American workers must be accepted with some reservation. However, if this value of 30 kcal./mol. is correct for the activation energy for the unimolecular homolysis of the oxygen to oxygen bond in peroxybenzoic acid, the abnormal value obtained by us suggests that the initiation might occur rather through some interaction between peroxybenzoic acid and the vinyl monomer. Moreover, the alternative possibility can not be overlooked that peroxybenzoic acid may decompose by interaction with a molecule of solvent (H–S), producing radicals, as represented in reaction (1a).

$$\mathrm{PhCO_3H + H{-}S \rightarrow PhCO_2\cdot + H_2O + S\cdot} \qquad (1a)$$

A similar mode of decomposition has been

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

[13] K. Akiba and O. Simamura, unpublished.

[14] G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950).

[15] O. Simamura, T. Suehiro and H. Terada, presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960; H. Terada, *J. Soc. Organic Synthetic Chem. Japan* (*Yuki-gosei Kagaku Kyokaishi*), **19**, 721 (1961); **20**, 74, 158 (1962).

[16] C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951). Similar data are tabulated in A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides", Interscience Publishers, New York (1954), p. 78.

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

suggested by Semenov[18] and Thomas and Harle[19] for the decomposition of hydroperoxides.

Summary

Decomposition of peroxybenzoic acid was studied in *n*-heptane, cyclohexane, cumene, and toluene. The hydrocarbons were oxidized to the corresponding alcohols, which were often oxidized further. For these decompositions, a radical chain mechanism was proposed, which involves the homolytic rupture of the oxygen-oxygen bond of peroxybenzoic acid as the initiation process and an induced decomposition of this bond by solvent radicals derived from hydrocarbon molecules.

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[18] N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity" (translated by J. E. S. Bradley), Vol. II, Pergamon Press, London (1959), p. 128.

[19] J. R. Thomas and O. L. Harle, *J. Phys. Chem.*, **63**, 1027 (1959).