tures which produce any change. Allyl benzenesulfinate yields allyl phenyl sulfone on heating and both crotyl benzenesulfinate and α-methylallyl benzenesulfinate rearrange on heating to a product which is principally crotyl phenyl sulfone, and probably contains small amounts of α-methylallyl phenyl sulfone.

The oxidation of crotyl phenyl sulfide yields crotyl phenyl sulfone, and the oxidation of α-methylallyl phenyl sulfide also yields crotyl phenyl sulfone. The product obtained by oxidizing α-methylallyl phenyl sulfide was characterized chemically and by infrared analysis. The spectral analysis confirmed its identity as crotyl phenyl sulfone and indicated the presence in the sample of about 10% of the secondary isomer, α-methylallyl phenyl sulfone.

CAMBRIDGE, MASS.
RECEIVED JUNE 21, 1949

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Decomposition of *p*-Methoxy-*p'*-nitrobenzoyl Peroxide

BY JOHN E. LEFFLER[1]

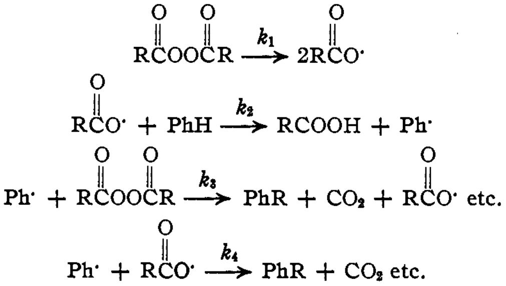
Part I. The Free Radical Decomposition

The present paper is part of a program of research on the mechanisms of peroxide decomposition and certain related oxidation reactions.[2] In particular it is desired to know: (a) the ionic or radical nature of the reaction mechanisms, (b) the role of the structure of the compound and the nature of the reaction medium in determining whether the reaction will be of radical or ionic type and (c) the extent to which a change in the ionic or radical character of the reaction changes the products.

Benzoyl peroxide has been shown to decompose by a free radical mechanism under most circumstances.[3] The reaction is of mixed first and higher order depending on the solvent and the nature of the processes by which chains of radical-induced decomposition are broken.[3] Evidence of the radical nature of the reaction is provided by the following facts: it is inhibited by oxygen; it goes at the same rate in the non-polar solvent benzene as it does in the polar solvent nitrobenzene; it initiates the polymerization of styrene. The reaction continues to be mainly radical in nature even under conditions favoring an ionic mechanism. Benzoyl peroxide acts as a polymerization initiator for the highly polar monomer acrylonitrile without any added solvent. Its decomposition. is only weakly catalyzed by acids and then only by the strongest acids in fairly high concentrations.[4] Such behavior is not surprising in view of the symmetrical structure of benzoyl peroxide.

The unsymmetrical analog, *p*-methoxy-*p'*-nitrobenzoyl peroxide, however, acts quite differently. Although it can decompose by a radical mechanism, a moderate change in the conditions of the reaction leads to decomposition by an ionic path.

The reaction in benzene at 70° is first order, the rate constant being $7.5 \pm 0.2 \times 10^{-2}$ hours^{-1}. The difference in rate constants between two runs differing in starting concentration by a factor of twelve is less than the experimental error. Unlike the decomposition of benzoyl peroxide the reaction is first order with no observable contribution from higher order terms. Figure 1 shows the kinetic runs in benzene at 70°, the black circle above the top curve shows the deviation from that curve caused by not removing oxygen from the ampoule containing the decomposing peroxide before sealing it. Since the reaction is slower in the presence of oxygen it is likely that the mechanism is similar to that of benzoyl peroxide decomposition, the oxygen inhibiting the reaction by combining with chain carrying radicals.



$$R\overset{O}{\overset{\|}{C}}O O\overset{O}{\overset{\|}{C}}R \xrightarrow{k_1} 2R\overset{O}{\overset{\|}{C}}O\cdot$$

$$R\overset{O}{\overset{\|}{C}}O\cdot + PhH \xrightarrow{k_2} RCOOH + Ph\cdot$$

$$Ph\cdot + R\overset{O}{\overset{\|}{C}}O O\overset{O}{\overset{\|}{C}}R \xrightarrow{k_3} PhR + CO_2 + R\overset{O}{\overset{\|}{C}}O\cdot \text{ etc.}$$

$$Ph\cdot + R\overset{O}{\overset{\|}{C}}O\cdot \xrightarrow{k_4} PhR + CO_2 \text{ etc.}$$

The observed kinetics will be first order if attack by radicals from the solvent is so much faster than attack by radicals from the peroxide that the former accounts for nearly all the induced decomposition. In such a case we have the equations[5]

(1) $-d[P]/dt = k_1[P] + k_3[Ph\cdot][P]$

(2) $0 = 2k_1[P] - k_2[RCOO\cdot] + k_3[P][Ph\cdot] - k_4[Ph\cdot][RCOO\cdot]$

(3) $0 = k_2[RCOO\cdot] - k_3[Ph\cdot][P] - k_4[Ph\cdot][RCOO\cdot]$

It can be shown that equations (2) and (3) are solvable for [Ph·] and that the expression obtained is not a function of [P]. It then follows that equation (1) is first order in [P].

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(1) Harvard University Ph.D. 1948; Cornell University Du Pont Post-Doctoral Fellow 1948-1949; present address, Department of Chemistry, Brown University, Providence, R. I.

(2) J. E. Leffler, "Cleavages and Rearrangements of Oxygen Radicals and Cations," to appear in *Chemical Reviews*.

(3) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

(4) J. E. Leffler, Thesis, Harvard University, 1948.

(5) [P] stands for the peroxide concentration. Equations (2) and (3) are the steady state assumptions for the radicals RCOO· and Ph·.

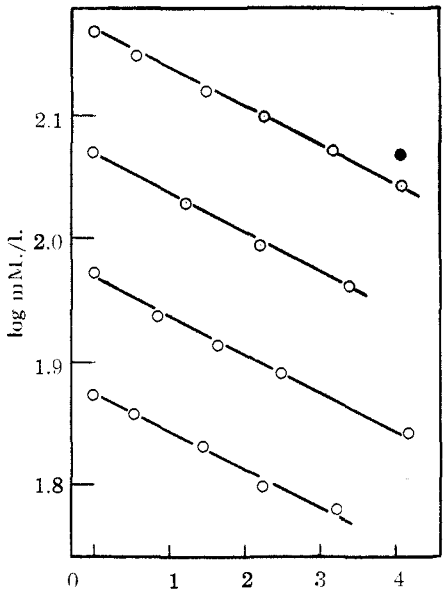
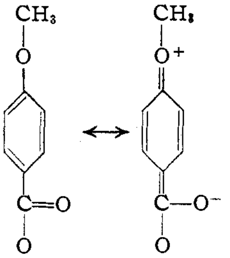
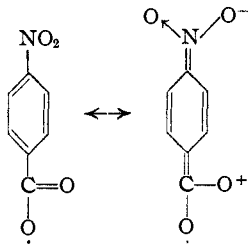


Fig. 1.—From top to bottom: Run I; Run III, ordinate log mM./l. +0.2; Run V, ordinate log mM./l. +0.5; Run IV, ordinate log mM./l. +0.8; ●, Run I with oxygen.

Thus the difference between *p*-methoxy-*p*′-nitrobenzoyl peroxide and benzoyl peroxide in benzene appears to be largely a matter of the induced decomposition in the former case being carried on entirely by radicals from the solvent. It may be that in this reaction aryl radicals are more reactive than aroyloxy radicals. Induced decomposition of benzoyl peroxide may go by both the paths (a) $PhCOO^{\cdot} \rightarrow Ph^{\cdot} + CO_2$ and (b) $PhCOO^{\cdot} + PhH \rightarrow Ph^{\cdot} + PhCOOH$, the aryl radicals being the agents which attack the peroxide. Path (a) leads to higher order kinetics, path (b) to first order kinetics.[6] In the case of *p*-methoxy-*p*′-nitrobenzoyl peroxide, path (b) is favored because resonance with the para substituents stabilizes the aroyloxy radicals against decarboxylation





In agreement with the above free radical interpretation, the products of the decomposition in benzene are *p*-methoxybenzoic and *p*-nitrobenzoic acids in approximately equal amounts, and the unsymmetrical *p*-nitro- and *p*-methoxy-biphenyls.

TABLE I

Run,	I	III		IV		V	
hr.	mM./l.[a]	hr.	mM./l.	hr.	mM./l.	hr.	mM./l.
0	148	0	74.1	0	11.87	0	29.7
0.574	141	1.246	67.4	0.528	11.40	0.857	27.3
1.485	132	2.238	62.2	1.448	10.72	1.664	25.9
2.271	125.5	3.382	57.6	2.254	9.96	2.503	24.5
3.177	118			3.221	9.55	4.183	22.0
4.096	110[b]						

[a] Millimoles of peroxide per liter of soln. [b] As compared with 4.071 and 117 for the air exposed ampoule.

Part II. The Ionic Decomposition and the Carboxy Inversion Reaction

As was shown in Part I the decomposition of *p*-methoxy-*p*′-nitrobenzoyl peroxide in benzene alone is a radical reaction. But the unsymmetrical distribution of polar substituents might be expected to make the reaction take an ionic path under favorable circumstances. That such is indeed the case will appear from the observations presented here.

In strong contrast to the decomposition of benzoyl peroxide, the decomposition of *p*-methoxy-*p*′-nitrobenzoyl peroxide is markedly accelerated by acids, the stronger acids having the greater effect. The rate in benzene at 70° in the presence of acids, HA, is given by

$$-d[P]/dt = k_1[P] + k_a[P][HA]$$

The constant k_1 is the same as the first order constant in benzene alone, 7.5×10^{-2} hours^{-1}. The constant k_a is a function of the acid HA. Figure 2

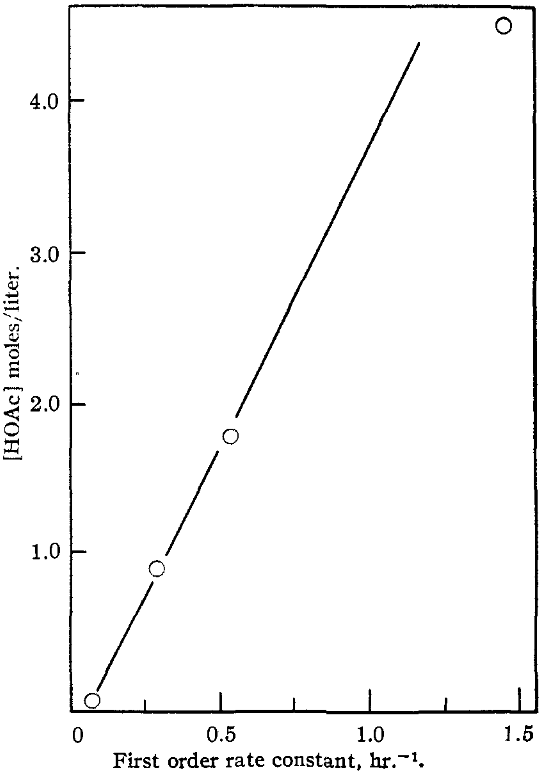


Fig. 2.

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[6] *Cf.* K. Nozaki and P. D. Bartlett, THIS JOURNAL, **69**, 2304 (1947). It is also necessary to assume that k_4 represents the only chain-terminating step.

and Table II show the relationship between the over-all rate constant and the concentration of acetic acid.

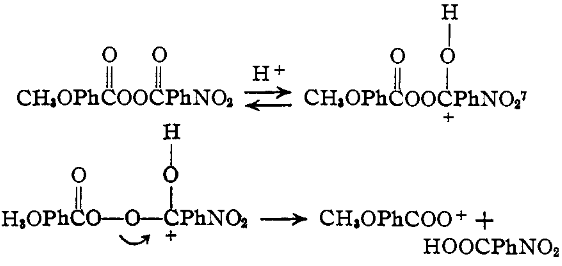
TABLE II

First order rate constant, hr.$^{-1}$	Acetic acid concentration, moles per liter
0.075	0
.289	0.895
.536	1.79
1.45	4.48

The straight line of Fig. 2 represents the equation

$$k_t = 0.075 + 0.26[\mathrm{HOAc}]$$

The last point, corresponding to 4.48 *M* acid is somewhat out of line, but this is to be expected since the concentration of acid is so high as to be an appreciable fraction of the solvent. Figure 3, data in Table III, shows the relationship between the logarithms of the catalysis constants, k_a, and the logs of the acid dissociation constants, K_a, for the series acetic, monochloroacetic, dichloroacetic and trichloroacetic acids. The phenomenon appears to be a case of general acid catalysis and it is likely that the acid-catalyzed part (superimposed on the radical decomposition) goes by an ionic mechanism in which the first step is heterolytic cleavage of the peroxide.



$$\mathrm{CH_3OPh\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}PhNO_2} \overset{H^+}{\rightleftarrows} \mathrm{CH_3OPh\overset{\overset{O}{\|}}{C}OO\underset{+}{\overset{\overset{\overset{H}{|}}{O}}{\overset{|}{C}}}PhNO_2}$$[7]

$$\mathrm{CH_3OPh\overset{\overset{O}{\|}}{C}{-}O{-}\underset{+}{\overset{\overset{\overset{H}{|}}{O}}{\overset{|}{C}}}PhNO_2} \longrightarrow \mathrm{CH_3OPhCOO^+ + HOOCPhNO_2}$$

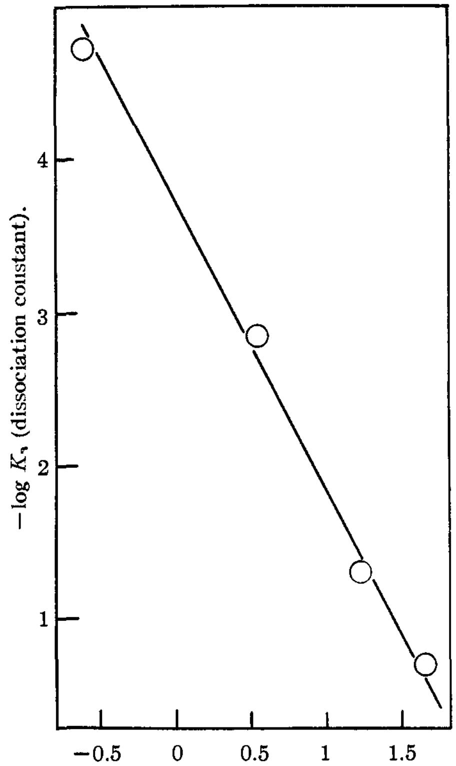


Fig. 3.—log k_a (catalysis constant).

TABLE III

Acid	− log K_a	log k_a
Acetic	4.73	−0.605
Monochloroacetic	2.85	0.536
Dichloroacetic	1.30	1.219
Trichloroacetic	0.70	1.656

In order to gain further information about the mechanism of the acid catalyzed reaction, a sample of the peroxide was decomposed in a benzene solution of trichloroacetic acid strong enough to ensure that the non-acid-catalyzed part of the reaction would be negligible. There was isolated the theoretical yield of *p*-nitrobenzoic acid containing less than 1.5% anisic acid. It will be remembered that in benzene alone the acid formed is an almost equal mixture of the two acids. Furthermore, the neutral product contains a derivative of hydroquinone monomethyl ether, presumably formed from the positive fragment by loss or rearrangement of carbon dioxide; the intermediate ester was not isolated.

Although the rate of decomposition of benzoyl peroxide is nearly the same in nitrobenzene as it is in benzene, the decomposition of *p*-methoxy-*p*′-nitrobenzoyl peroxide is nearly eight times as fast in the former as in the latter solvent. The first order rate constant in nitrobenzene at 70° is 58.7 × 10^{-2} hours^{-1}. Such a large increase in rate is due to the fact that *p*-methoxy-*p*′-nitrobenzoyl peroxide, unlike benzoyl peroxide, will decompose by a polar mechanism in polar solvents. It will be noted (Fig. 4, Table IV) that the run at the higher

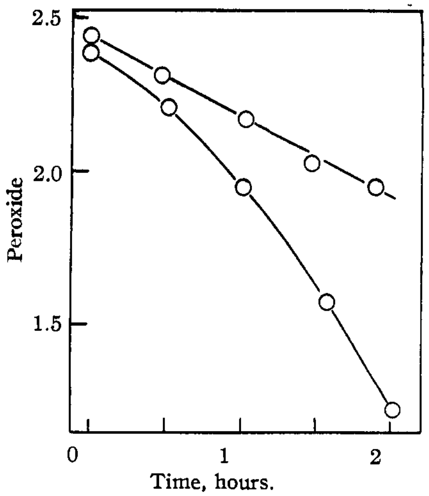


Fig. 4.—Top curve, ordinate, log mM./l. +0.75; bottom curve, ordinate, log mM./l.

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[7] Although the proton might be expected to attach itself more frequently to the other carbonyl, it is only the intermediate shown here that leads to reaction.

concentration in nitrobenzene appears to be autocatalytic; acids are formed by the reaction and should cause autocatalysis as the concentration builds up.

TABLE IV

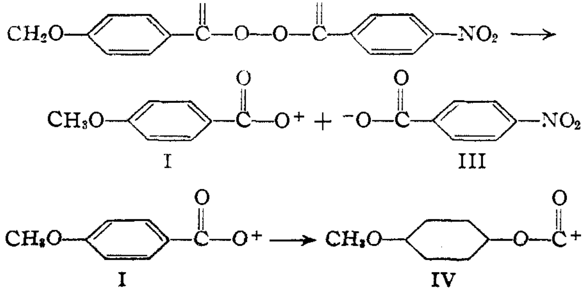
THE DECOMPOSITION OF *p*-METHOXY-*p*'-NITROBENZOYL PEROXIDE IN NITROBENZENE AT 70°

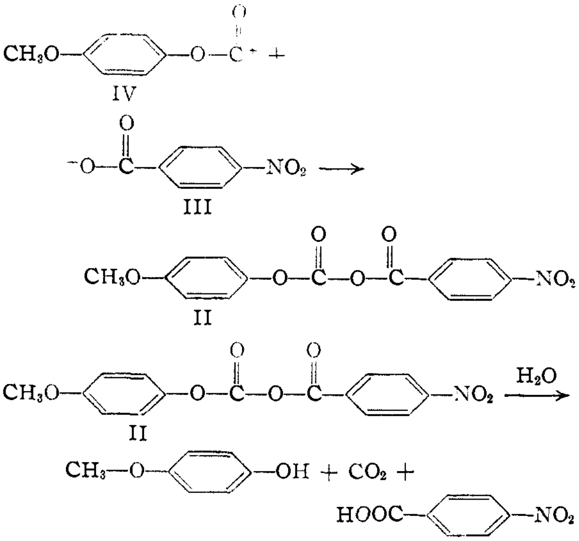
mM./l.[a]	Hr.	mM./l.	Hr.
246	0	49.2	0
164	0.520	36.8	0.472
90.8	1.020	26.8	1.027
38.1	1.575	19.2	1.471
16.7	2.018	16.2	1.896

[a] Millimoles per liter.

From the nitrobenzene solution, after decomposition of the peroxide, was isolated a mixture of acids consisting of 86% *p*-nitrobenzoic acid. This is in contrast to the 58% of *p*-nitrobenzoic acid found in the mixture of acids from the reaction in benzene and supports the theory that the decomposition in nitrobenzene is accelerated by a contribution from an ionic mechanism. An ionic reaction would presumably favor cleavage in the direction leading to *p*-nitrobenzoate anion and *p*-methoxybenzoyloxy cation which would lose carbon dioxide or rearrange. The reaction in refluxing methanol is also very fast, being nearly complete in half an hour. The melting point of the acid formed corresponds to 96% *p*-nitrobenzoic acid. The reaction in acetone at 70° gives a mixture of acids having a melting point corresponding to 91% *p*-nitrobenzoic acid.

Because of the somewhat complicated course of the reaction in nitrobenzene and in solvents having active hydrogen it was decided to try the reaction in thionyl chloride, a polar solvent, but not a nucleophilic one. The main product of the reaction, isolated in 38% yield, is II. Conversion of the peroxide to II involves inversion of the carboxy group attached to the *p*-methoxyphenyl part of the molecule. That this is the structure of II is shown by the following facts: (a) it is not a peroxide, and (b) it is hydrolyzed quantitatively to *p*-methoxyphenol, *p*-nitrobenzoic acid and carbon dioxide. There is also formed in the thionyl chloride reaction a mixture of acid, about 77% *p*-nitrobenzoic acid.





Although this rearrangement is probably the first example of its kind, it is not entirely surprising in view of the previously noted rearrangements of alkyloxygen cations involving cleavage of an adjacent carbon to carbon bond.[8,9,2] Thus a plausible mechanism may be written involving heterolytic cleavage of the peroxide to the fragments I and III, rearrangement of I to IV, and recombination of III and IV.

A prediction based on the effect of the polarity of the medium on the course of the decomposition is that the peroxide, because of wastage through ionic decomposition, should not be an efficient polymerization initiator whenever the medium is polar.[10] To test this, the *p*-methoxy-*p*'-nitrobenzoyl peroxide was compared with benzoyl peroxide as a polymerization catalyst. In styrene, which is not very polar, the polymerization proceeds with about half the yield as if benzoyl peroxide is used. But in the highly polar acrylonitrile, benzoyl peroxide leads to an explosive polymerization or to complete solidification whereas *p*-methoxy-*p*'-nitrobenzoyl peroxide gives only a very small amount of polymer. Again, in acidified styrene, the former gives a good yield of polymer, the latter does not.

Acknowledgment.—The author wishes to express his appreciation for many interesting discussions with Professor Paul D. Bartlett of Harvard University and with the members of the Department of Chemistry of Cornell University.

Experimental

***p*-Methoxy-*p*'-nitrobenzoyl Peroxide.**—To a cold solution of 13 g. of sodium hydroxide in 32 cc. of water is added 18 cc. of 30% hydrogen peroxide. The mixture is stirred in an ice-bath for a few minutes and then a filtered solution of 18.5 g. of *p*-nitrobenzoyl chloride in 50 cc. of toluene

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[8] R. Criegee, *Ann.*, **560**, 127 (1948).

[9] W. A. Mosher and F. C. Whitmore, THIS JOURNAL, **70**, 2544 (1948).

[10] A suggestion for which the author is indebted to Professor P. D. Bartlett.

is added with stirring during the course of one hour. After an additional forty-five minutes of stirring in the ice-bath, the precipitate of sodium *p*-nitroperbenzoate is removed and dissolved in 800 cc. of 5% sodium carbonate solution. To the cold, stirred solution is added dropwise during ten minutes 15 g. of *p*-methoxybenzoyl chloride. The mixture is stirred until the oil has all solidified, the crude *p*-methoxy-*p*'-nitrobenzoyl peroxide is dissolved in methylene chloride and washed twice with 10% sodium bicarbonate, and the methylene chloride removed in a nitrogen stream at room temperature. The yield is 5 g. of material melting at 105–108°. The use of sodium carbonate solution in the above procedure is critical; if smaller amounts of sodium carbonate are employed, *p*-methoxybenzoyl peroxide is formed instead of the desired product. Two crystallizations from cold acetone by addition of 60–70° petroleum ether gave the material used in the present work. It had the following properties: m. p. 108° with decomposition and resolidification; peroxide titer by the method of Nozaki[11] 99.3% and 100.0% of the theoretical; *anal.* calcd. for $C_{15}H_{11}O_7N$: C, 56.78; H, 3.50; N, 4.42. Found:[12] C, 57.09, 56.88; H, 3.72, 3.53; N, 4.40, 4.40. Because neither the melting point nor the peroxide titer is a sensitive index of the amount of *p*-methoxybenzoyl peroxide present as an impurity, and because a nitrogen analysis is a rather tedious method of checking the results of a preparative run, an ultraviolet absorption spectrum is given in Fig. 5.

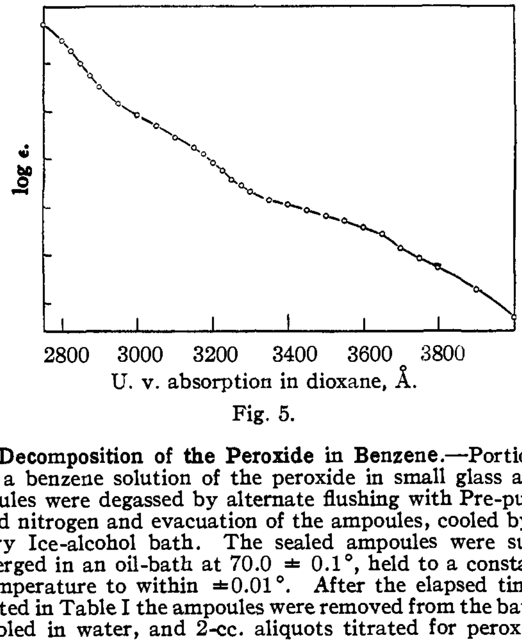

Fig. 5.

Decomposition of the Peroxide in Benzene.—Portions of a benzene solution of the peroxide in small glass ampoules were degassed by alternate flushing with Pre-purified nitrogen and evacuation of the ampoules, cooled by a Dry Ice-alcohol bath. The sealed ampoules were submerged in an oil-bath at 70.0 ± 0.1°, held to a constant temperature to within ±0.01°. After the elapsed times noted in Table I the ampoules were removed from the bath, cooled in water, and 2-cc. aliquots titrated for peroxide by the method of Nozaki.[11]

The Products of the Decomposition in Benzene.—Five cc. of a benzene solution of the peroxide, 148 mM./l., was heated in an ampoule under nitrogen at 70° for two days. Extraction with 10% sodium bicarbonate gave 0.093 g. of a mixture of acids, m. p. *ca.* 220–225°. Comparison with a melting point curve for the system anisic acid–*p*-nitrobenzoic acid (Fig. 6) indicated a composition of 42 ± 5% anisic acid. This was confirmed by a counter-current distribution of the mixture between a *p*H 5 citric acid–phosphate buffer and chloroform. Both acids were isolated and identified by their m. p.'s and mixed m. p.'s with authentic samples. The neutral residue from the bicarbonate extraction was subjected to counter-current distribution between methanol and 60–70° petroleum ether, giving 6 mg. of *p*-nitrobiphenyl, m. p. 110–112°, mixed melting point with an authentic sample 110–114°, and 1 mg. of *p*-methoxybiphenyl, m. p. 81–83°, mixed with an authentic sample, 82–86°. All m. p.'s were taken in capillary tubes under observation through a microscope.

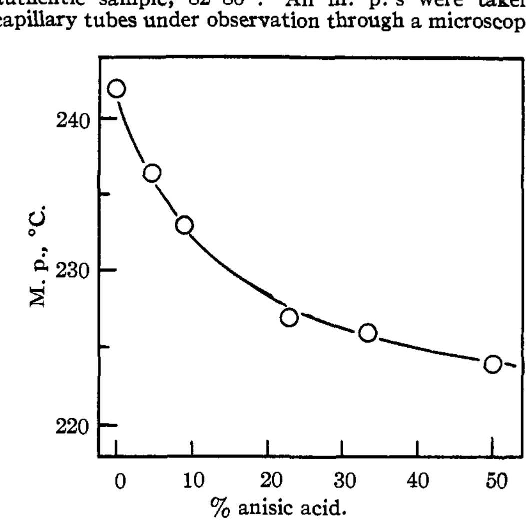

Fig. 6.—Anisic acid–*p*-nitrobenzoic acid.

Analyses.—The analyses for peroxide in the nitrobenzene runs were done by the Nozaki method but with added chloroform and excess potassium iodide to improve the end point.[11] Aliquots from the acid benzene runs were added to 15 cc. of acetic acid containing 1 cc. of saturated aqueous potassium iodide solution and a pellet of Dry Ice, letting the mixture stand for twenty minutes, adding another Dry Ice pellet and 50 cc. of water, and titrating with sodium thiosulfate to a starch–iodide end-point. Blank corrections were applied.

The Decomposition in Nitrobenzene.—A 5-cc. portion of a 0.246 *M* solution of *p*-methoxy-*p*'-nitrobenzoyl peroxide in nitrobenzene was degassed, sealed in an ampoule and heated overnight at 70°. After removal of the nitrobenzene in an air stream, the residue was extracted with 10% sodium bicarbonate and the resulting solution washed with methylene chloride. There was isolated a mixture of acids weighing 85 mg., m. p. 225–231°, separated into *p*-nitrobenzoic and *p*-methoxybenzoic acids by counter-current distribution between chloroform and a *p*H 5 citric acid–phosphate buffer. Both components were identified by mixed melting points with authentic samples. The yields agreed with the composition of the mixture estimated from its m. p., 87% *p*-nitrobenzoic acid. Repetition of the experiment with extraction of the bulk of the acid before evaporation of the nitrobenzene gave two portions of mixed acid, 0.12 g. of m. p. 229–235°, 0.027 g. of m. p. 213–223°. The percentage of nitrobenzoic acid estimated from these melting points is 86%.

The Decomposition in Benzene with Trichloroacetic Acid.—To a 5-cc. portion of a 148 mM./l. solution of *p*-methoxy-*p*'-nitrobenzoyl peroxide in benzene was added 1 cc. of benzene containing 0.1 g. of trichloroacetic acid. The mixture was degassed in the usual way and held at 70° overnight. Extraction with 10% sodium bicarbonate gave 0.13 g. of *p*-nitrobenzoic acid, m. p. 238–240° corresponding to a 1.5% anisic acid content. The neutral residue was converted into *p*-methoxyphenyl benzoate, m. p. 84–86°, mixed m. p. with an authentic sample, 84–86°, yield 0.016 g., by treatment with benzoyl chloride and sodium hydroxide.

The Decomposition in Methanol.—0.3 g. of the peroxide was refluxed for thirty minutes in 50 cc. of methanol. At the end of this time most of the peroxide had been destroyed. Extraction of the residue, after removal of methanol, with 10% sodium bicarbonate gave 0.093 g. of acid, m. p. 233–237° corresponding to a mixture containing 96% *p*-nitrobenzoic acid.

The Decomposition in Acetone.—1.00 gram of the peroxide and 7 cc. of acetone were heated at 70° in a nitrogen

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(11) K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

(12) Analyses by Clark Microanalytical Laboratory.

flushed ampoule for twelve hours. The cooled ampoule was opened by pressing a hot glass rod against a scratch; the top blew off indicating considerable pressure inside. Extraction of the residue from evaporation of the acetone gave 0.39 g. of acid, m. p. 230–233° corresponding to 91% *p*-nitrobenzoic acid. The bicarbonate-insoluble part was a tar.

The Carboxy Inversion Reaction.—Because of the complicated nature of the neutral products in other polar solvents it was decided to try the peroxide decomposition in thionyl chloride. A 0.500-g. sample of *p*-methoxy-*p*′-nitrobenzoyl peroxide was dissolved in 40 cc. of thionyl chloride and refluxed for one hour, the condenser being cut off from the atmosphere by a calcium chloride tube. The thionyl chloride was then removed in a stream of nitrogen and the residue crystallized from acetone–petroleum ether (60–70°), giving 0.189 g. of a substance melting at 126–129°. Extraction of the mother liquor with 10% sodium bicarbonate gave 0.058 g. of acid melting at 220–227° corresponding to a 77% *p*-nitrobenzoic acid content. Recrystallization of the 126–129° material raised the melting point to 127–129°; 10 mg. was refluxed for three minutes with 0.2 g. of sodium hydroxide and 2 cc. of water, the mixture neutralized and extracted with benzene. The benzene extract gave an oil which crystallized on seeding with *p*-methoxyphenol, m. p. 51–53.5°, mixed m. p. with an authentic sample, 53–56°. Addition of excess acid and extraction with ether gave 5 mg. of *p*-nitrobenzoic acid, m. p. 239–240°, mixed m. p. with an authentic sample, 239–241°. The 127–129° material was shown *not* to be an allotropic form of *p*-methoxyphenyl *p*-nitrobenzoate by a mixed melting point. Twenty-eight mg. of the 127–129° material was placed in an ampoule with 5 cc. of a 1% sodium hydroxide solution saturated with barium hydroxide, sealed and heated with occasional shaking at 70° for half an hour. The resulting precipitate was centrifuged down, washed thrice with water and once with acetone, then dried to constant weight *in vacuo* over potassium hydroxide, yielding 0.018 g., the theoretical yield, of barium carbonate. The product was identified by the fact that acidification gave an odorless gas and that the residue was not ether-soluble. *Anal.* Calcd. for $C_{15}H_{11}O_7N$: C, 56.78; H, 3.50; N, 4.42. Found: C, 56.97, 57.03; H, 3.72, 3.73; N, 4.49, 4.51.[12]

Polymerization of Styrene.—A 5-cc. sample of freshly distilled styrene containing 1% *p*-methoxy-*p*′-nitrobenzoyl peroxide, heated for eight and one-half hours under nitrogen at 70°, remained fluid and gave 0.66 g. of polystyrene, isolated by precipitation from ether on addition of methanol. The control run, using benzoyl peroxide, gave 1.27 g. of polystyrene. To 5 cc. of 1% solution of *p*-methoxy-*p*′-nitrobenzoyl peroxide in styrene was added 1 cc. of styrene containing 0.1 g. of trichloroacetic acid, the mixture degassed, sealed and allowed to stand at 30° for one week. At the end of this time the ampoule was opened and the viscosity of the solution compared with that from a control run using benzoyl peroxide and trichloroacetic acid by measuring the time of flow of 5 cc. between two marks on a standard pipet: the *p*-methoxy-*p*′-nitrobenzoyl peroxide run, 15.4 seconds; the benzoyl peroxide run, 296 seconds; pure benzene, 14.9 seconds.

Polymerization of Acrylonitrile.—Five cc. of a 1% solution of *p*-methoxy-*p*′-nitrobenzoyl peroxide in freshly distilled acrylonitrile, heated under nitrogen at 70°, gave a milky precipitate in five minutes. After seven and one-half hours the acrylonitrile was removed in a nitrogen stream leaving 0.294 g. of solid residue. A control run using benzoyl peroxide exploded; another control run did not explode but became completely solid in less than six minutes of heating.

Summary

The decomposition of *p*-methoxy-*p*′-nitrobenzoyl peroxide is subject to general acid catalysis, and in sufficiently polar media goes by an ionic mechanism. The decomposition in thionyl chloride leads to a novel rearrangement of the peroxide to a mixed ester and anhydride of carbonic acid.

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[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

β-Propiolactone. VIII.[1,2] Reactions with Organic and Inorganic Acids, Acid Chlorides and Anhydrides

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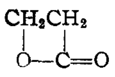
β-Propiolactone (I) reacts with thionyl chloride or phosphorus pentachloride to give β-chloropropionyl chloride[3] (II). With thionyl chloride an



I

$ClCH_2CH_2COCl$

II

intermediate compound seems to be formed, with little heat of reaction, from which sulfur dioxide is evolved slowly on heating. Acrylyl chloride is readily obtained by heating II with barium chloride.

β-Halogenopropionic acids are formed from I and aqueous halogen acids.[4] The yields of the reaction products decrease in the order: HI > HBr > HCl.

The reaction of I with organic acid halides[5] is extremely slow unless catalyzed with acid. β-Acetoxypropionyl chloride (III) is formed rapidly from I and acetyl chloride in the presence of a trace of sulfuric acid.

$CH_3COOCH_2CH_2COCl$ III $CH_3COOCH_2CH_2COOCOCH_3$ IV

The catalyzed reaction of acetic anhydride with I gives acetic β-acetoxypropionic anhydride (IV) which disproportionates into β-acetoxypropionic anhydride (V) and acetic anhydride on distilla-

$(CH_3COOCH_2CH_2CO)_2O$ V $CH_3COOCH_2CH_2COOH$ VI

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(1) Given in part at the San Francisco Meeting of the American Chemical Society, March, 1949.

(2) For Paper VII of this series see Gresham, Jansen, Shaver and Bankert, THIS JOURNAL, **71**, 2807 (1949).

(3) Gresham and Shaver, U. S. Patent 2,411,875 (1946).

(4) Gresham and Shaver, U. S. Patent 2,449,993 (1948).

(5) Gresham and Shaver, U. S. Patent 2,449,994 (1948).