A Kinetic and Isotopic Study of the Decomposition of Monoperoxyphthalic Acid

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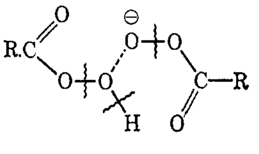
Contribution from the Metcalf Chemical Laboratory of Brown University, Providence, Rhode Island, and the Department of Physical Chemistry of the University of Newcastle, Newcastle upon Tyne, England. *Received January 10, 1967*

Abstract: The mechanism of the decomposition of monoperoxyphthalic acid has been investigated. The rate law is analogous to those found for other monosubstituted peroxides (second order in peroxide with a maximum rate at pH equal to pK_a of peroxidic proton). The isotope data are consistent with previously observed cases in that the data are explicable in terms of two competing transition states of identical composition but different configuration.

The thermal decomposition of peroxy acids in aqueous solution to form the parent acid and oxygen has been the subject of a number of recent investigations. Edwards, *et al.*,[2-4] have studied the kinetics of the decomposition of two aliphatic peroxy acids and the inorganic peroxy acids Caro's acid and peroxymonophosphoric acid. Goodman and Robson[5,6] have studied the decomposition of peroxybenzoic acid and a number of substituted peroxybenzoic acids. The latter workers have also investigated Caro's acid and have obtained results in agreement with those reported by Edwards. Independent data on peroxybenzoic acids are also in good agreement.[7]

In all cases it has been found that the rate of peroxy acid decomposition is second order in total peroxy acid concentration, with a maximum rate constant at a pH equal to the pK of the proton bound to the peroxide group. The results are consistent with the idea that reaction occurs by nucleophilic attack of the peroxy acid anion upon the undissociated peroxy acid molecule, but there has been some question as to the electrophilic center at which this attack occurs. Whereas Edwards favored attack at the outer peroxidic oxygen atom (I), Goodman and Robson advanced arguments which led them to conclude that attack was at the carbonyl carbon atom of the peroxy acid (II) (sulfur or phosphorus in the case of Caro's acid and peroxymonophosphoric acid, respectively). These two activated complexes can be distinguished by a tracer technique. Mechanism I predicts that, from a mixture of doubly oxygen-18-labeled peroxy acid and unlabeled peroxy acid, some scrambled molecular oxygen (mass 34) should be obtained. Mechanism II predicts that under the same condition no scrambling should occur. Two cases have so far been investigated. In the case of peroxyacetic acid Edwards and co-workers[3] found a distribution of isotopic label in product oxygen corresponding to 83% of the reaction occurring *via* II. Studies of Caro's acid[4] yield the result that 91% of the reaction occurs *via* I. Thus it appears likely that the two mechanisms, which yield identical kinetic form and differ only in the conformation of the transition state, are operating simultaneously.



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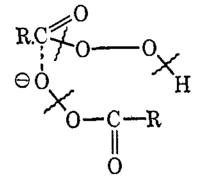

II

The double-labeling method has not yet been applied to the case of substituted peroxybenzoic acids, but the experiments cited above suggest that if the carbonyl carbon electrophilic site is sterically hindered, then attack at outer peroxidic oxygen (I) may be favored. Monoperoxyphthalic acid is a most suitable peroxy acid to test this idea since the pK of the peroxy acid proton is 8.2, and the pK of the carboxylic acid proton is -0.5,[8] so that around pH 8 decomposition would arise from attack of the dinegative ion upon the mononegative ion. Thus the electrostatic situation is similar to that with Caro's acid (attack of SO_5^{2-} on HSO_5^-) and additional steric hindrance is provided by the *o*-carboxylate group.

This paper describes the results of our investigation of the decomposition of monoperoxyphthalic acid. Studies of the hydrolysis of monoperoxyphthalic acid are reported elsewhere.[8]

Experimental Section

Monoperoxyphthalic acid was prepared according to the method of Bohme.[9] The product was a mixture of peroxy acid and phthalic acid. Various preparations yielded samples containing 40–60% w/w monoperoxyphthalic acid. The preparation of doubly oxygen-18-labeled monoperoxyphthalic acid followed the same procedure except that, to the hydrogen peroxide used, was added sufficient $H_2O_2^{18,18}$ to give a mole fraction of $H_2O_2^{18,18} \simeq 0.04$. $H_2O_2^{18,18}$ was prepared from water containing 97 atom % O^{18} (Yeda Research and Development Co., Ltd., Rehovoth, Israel) by the electric discharge method.[10]

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[2] D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).

[3] E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *ibid.*, **85**, 2263 (1963).

[4] E. Koubek, G. Levey, and J. O. Edwards, *Inorg. Chem.*, **3**, 1331 (1964).

[5] J. F. Goodman and P. Robson, *J. Chem. Soc.*, 2871 (1963).

[6] J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).

[7] R. Curci and G. Modena, *Tetrahedron Letters*, 1749 (1963); *Gazz. Chim. Ital.*, **94**, 1257 (1964).

[8] M. L. Haggett, D. Holden, P. Jones, P. J. Robinson, and A. Suggett, in preparation.

[9] H. Bohme, *Org. Syn.*, **20**, 70 (1940); H. Bohme, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 619.

[10] R. E. Ball, J. O. Edwards, and P. Jones, *J. Inorg. Nucl. Chem.*, **28**, 2458 (1966).

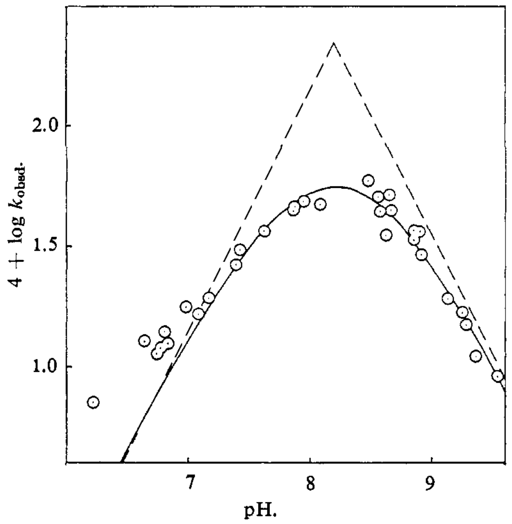

Figure 1. Second-order rate constant for decomposition of peroxyphthalic acid as a function of pH, temperature 24.6°.

Buffer Components. Analar Na_2CO_3, $NaHCO_3$, Na_2HPO_4, and KH_2PO_4 were used. Reagent grade phosphates were found to give an enhanced decomposition rate (about 8%) compared with Analar materials. Analar 72% perchloric acid and 1 *M* NaOH (diluted to suitable concentrations) were used to adjust pH where necessary. EDTA, which was added to sequester trace metal cations, was recrystallized as described by Blaedel and Knight.[11] Laboratory distilled water was further purified, either by using a mixed-bed ion exchanger, or by two further distillations from alkaline $KMnO_4$ and dilute phosphoric acid, respectively. Other reagents were of Analar grade where possible.

Procedures. For the decomposition kinetic studies about 0.5 g of peroxyphthalic acid–phthalic acid mixture was weighed directly into a flask and the required volume of 1 *M* NaOH added to neutralize the phthalic acid and also the carboxylic acid proton of the peroxy acid. Buffer solution (50 ml) consisting of x ml of 0.33 *M* Na_2HPO_4 (or 0.67 *M* $NaHCO_3$) + $(60 - x)$ ml of 0.33 *M* KH_2PO_4 (or 0.67 *M* Na_2CO_3) + 0.65 ml of 0.1 *M* EDTA solution was added, the solid dissolved, and the solution allowed to come to thermostat temperature. Samples (5 ml) were withdrawn by pipet, quenched in 30 ml of acetate buffer ($\text{pH} \simeq 3$) containing KI, and titrated with 0.1 *N* sodium thiosulfate using starch indicator.

Second-order graphs of the results were linear for at least two half-lives. Deviations at longer reaction times were observed, and the experiments at $\text{pH} \leq 7$ were less satisfactory because hydrolysis of the peroxy acid occurred. Two other buffers were tried out near pH 8. Tris buffer ($pK = 8.1$) was very rapidly oxidized. With NH_3–$NH_4H_2PO_4$ buffers, the reaction became first order in peroxyacid. Botvinnik[12] has reported a reaction between ammonia and peroxybenzoic acid.

The apparatus and technique used in the isotopic-labeling experiments was the same as that described previously.[3,4]

Results

Figure 1 shows the experimental values of the second-order rate constants for the decomposition reaction at 24.6° as a function of pH. The points lie on a curve with a maximum rate constant of 5.6×10^{-3} l. mole^{-1} sec^{-1} at pH 8.2. The proton bound to the peroxide group in peroxyphthalic acid has a $pK = 8.2 \pm 0.1$ at 25°.[8] Since the dissociation of the carboxylic acid proton in peroxyphthalic acid has $pK \simeq 0.5$, the decomposition reaction may be formulated, following Ball and Edwards,[2] as an attack of the dianion $^{-}O_2CC_6H_4CO_3^{-}$ upon the monoanion $^{-}O_2CC_6H_4CO_3H$. The curve in Figure 1 was constructed using this model and the numerical values noted above. At $\text{pH} \leq 7$, the experimental rate constants deviate appreciably from the theoretical curve. In this region the decomposition and hydrolysis reactions[8] overlap so that kinetic data for the decomposition reaction alone become much less reliable.

Table I shows the results of isotopic-labeling experiments carried out at pH 8.5 and room temperature ($\simeq 20°$). The composition of the hydrogen peroxide used in the preparation of labeled peroxyphthalic acid was determined by mass spectrometric analysis of the evolved oxygen from reaction with ceric ammonium sulfate in acid solution. The values quoted are the means of four experiments. Some samples were analyzed on a Consolidated-Electronics 21-103 mass spectrometer at Harvard University; the remainder on a Hitachi-Perkin-Elmer mass spectrometer. The results from the two instruments were in good agreement. As a check that scrambling did not occur during synthesis of peroxyphthalic acid, a sample of the labeled peroxy acid was hydrolyzed in phthalate buffer solution at pH 4 in the presence of 10^{-2} *M* EDTA, and the hydrogen peroxide produced was then allowed to react with acid ceric ammonium sulfate solution. The results of the check experiment are shown in the third line of Table I. It must be concluded from the data in the second line that the amount of scrambling (indicated by per cent O_2^{34}) is extensive but not complete, and that this scrambling occurred during the process of decomposition.

Table I. Isotopic Tracer Results for Peroxyphthalic Acid Decomposition

Source of oxygen	Composition of oxygen gas, mole % O_2^{32}	O_2^{34}	O_2^{36}
H_2O_2	95.8 ± 0.1	0.6 ± 0.1	3.6 ± 0.1
Peroxyphthalic acid decomposition (pH 8.5 phosphate buffer)	93.6 ± 0.2	5.4 ± 0.3	1.0 ± 0.1
H_2O_2 from hydrolysis of peroxyphthalic acid	95.2	0.8	3.9

Discussion

The kinetic data conform well to the pattern found for other peroxy acids and are described equally well by either mechanism I or II. The isotopic tracer results cannot be explained by either mechanism alone. If it is assumed that both mechanisms contribute to the total reaction, then a statistical analysis, in which it is assumed that peroxy acid species of all isotopic distributions will react with each other at a rate unaffected by isotopic mass, yields the result that 74 ± 4% of the product oxygen molecules derive from mechanism I. Thus, in this reaction, decomposition *via* displacement on oxygen by oxygen (I) predominates over decomposition *via* attack at the alternative carbonyl carbon electrophilic center (II). This result was expected since, in peroxyphthalic acid, we have chosen a molecule in which the latter reaction path would be disfavored. It must be concluded that the decomposition of derivatives of peroxycarboxylic acids will not generally occur exclusively by attack at carbonyl carbon. Indeed the present results reinforce the idea[4] that peroxy acid decompositions occur by two competing pathways having identical rate laws and differing only in the conforma-

(11) W. J. Blaedel and H. T. Knight, *Anal. Chem.*, **26**, 741 (1954).
(12) M. M. Botvinnik, *J. Gen. Chem. USSR*, **16**, 863 (1946).

tion of the transition state. In no case so far investigated does either mechanism alone completely satisfy both kinetic and isotopic tracer results.

The investigation of the decomposition of a series of substituted peroxybenzoic acids by Goodman, *et al.*[6] is at present the most complete study of a group of structurally closely related acids and the data suggest that the contribution of decomposition by path I may not be inappreciable in this series. For this series of reactions there is no simple Hammett $\sigma\rho$ relationship between the logarithm of the rate constant and σ since substituents in the aromatic ring affect both substrate and nucleophile instead of only the substrate and also since the two mechanisms should have different ρ values. Indeed it was found[6] that the decomposition rate constants exceeded that for peroxybenzoic acid whether electron-releasing or -attracting groups were substituted in the benzene ring.

The convenience and the usefulness of the double-labeling method for study of peroxide decompositions is exemplified well by the present investigation. Some other systems to which this technique is being applied at present are the paramagnetic peroxyborates,[13] the tetraperoxychromate ion,[14] and peroxypivalic acid.[15] A combined kinetic and isotope study of the decompositions of substituted peroxybenzoic acids would give data of considerable value in understanding the factors which govern the reactivities of carbonyl carbon and peroxide oxygen to peroxyanions.

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[13] K. Watters, private communication; *cf.* R. Bruce, J. O. Edwards, D. Griscom, R. A. Weeks, L. R. Darbee, W. DeKleine, and M. McCarthy, *J. Am. Chem. Soc.*, **87**, 2057 (1965).

[14] S. B. Brown, private communication; *cf.* D. Quane and J. E. Earley, *ibid.*, **87**, 3823 (1965).

[15] E. Koubek, private communication.

The Decomposition of Aryl Iodine Diacetates

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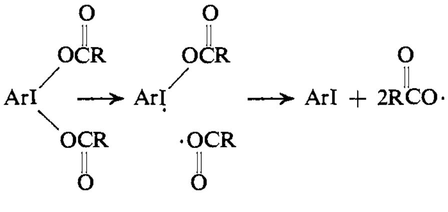
Abstract: The decomposition of aryl iodine diacetates takes place by three mechanisms: nucleophilic displacement within an ion pair to give aryl acetate and iodine acetate (the major reaction), homolysis to aryl iodide and acetoxy radicals, and induced homolysis. The intermediate iodine acetate decomposes rapidly to carbon dioxide and methyl iodide, but may be trapped completely by cyclohexene. The radical chain homolysis of phenyl iodine diacetate is enhanced by di-*t*-butyl peroxide.

The decomposition of phenyl iodine dibenzoate[2] in aromatic solvents gives clear indications of the presence of phenyl radicals,[3a,b,c] and it was at one time widely presumed to consist entirely of homolysis to benzoyloxy radicals, in a process such as eq 1 or the corresponding single-step mechanism. However, a more detailed study of the products and kinetics revealed a reaction of considerable complexity.[3a] One of the products, in 8–25% yield, is phenyl benzoate. Labeling experiments established that the phenyl moiety of that ester comes exclusively from the aryl iodine moiety of the dibenzoate and not at all from benzoyloxy-derived phenyl radicals. This suggested that at least part of the reaction goes by way of an internal nucleophilic displacement (eq 2), closely analogous to a well-established major route for the decomposition of diaryliodonium compounds.[4] Kinetic and other evidence indicated that the intermediate iodine benzoate interacted with additives such as benzoic anhydride or benzaldehyde to induce a radical chain decomposition of the dibenzoate, but the details of the mechanism remained conjectural. The behavior of the diacetate, as reported in the present paper, appears to be simpler and more amenable to mechanistic interpretation.



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The Ion Pair Process. Table I and Figure 1 show the products and typical kinetic behavior of the decomposition of phenyl iodine diacetate in chlorobenzene under anhydrous conditions.[5] The second yield col-

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[1] Petroleum Research Foundation Predoctoral Fellow.

[2] The *Chemical Abstracts* name is (dihydroxyiodo)benzene diacetate.

[3] (a) J. E. Leffler, W. J. M. Mitchell, and B. C. Menon, *J. Org. Chem.*, **31**, 1153 (1966); (b) B. M. Lynch and K. H. Pausacker, *Australian J. Chem.*, **10**, 329 (1957); (c) D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 1475 (1956).

[4] See, for example, F. M. Beringer and R. A. Falk, *ibid.*, 4442 (1964).

[5] Unless otherwise noted, the solvent is chlorobenzene containing 0.1 M acetic anhydride to reacetylate any diacetate that may be hydrolyzed by traces of water. Within experimental error, the presence of this amount of acetic anhydride has no effect on the decomposition rate. Although the direct reaction between traces of water and acetic anhydride in chlorobenzene at 126.8° is very slow, the indirect reaction in the presence of phenyl iodine diacetate is extremely fast. Unless