beryllium source of neutrons was used to bombard manganese in order to get Mn^{56}. Several devices were tried. Bombardment of the potassium manganate solution was poor because retention of activity in the manganate is low,[1] and non-exchangeable activity is not easily centrifuged out. More satisfactory was the bombardment of a neutral, saturated solution of potassium permanganate. A small amount of manganous sulfate was added to form manganese dioxide carrier, and nearly all of the activity was filtered out with the MnO_2.[1] This manganese dioxide with high specific activity was transferred to a platinum crucible, carefully dried, and then air-oxidized to potassium manganate in fused KOH at just below red heat. The potassium manganate was dissolved in water, centrifuged and standardized. In the best method for incorporating the tracer, a basic potassium permanganate solution 0.1–0.2 *M* in KOH, in which retention of activity is high,[1] was bombarded with neutrons, neutralized with hydrochloric acid to decompose the manganate that formed, centrifuged, and cooled to 0°. Crystallization of potassium permanganate usually occurred, and the saturated solution was decanted, centrifuged, and standardized spectrophotometrically using a Beckman model DU spectrophotometer.

In general, the manganate and permanganate solutions were always centrifuged before a run in order to remove any manganese dioxide that may be accumulated.

Results.—The data are presented in Table I. Zimmerman,[6] Hall and Alexander,[7] and Mills[8] have shown that under the conditions of this experiment there is negligible exchange of oxygen between water and permanganate ion. Zimmerman showed that in dilute, neutral solution of potassium permanganate at 25°, O^{18} exchange was only 0.5% per hour. Similar results for other oxygenated cations have been reported.[6,7,9,10,11]

These results together with the earlier results with precipitation separation constitute strong evidence for the existence of rapid electron exchange between the two ions, probably involving 3d orbitals in the manganese atoms, the argument being that exchange of the manganese atoms could hardly occur without the surrounding oxygen atoms exchanging with water in the process.

(6) G. L. Zimmerman, Ph.D. Thesis, University of Chicago, 1949, p. 46.

(7) N. F. Hall and O. R. Alexander, THIS JOURNAL, **62**, 3455 (1940).

(8) G. A. Mills, *ibid.*, **62**, 2833 (1940).

(9) G. A. Mills and H. C. Urey, *ibid.*, **61**, 534 (1939), and **62**, 1019 (1940).

(10) E. R. S. Winter and H. V. A. Briscoe, *J. Chem. Soc.*, 631 (1942).

(11) E. R. S. Winter, M. Carlton and H. V. A. Briscoe, *ibid.*, 131 (1940).

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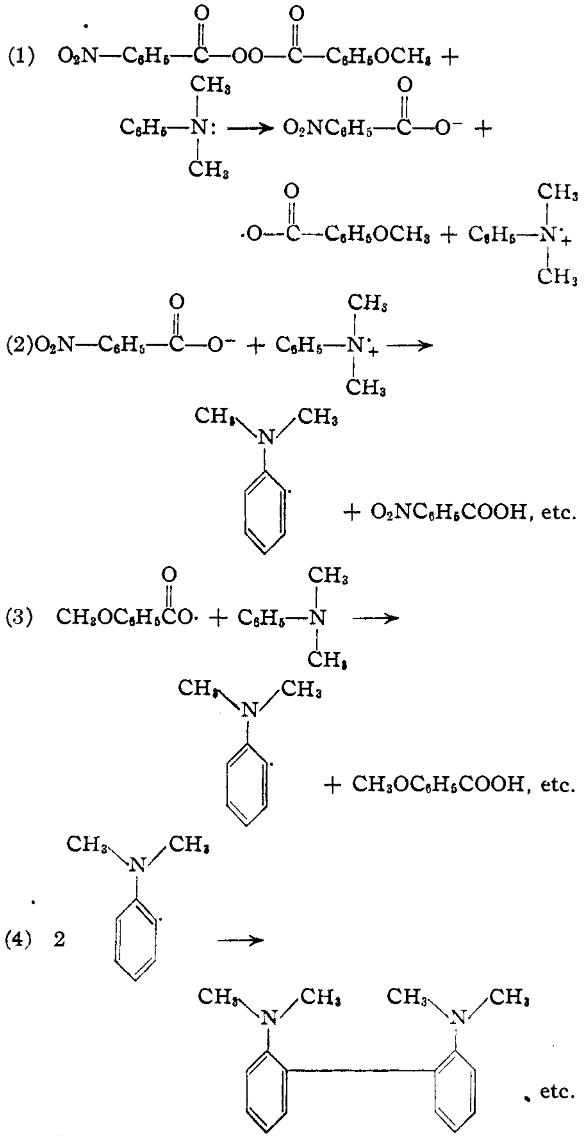
The Reduction of *p*-Methoxy-*p*′-nitrobenzoyl Peroxide by Dimethylaniline

BY JOHN E. LEFFLER

Horner and Schwenk[1] have recently shown that benzoyl peroxide is reduced *quantitatively* to benzoic acid by dimethylaniline. This result excludes the possibility of the usual[2] radical induced decomposition of the peroxide into a stable molecule (not an acid) and a new radical. A strictly unimolecular decomposition into radicals, on the other hand, should be a rather slow reaction, with a rate like that of the uninhibitable part of the reaction in benzene.

The decomposition of *p*-methoxy-*p*′-nitrobenzoyl peroxide in dimethylaniline gives anisic and *p*-nitrobenzoic acids in high yield. This excludes not only the radical chain mechanism but also the expected rearrangement reaction to which *p*-methoxy-*p*′-nitrobenzoyl peroxide is subject in polar media.[3] Furthermore, since the reaction is very fast, almost instantaneous at room temperature, the strictly unimolecular decomposition into radicals need not be considered. It therefore



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[1] Horner and Schwenk, *Angew. Chemie*, **61**, 411 (1949).

(2) Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946).

(3) Leffler, *ibid.*, **72**, 67 (1950).

seems probable that an electron transfer occurs like that postulated for the reaction of benzoyl peroxide with dimethylaniline.[1]

Recently[4] it has been reported that phenol reacts with benzoyl peroxide in chloroform to give a high yield of benzoic acid and only a minor amount of catechol monobenzoate. The high yield of benzoic acid means that the radical chain reaction cannot be important in this case either. But since the decomposition in chloroform is not appreciably accelerated by phenol, Cosgrove and Waters' explanation in terms of unimolecular decomposition into radicals need not be abandoned.

Experimental

To 13 g. of freshly distilled dimethylaniline, b. p. 192°, was added 1.13 g. of *p*-methoxy-*p*'-nitrobenzoyl peroxide.[3] The addition of the peroxide was carried out very cautiously, since if a mass of several mg. of the peroxide is added all at once it usually explodes instead of dissolving quietly. Before the addition of the peroxide was complete a mixture of anisic and *p*-nitrobenzoic acids began to precipitate. The total yield of acids was 0.98 g.

The melting point of the mixed acids was 225° (end of melting), raised by addition of *p*-nitrobenzoic acid. The melting point of an equimolar mixture of anisic and *p*-nitrobenzoic acids is 224.5°.[3]

Two flasks, one containing 7.75 g. of benzoyl peroxide in 50 cc. of chloroform, the other containing *in addition* 3.0 g. of phenol, were heated together on the same hotplate under reflux for one hour. Aliquots removed at the end of the reflux period and analyzed by the method of Nozaki[5] showed that there remained in the control run 6.7 g. of benzoyl peroxide compared with 6.6 g. for the run containing phenol.

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(4) Cosgrove and Waters, *J. Chem. Soc.*, 3193 (1949).

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

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Oxygen Exchange between Nitrates and Water[1]

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In connection with research on the mechanism of burning of propellants, studies have been made of the mechanism of thermal decomposition of nitrocellulose containing O^{18}. In the course of the preparation of O^{18}-enriched nitrocellulose it became necessary to study a number of oxygen-exchange reactions, among them oxygen exchange between nitrates and water.

Investigation has shown no oxygen exchange between nitrate ions and water in neutral solution,[2] and Hall and Alexander have determined that no exchange occurs in basic solutions. Winter, Carlton and Briscoe reported complete exchange at 100° in twenty-four hours in approximately 1 *N* sulfuric acid. On the other hand, Hall and Alexander found no exchange for potassium nitrate in 0.2 *N* nitric acid within the precision limits of their experiments. If their results are correct (the experimental method consisted in careful measurements of the density of the water before and after the reaction and appears to be rather precise), it would seem that the reaction is *p*H-dependent. We have found, using mass-spectrometer analysis, that nitric acid in a 40% solution undergoes an oxygen exchange with water at 30°. The question may be raised whether the nitrate groups need be present in an ionizable form for exchange. This may be tested with cellulose nitrate, which is known to be only slightly hydrolyzed by dilute sulfuric acid.[3] No exchange was observed experimentally between cellulose nitrate (12.9% nitrogen) in a 1 *N* sulfuric acid solution at 23° or 100°.

Experimental

The O^{18} enrichment of the water was determined by means of a mass spectrometer (Consolidated Model 21-102). The use of this instrument for quantitative analysis[4] of water and for isotopic analysis is complicated by adsorption of ordinary water on the walls of the high-vacuum system, which is gradually desorbed and thus interferes considerably with the determination of isotopes in enriched water. The difficulty is overcome by repeated flushing and pumping out of the system, using the enriched water to be analyzed. After three such cycles, consisting of three minutes flushing and three minutes pumping, the ratio $H_2O^{18}:H_2O^{16}$ approaches a constant value, indicating that the ordinary water on the walls has been substantially removed or diluted to a negligibly low value.

Cellulose nitrate and 1 *N* sulfuric acid were agitated at 23° in a 1:3.5 weight ratio in a cell similar to that of Frilette, Hanle and Mark.[5] The water had an O^{18} content of 1.31 ± 0.01%. The natural abundance being 0.2%, this corresponds to an enrichment factor of 6.55 ± 0.05. If oxygen exchange occurred, the enrichment factor should have been decreased. Assuming that two oxygen atoms per nitrate group are exchangeable, the enrichment factor should have dropped from 6.5 to 6.0, calculated on the basis of the weight ratio of cellulose nitrate to water. Table I shows that under the conditions of this

TABLE I

O^{18} ENRICHMENT OF WATER MIXED WITH NITROCELLULOSE

Time after mixing	O^{18} enrichment factor
0	[a]6.55 ± 0.05
12 minutes	[b]6.3
19 minutes	[b]6.4
28 minutes	6.5
35 minutes	6.7
47 minutes	6.6
56 minutes	6.7
66 minutes	6.6
24 hours	6.5
25 hours	6.6
2 days	[a]6.65 ± 0.08
7 days	[a]6.51 ± 0.06

[a] Average of 4 runs, each in duplicate. [b] Initial low values due to incomplete flushing or to slight contamination.

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(1) Publication approved by the Public Information Division, National Defense Department. Article not copyrighted.

(2) (a) R. Titani and K. Goto, *Bull. Chem. Soc. Japan*, **14**, 77-85 (1939); (b) E. R. S. Winter, M. Carlton and H. V. A. Briscoe, *J. Chem. Soc.*, 131-138 (1940); (c) N. F. Hall and O. R. Alexander, THIS JOURNAL, **62**, 3455-3462 (1940).

(3) J. Desmaroux, *Compt. rend.*, **206**, 1483-1484 (1948).

(4) R. C. Taylor, R. A. Brown, W. S. Young and C. E. Headington, *Anal. Chem.*, **20**, 396-401 (1948).

(5) V. J. Frilette, J. Hanle and H. Mark, THIS JOURNAL, **70**, 1107-1113 (1948).