color characteristic of the starting material. The specific rotation was also unchanged from that of the starting material. (b) Fifty milligrams was refluxed with an aqueous hydrochloric acid–toluene mixture for one hour. Thirty milligrams (82%) of crude residue was obtained and recrystallized from aqueous ethanol to yield 20 mg. (55%) of estradiol, m. p. 167–170°.

RESEARCH LABORATORIES
CHARLES E. FROSST & COMPANY
MONTREAL, CANADA
RECEIVED JANUARY 27, 1950

Electron Exchange between Manganate and Permanganate Ions by Solvent Extraction[1]

BY HOWARD C. HORNIG, GEORGE L. ZIMMERMAN AND W. F. LIBBY

The electron exchange reaction between manganate and permanganate ions in basic solution was reëxamined by using pyridine extraction to separate the permanganate from the reaction solution. With 4 *M* potassium hydroxide solutions pyridine has a fairly low solubility and it is observed that an essentially quantitative removal of MnO_4^- into the pyridine layer occurs while MnO_4^{--} is extracted to a negligible extent. The exchange was followed with the radioactive tracer Mn^{56} with 2.5 hour half life. The manganate–permanganate exchange was previously reported to be rapid when separation was made by precipitation of barium manganate,[2] but in view of the possibility of catalysis by precipitation, *viz.*, Prestwood and Wahl's study of thallous–thallic exchange[3] the solvent extraction method was tried. The exchange was again found too rapid to measure; even at 0° exchange was complete in thirty-five seconds.

TABLE I

Data on Exchange between MnO_4^{--} and MnO_4^- (both at 0.013 *M*)

Run	Temp., °C.	Contact time, sec.	Exchange, %	Active specie	Loss MnO_4^-, (%)	Material balance, %	Remarks
6	0	50	102 ± 3	MnO_4^{--}	1.2	4.4	Low activity
7	0	50	98.5 ± 3	MnO_4^{--}	8.2 gain	0.9 gain	Low activity
11	− 3	45	97.8 ± 2	MnO_4^{--}	1.4	2.3 loss	
12	− 3	45	99.1 ± 2	MnO_4^{--}	5.4	1.1 loss	
13	0	45	101.8 ± 2	MnO_4^{--}	24	12.5 loss	Very poor material balance
14	− 3	43	100	MnO_4^-	2.9	1	Good activity balance
15	− 3	42	100	MnO_4^-	0.6	1.6	Good activity balance
17	− 3	40	99.5 ± 2	MnO_4^-	2.1 gain	0.2 loss	$(MnO_4^-)/(MnO_4^{--}) = 0.37$
22	− 3	38	100	MnO_4^-			
25	− 4	40	99.4	MnO_4^-	0.5 gain	2.6 loss	
26	− 4	35	99.5	MnO_4^-	1 gain	1.7 loss	
27	−14	42	93.9 ± 2	MnO_4^-	7.8 gain	1.6 loss	Probably MnO_2 in system
28	−14	35	93.4 ± 2	MnO_4^-	6.8	3.6 loss	

Experimental

The manganate–permanganate exchange in 3.5 and 4 *M* aqueous potassium hydroxide solution was performed at 0° in order to retard the decomposition of permanganate in basic solution and to afford the best chance of finding a measurable rate of exchange. The loss of permanganate by reduction was between 2 and 5%, and material balance was found within 2 or 3%.

In a typical run 7.35 ml. of 0.0893 *M* K_2MnO_4 in 4 *M* KOH was added to 35 ml. of 4 *M* KOH in a separatory funnel; 7.0 ml. of 0.0939 *M* $KMnO_4$ containing radioactive Mn^{56} was delivered rapidly with a hypodermic syringe and mixed to give an equimolar solution of 0.013 *M*; 40 ml. of pyridine saturated with KOH was immediately added, shaken, and the layers separated. The probable time of contact was measured from the addition of permanganate until the two layers separated with a sharp interface; the total time was measured to the complete separation of the two phases. The pyridine, potassium manganate, and potassium hydroxide solutions were precooled to −3 or −4° in an ice-salt-water-bath, the potassium permanganate was cooled to 0°, and the entire experiment was performed in a refrigerated room at 7°. After the separation, the solutions were analyzed by precipitating $MnNH_4PO_4$, weighing as the monohydrate, and counting the activity of this precipitate.

It was found that the presence of large amounts of pyridine strongly interfered with the precipitation of $MnNH_4PO_4$, and its presence in small amounts discolored the precipitate. The pyridine which was dissolved in the aqueous phase was removed sufficiently well by heating to a slow boil for ten to fifteen minutes. To the pyridine phase was added 40 ml. of water and 5–10 ml. of 4 *M* KOH solution and stirred to form a pyridine–water solution saturated with KOH (a small amount of a second heavy phase separated). The permanganate was reduced to MnO_2 with 5% hydrogen peroxide. Then 10–15 pellets of KOH were added and, after vigorous stirring, a deep aqueous layer separated into which all of the MnO_2 settled. The pyridine was drawn off the top with a pipet and discarded, and the aqueous layer boiled ten to fifteen minutes to remove the remaining pyridine.

Both solutions were then acidified with hydrochloric acid and the manganese reduced to Mn^{++} with 5% hydrogen peroxide. According to the procedure described by Hillebrand and Lundell,[4] the volume of the solution was adjusted to about 130 ml., 15 g. ammonium chloride and 1.5 g. dibasic ammonium phosphate were added. The $MnNH_4PO_4$ was precipitated from the boiling solutions by adding dropwise dilute ammonium hydroxide. The cooled solutions were filtered and washed with water onto a previously washed and weighed filter paper and dried for forty minutes at 75–80° to the monohydrate,[5] weighed, mounted, and counted using an Eck and Krebs thin-wall counter tube.

The University of Chicago cyclotron or a radium–

---

[1] This work was assisted by the Office of Naval Research under Task Order III of Contract N6ori-20.

[2] W. F. Libby, THIS JOURNAL, 62, 1930 (1940).

[3] R. J. Prestwood and A. C. Wahl, *ibid.*, 71, 3137 (1949).

[4] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Son, New York, N. Y., 1929.

[5] J. W. Mellor, "Treatise on Inorganic and Theoretical Chemistry," 12, 452, Longmans, Green, New York, N. Y., 1932.

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).

DEPARTMENT OF CHEMISTRY AND
INSTITUTE FOR NUCLEAR STUDIES
THE UNIVERSITY OF CHICAGO
CHICAGO 37, ILLINOIS

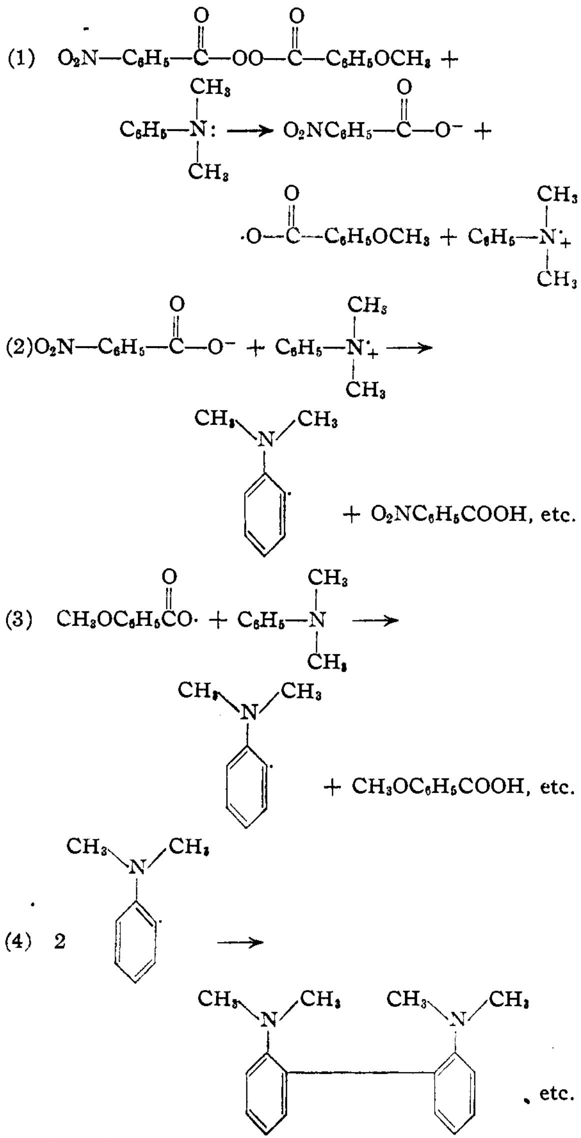
RECEIVED MARCH 27, 1950

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



---

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

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

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