[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Mechanisms of Permanganate Oxidation. IV. Hydroxylation of Olefins and Related Reactions

BY KENNETH B. WIBERG AND KLAUS A. SAEGEBARTH

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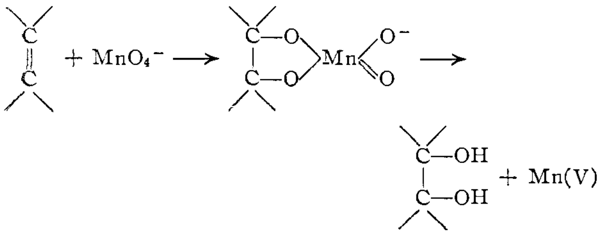
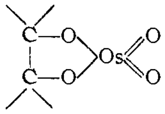
The oxygen introduced into oleic acid in its conversion to 9,10-dihydroxystearic acid by permanganate has been found to arise from the oxidizing agent. The reaction of bicyclo[2.2.1]-2-heptene with permanganate in neutral solution led to a new type of reaction, cleavage to a dialdehyde. The mechanisms for the formation of the diol, ketol and dialdehyde from a common intermediate are discussed.

Introduction

The hydroxylation of olefins by potassium permanganate has been known for many years and has proved a useful method for this conversion. Wagner, who did much of the early work on this reaction, proposed that it involved the formation of a cyclic ester between the permanganate ion and the olefin.[1] Decomposition of the intermediate with cleavage of the manganese–oxygen bonds would lead to the formation of the glycol.



This hypothesis received strong support from the careful stereochemical investigations of Böeseken and his co-workers[2] who determined that the reaction invariably gave the glycol formed by *cis*-addition of the hydroxyl groups. The formation of a cyclic ester intermediate has been well accepted, particularly since osmium tetroxide, which also gives *cis*-hydroxylation, has been shown by Criegee[3] to give an isolable intermediate which almost certainly has the structure



The most important evidence which now could be obtained would be a demonstration that the oxygens introduced into the olefin did arise from the permanganate. Since an excellent method for analyzing for O^{18} in organic molecules is now available,[4] we have studied the oxidation of an olefin with O^{18}-labeled permanganate. The olefin chosen was oleic acid since it gives an excellent yield of the diol and since the product is easily isolated.[5]

It was also of interest to study the effect of reaction conditions on the oxidation of other olefins, since whereas oleic acid gives quantitatively 9,10-dihydroxystearic acid in alkaline solution, the main product in a neutral solution is a mixture of 9,10- and 10,9-ketohydroxystearic acids.[6]

Results and Discussion

In studying the oxygen transfer from permanganate to oleic acid, it is desirable to effect the reaction under conditions which will minimize oxidation of the double bond by manganate, since it is known that manganate will exchange oxygens with water whereas permanganate will not,[7] and since the rate of oxidation by manganate is considerably lower than that for permanganate. Thus, if a large part of the oxidation were effected by manganate, the extent of oxygen transfer would be quite low Even with a large excess of permanganate, incomplete oxygen transfer would be expected since it is known that the rate of electron transfer between manganate and permanganate is very rapid,[8] permitting some exchange of O^{18} with the solvent to occur as the reaction proceeds.

The oxidation of oleic acid was effected at about *p*H 12 using the conditions of Lapworth and Mottram[5] (1.45 $KMnO_4$:1 oleic acid) and also using a larger excess of permanganate (2 $KMnO_4$:1 oleic acid). The large excess of permanganate is permissible since it is known that the oxidation of the diol under these conditions is very slow relative to the rate of oxidation[6] and since a nearly quantitative yield of diol was obtained in each case. The results are shown in Table I.

TABLE I

OXYGEN TRANSFER IN THE OXIDATION OF OLEIC ACID

Excess atom %O^{18} in $KMnO_4$[a]	$[KMnO_4]$ / [oleic acid]	Excess atom %O^{18} in CO_2[a,b]	No. of oxygens from $KMnO_4$
0.910	1.45:1	0.117	1.03
.910	2.00:1	.176	1.55

[a] Excess over normal abundance, 0.204%. The precision of the results is ±0.002%. [b] Carbon dioxide from the oxygen analysis. In calculating the oxygen transfer, a dilution factor of four is used, two for the conversion of carbon monoxide to carbon dioxide and two for the oxygens in the carboxylate group of the acid.

It is clear from these results that over 1.5 atoms of oxygen are transferred from the oxidizing agent to the oleic acid in the course of the hydroxylation. A consideration of the effect of the permanganate–oleic acid ratio on the extent of oxygen transfer leads to the conclusion that the true extent of trans-

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[1] G. Wagner, *J. Russ. Phys.-Chem. Soc.*, **27**, 219 (1895).

[2] J. Böeseken, *Rec. trav. chim.*, **40**, 553 (1921); J. Böeseken and M. C. de Graaff, *ibid.*, **41**, 199 (1922); J. Böeseken, *ibid.*, **47**, 683 (1928).

[3] R. Criegee, *Ann.*, **522**, 75 (1936); *Angew. Chem.*, **51**, 519 (1938); R. Criegee, B. Marchand and H. Wannowius, *Ann.*, **550**, 99 (1938).

[4] W. v. E. Doering and E. Dorfman, THIS JOURNAL, **75**, 5595 (1953).

[5] A. Lapworth and E. N. Mottram, *J. Chem. Soc.*, **127**, 1628 (1925).

[6] G. King, *ibid.*, 1788 (1936); J. E. Coleman, C. Ricciuti and D. Swern, THIS JOURNAL, **78**, 5342 (1956).

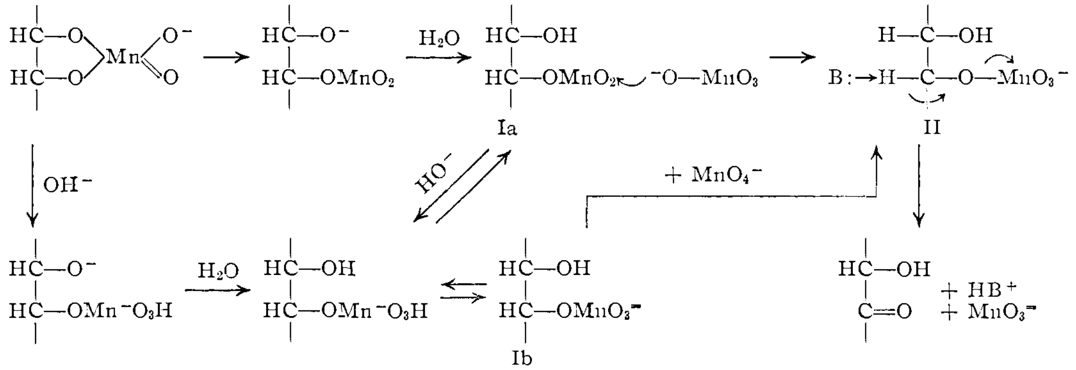
[7] M. C. R. Symons, *J. Chem. Soc.*, 3676 (1954).

[8] J. C. Sheppard and A. C. Wahl, THIS JOURNAL, **75**, 5133 (1953).

fer is close to 2. These results are then a confirmation of the proposal of Wagner and Böeseken.

As was mentioned previously, the high yield of diol from oleic acid is obtained only in basic solution, and a mixture of 9,10- and 10,9-ketohydroxystearic acids is obtained in neutral solution. That oleic acid is not an isolated case is shown by the observations of Lemieux and von Rudloff[9] that other olefins probably give ketols as intermediates in the permanganate–periodate oxidation at *p*H 7–8. It may also be noted that the hydroxylation of 2,3-dimethylbicyclo[2.2.2]-5-octene-2,3-dicarboxylic anhydride was best effected in 2 *N* sodium hydroxide (80% yield)[10] and that the hydroxylation of oleyl and elaidyl hydrogen phthalates were also best effected in basic solution.[11]

Since it is known that the ketol is not formed from the diol, it is reasonable to believe that the ketol and the diol are formed from a common intermediate which has two modes of reaction.[6] The formation of the ketol requires a four-electron oxidation. Since permanganate usually undergoes only a three electron change under the conditions used, two molecules of permanganate probably are involved in the formation of the ketol. Ketol formation is favored by low base concentration and relatively high permanganate concentration, and diol formation is favored by low permanganate and relatively high base concentration. Thus it appears that permanganate and hydroxyl ions compete for reaction with a common intermediate. A reasonable scheme for the reactions is

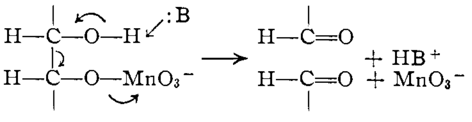


The first step in the hydrolysis of the cyclic permanganate ester would lead to the intermediates Ia or Ib depending on how the manganese–oxygen bond was broken. If both intermediates could be formed, one would expect that they could be interconverted, depending on reaction conditions. The intermediate (Ia or Ib) could be converted to the diol by reaction with hydroxyl ion and to the ketol by oxidation of the Mn(V) in the intermediate to Mn(VI) by permanganate, followed by cleavage of the remaining manganese–oxygen bond in such a way as to produce a carbonyl group. The oxidation would involve the transfer of either an electron or an oxygen ion-radical depending on which intermediate was involved.

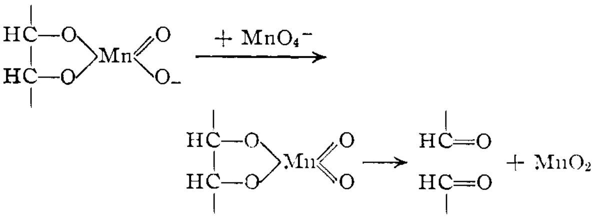
The conclusions reached above apply only to oxidations carried out in aqueous solution. In no case has the isolation of a ketol been reported when a mixture of an organic solvent and water was employed as the reaction medium, and in no case has base been added when these conditions were used. In fact, the recent procedures usually employ a neutral medium.

Straus and Rohrbacher[12] appear to have been the first to use a neutral solution for the hydroxylation reaction. They added magnesium sulfate to precipitate hydroxyl ions as magnesium hydroxide, presumably to avoid oxidation of the ethanol they used as the solvent, for the permanganate oxidation of ethanol is strongly base catalyzed. Subsequent workers have for the most part continued to use this procedure with either ethanol or acetone as the solvent. It is interesting to note that Straus and Rohrbacher reported the hydroxylation of 1,2-dihydronaphthalene to give, in addition to the diol, an unidentified non-crystalline neutral compound, which may have been a ketol.

In order to see whether a ketol might be obtained in a neutral permanganate oxidation, the reaction of bicyclo[2.2.1]-2-heptene was studied and was found to give a small amount of diol and cyclopentane-1,3-dicarboxaldehyde in 54–66% of the theoretical amount. There are two paths which might lead to this product. First, the intermediate II which led to the ketol could also give the dialdehyde by attack of base on a different position (reaction (A)). Second, further oxidation of the original cyclic permanganate ester, before the initial cleavage, might occur. This would lead to an intermediate similar to that in the periodic acid oxidation of diols to carbonyl compounds.



(A)



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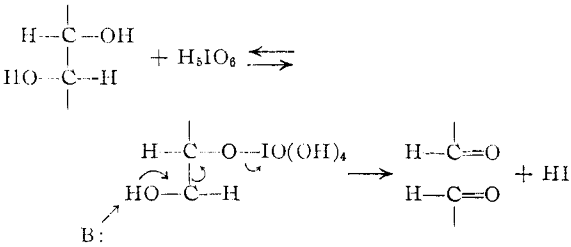
[9] R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

[10] K. Ziegler, G. Schenk, E. W. Krockow, A. Siebert, A. Wenz and H. Weber, *Ann.*, **551**, 1 (1942).

[11] G. Collin and T. P. Hilditch, *J. Chem. Soc.*, 246 (1933).

[12] F. Straus and A. Rohrbacher, *Ber.*, **54**, 69 (1921).

If the first of these possibilities were correct, one might expect that the first-formed intermediate in the periodate cleavage of diols (the periodate ester of one of the hydroxyl groups) should also be able to undergo this type of reaction, in which case the *trans*-glycol should react as fast or faster than the *cis*-glycol. However, the opposite order of reactivity is found[13] and thus the cleavage cannot occur in this manner. The possible similarity between the permanganate and periodate reactions therefore leads us to favor the second path at this time. Further work on the effect of solvent and structure on this reaction is now in progress.



It was also of interest to determine whether alkaline permanganate would have any advantages over neutral permanganate for the hydroxylation reaction in mixed solvents. The oxidations of cyclopentene, cyclohexene and cycloheptene were effected in *t*-butyl alcohol–water solution at about *p*H 13 giving 55, 38 and 38% of the theoretical amounts of diol, respectively. The maximum yields reported for the oxidation in neutral solution are 34, 33 and 35% for the three olefins.[14] Furthermore, the oxidation in basic solution is effected more easily and gives a purer product than does the other procedure.

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Experimental[15]

Hydroxylation of Oleic Acid with Potassium Permanganate O^{18}.—A solution prepared by heating a mixture of 1.00 g. (3.5 mmoles) of oleic acid (Fisher Scientific Co. purified grade), 1.0 g. (25 mmoles) of sodium hydroxide and 100 ml. of water was cooled and diluted with 800 ml. of ice-water and 100 g. of crushed ice. To the cold mixture (5°) was added a solution of 0.80 g. (5.1 mmoles) of labeled potassium permanganate ($\%O^{18} = 1.114$)[16] in 80 ml. of water as rapidly as possible with vigorous stirring. After five minutes, the reaction mixture was decolorized with sulfur dioxide, 30 ml. of concentrated hydrochloric acid was added and the mixture was cooled in ice-water for 1 hr. The precipitate was filtered and dried at room temperature in a vacuum desiccator giving 1.05 g. (94%) of crude *erythro*-9,10-dihydroxystearic acid. One recrystallization from 95% ethanol gave the pure diol (0.90 g. 81%), m.p. 130–131°.[17]

The reaction was repeated using 1.10 g. (7 mmoles) of labeled potassium permanganate in 110 ml. of water. The solution was decolorized after one minute, and the diol was obtained as above (1.10 g. (98%) crude; 0.88 g. (79%) pure, m.p. 130–131°).

Oxygen-18 Analysis.—The apparatus and procedure was essentially that described by Doering and Dorfman,[4] except that the bubbler containing 2–3% bromine in 1:1 chloroform–carbon tetrachloride was not used. The high temperature furnace (1120°) consisted of a heating coil enclosed in a cylindrical sheet nickel housing which was constructed in two halves which were hinged together. The coil was approximately 15 mm. i.d. and 280 mm. long (73 turns spaced 2 mm. apart) of 12 gage Kanthal A-1 wire, having a resistance of 1.5 ohms. The electrical connections were made using pure nickel machine screws and nuts. The heating current was supplied from an 18 amp. Powerstat followed by a 2:1 stepdown transformer. At 1120°, the coil draws approximately 27 amp. at 50 volts.

The analyses were conducted in quadruplicate, and in each case the third and fourth analyses agreed to ±0.002%.

Oxidation of Bicyclo[2.2.1]-2-heptene with Potassium Permanganate. A. Dilute Basic Permanganate.—A solution of 23.4 g. (0.148 mole) of potassium permanganate and 5 g. (0.125 mole) of sodium hydroxide in 800 ml. of water, cooled to 0°, was added quickly with vigorous stirring to a cold mixture (−10°) of 1 l. of *t*-butyl alcohol, 200 ml. of water and 500 g. of cracked ice containing 9.42 g. (0.1 mole) of bicyclo[2.2.1]-2-heptene.[18] After 3–5 min., most of the permanganate color had been discharged, and sulfur dioxide was added to ensure complete reduction of the permanganate. The precipitate of manganese dioxide was filtered through a layer of Filter-Aid, most of the *t*-butyl alcohol was removed by distillation at atmospheric pressure, and the resultant solution was concentrated to about 250 ml. under reduced pressure with steam-bath heating. The solution was continuously extracted with ether for 48 hr., and the ether solution was dried over anhydrous sodium sulfate. Evaporation of the solvent gave 5.77 g. (45%) of a white crystalline solid which was purified by sublimation at 105–110° at 18 mm. giving 5.38 g. (40%) of *exo-cis*-bicyclo[2.2.1]heptane-2,3-diol, m.p. 139.5–140.5°.[19] The infrared spectrum (carbon tetrachloride solution) of the crude reaction product and of the purified material were identical and showed no absorption in the 6 μ region.

The hydroxylations of cyclopentene, cyclohexene and cycloheptene were effected using this procedure.

B. Neutral Permanganate.—A solution of 12.6 g. (0.08 mole) of potassium permanganate and 9.6 g. (0.08 mole) of anhydrous magnesium sulfate in 300 ml. of water was added dropwise to a vigorously stirred suspension of 9.42 g. (0.1 mole) of bicyclo[2.2.1]-2-heptene in 200 ml. of acetone at such a rate as to maintain a reaction temperature of −15 to 20° while immersed in a Dry Ice-acetone-bath. The addition required 1 hr. The reaction mixture was allowed to warm to room temperature and was then filtered. The resultant solution was made basic by the addition of 5 ml. of 40% sodium hydroxide solution and then evaporated to about 250 ml. at 60–70° under reduced pressure. The remaining solution was continuously extracted with ether for 48 hr., and the ether solution was dried over anhydrous magnesium sulfate. Distillation gave 4.1–5.0 g. (54–66%) of cyclopentane-1,3-dicarboxaldehyde, b.p. 80–87° at 2 mm. Redistillation through a 15-inch twisted wire gauze column gave the pure dialdehyde, b.p. 74–75° at 1.5 mm., n^{25}D 1.4759, with good recovery.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.6; H, 8.0. Found: C, 66.2; H, 8.3.

The phenylhydrazone (m.p. 121–122°), dinitrophenylhydrazone (m.p. 225.5–226°) and the semicarbazone (m.p. 203–203.5°) were prepared.

Anal. Calcd. for $C_{19}H_{18}N_8O_8$ (2,4-dinitrophenylhydrazone): C, 46.9; H, 3.7. Found: C, 46.7; H, 3.8. Calcd. for $C_9H_{16}N_6O_2$ (semicarbazone): C, 45.0; H, 6.7. Found: C, 45.1; H, 6.8.

The above 2,4-dinitrophenylhydrazone did not on admixture depress the m.p. of the dinitrophenylhydrazone of cyclopentane-1,3-dicarboxaldehyde prepared by the lead tetraacetate cleavage of *exo-cis*-bicyclo[2.2.1]heptane-2,3-diol.

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[13] R. Criegee, *Sitzber. Ges. Beförder. ges. Naturw. Marburg*, **69**, 25 (1934).

[14] L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4026 (1952); M. F. Clarke and L. N. Owen, *ibid.*, 315 (1949); L. N. Owen and G. S. Saharia, *ibid.*, 2582 (1953).

[15] Melting points are corrected and boiling points are uncorrected. The microanalyses were performed by B. J. Nist and C. L. Ludwig.

[16] K. B. Wiberg and R. Stewart, THIS JOURNAL, **77**, 1786 (1955).

[17] Reference 5 reported m.p. 130.5–131°.

[18] Obtained through the courtesy of the Universal Oil Products Co.

[19] H. Kwart and W. G. Vosburgh, THIS JOURNAL, **76**, 5400 (1954), reported m.p. 140.2–140.6°.