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

The Mechanisms of Permanganate Oxidation. II. The Oxidation of Formate Ion

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The observations of Tompkins[2] that the rate of permanganate oxidation of formate ion is independent of *p*H, that the reaction shows a large positive salt effect and that formate ion is oxidized more rapidly than formic acid have been confirmed. The reaction showed a deuterium isotope effect of 7.4, and over one-third of the oxygen introduced into the product arose from the oxidizing agent. The rate of oxidation by manganate was much slower than the rate of oxidation by permanganate.

Introduction

The permanganate oxidation of formate ion has been studied by Tompkins, Mann and Hill.[2] They found that the rate of oxidation was not dependent on *p*H provided it was not so low as to permit formic acid to form. Formic acid was found to be oxidized at a much smaller rate than formate ion. A primary salt effect was also observed, indicating that the reaction involved two similarly charged ions. The following mechanism was proposed

$$\begin{aligned}&MnO_4^- + HCO_2^- \longrightarrow MnO_3^- + CO_2 + HO^- &&\text{(slow)}\\&2MnO_3^- + H_2O \longrightarrow MnO_2 + HMnO_4^- + HO^- &&\text{(fast)}\\&HMnO_4^- + HCO_2^- \longrightarrow MnO_2 + CO_2 + 2HO^- &&\text{(fast)}\end{aligned}$$

Since this mechanism was clearly different from that observed in the oxidation of aromatic aldehydes,[3] some details of this reaction have now been reinvestigated.

Experimental

Kinetic Method.—A solution containing 5 ml. of 0.0200 *M* formic acid, 1 ml. of 1.00 *M* dipotassium hydrogen phosphate and 42 ml. of water was brought to the desired *p*H by the addition of either concentrated sulfuric acid or solid potassium hydroxide. The reaction was started by the addition of 2 ml. of 0.0331 *M* potassium permanganate, and at regular intervals 5-ml. aliquots were removed and analyzed for permanganate by the method of Tompkins.[2] The results obtained were in good agreement with those previously reported.[2]

Deuterioformic Acid.—Oxalic acid was equilibrated with deuterium oxide[4] several times and then converted to formic acid by heating at atmospheric pressure[5] in a flask with a long heated neck. The latter was necessary in order to avoid sublimation of unconverted oxalic acid.

The deuterioformic acid was analyzed by treating 1 ml. of the acid with 2 ml. of methanol and 0.1 g. of *p*-toluenesulfonic acid. The methyl formate thus formed was distilled from the reaction solution through an 18-inch twisted wire gauze column. The methyl formate was analyzed by means of the mass spectrometer. It was assumed that the isotope effect associated with the cracking pattern would have little effect on the parent and parent-1 peaks. This is reasonable since the p-1 peak was quite small, about 2% of the parent peak. The deuterium content could then be calculated easily giving the value of 96.9% formic acid-d_1.

Oxidation with Potassium Permanganate-O^{18}.—A typical experiment was conducted as follows using the apparatus previously employed for the oxidation of benzaldehyde.[3] Formic acid (0.53 ml., 0.0144 mole) was added to 750 ml. of boiled distilled water containing 7.4 g. of potassium acetate. Four drops of concentrated sulfuric acid was added to bring the *p*H to 5.2. With the solution temperature at 25.0°, 25 ml. of a solution containing 1.58 g. of labeled potassium permanganate (O^{18} = 1.114%) per 26 ml. of solution was added. After 48 seconds, the reaction was quenched with 30 ml. of 2 *M* sodium hypophosphite, and 50 ml. of 1 *N* carbonate free potassium hydroxide was added at once. The mixture was filtered through coarse filter paper, and 30 ml. of 1 *N* barium chloride was added to the filtrate after about one-third of the solution had passed through. The precipitate of barium carbonate was filtered and dried thoroughly. A second fraction of barium carbonate was obtained from the subsequent filtrate. No appreciable difference in O^{18} content was found between the two fractions.

In order to determine the O^{18} content of the carbonate, two ml. of concentrated sulfuric acid was frozen in a small bulb which was attached to a larger bulb by means of a stopcock. The sample of barium carbonate was poured on the solid acid and the system was evacuated. The bulb was immersed in cold water for about one minute. The sulfuric acid melted at once and liberated carbon dioxide from the barium carbonate. The stopcock was closed, and the carbon dioxide in the large bulb was analyzed with the mass spectrometer. The extent of oxygen transfer was calculated using the equation

$$\%\ \text{O from } KMnO_4 = \frac{3y - 0.612}{1.114 - 0.204} \quad \text{where } 2y = \frac{I_{46}}{I_{46} + I_{44}}$$

The procedure was checked as follows. A solution of 4 g. (0.1 mole) of sodium hydroxide in 20 ml. of water containing about 1.5% O^{18} was divided in two equal portions. One portion was saturated with carbon dioxide, diluted with 5 ml. of labeled water, and allowed to stand in contact with carbon dioxide in a small closed vessel with occasional shaking. After several days, the second portion of the base solution was added and the resultant solution of sodium carbonate-O^{18} was evaporated to dryness under vacuum.

A solution of 1.06 g. (0.01 mole) of sodium carbonate-O^{18} in 100 ml. of 0.01 *N* sodium hydroxide solution was treated with 25 ml. of 1 *N* barium chloride solution. The barium carbonate was filtered, dried and analyzed as described above. It contained 1.20% O^{18}. When the sodium carbonate was analyzed in the same way, it was found to contain 1.23% O^{18}. These values indicate that only a very small amount of exchange occurred in the precipitation of the barium carbonate. The O^{18} content of the sodium carbonate was somewhat lower than that of the water used in its preparation, and this is probably caused by incomplete exchange since sodium bicarbonate was not completely soluble in the quantity of water used.

The oxidation of formate ion was carried out as described above, except that an equivalent amount of sodium carbonate-O^{18} was added prior to the start of the reaction. The reaction was conducted at *p*H 10, and was allowed to proceed to completion. The barium carbonate was found to contain 0.68% O^{18}, whereas 0.70% is the calculated value. The good agreement between these values indicates that the carbonate does not exchange appreciably with water under the reaction conditions.

Results and Discussion

The kinetic results of Tompkins' were confirmed except that at high *p*H (above 11) the rate of oxidation was found to decrease with time. This is similar to behavior of piperonal,[3] and to see if there were a similar explanation, the rate of oxidation of formate

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[1] Taken from part of a thesis submitted by Ross Stewart to the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] D. R. Mann and F. C. Tompkins, *Trans. Faraday Soc.*, **37**, 201 (1941); L. M. Hill and F. C. Tompkins, *Trans. Roy. Soc. S. Africa*, **29**, 309 (1942).

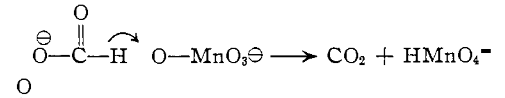
[3] K. B. Wiberg and R. Stewart, THIS JOURNAL, **77**, 1786 (1955).

[4] Obtained from the Stuart Oxygen Co. on allocation from the U. S. Atomic Energy Commission.

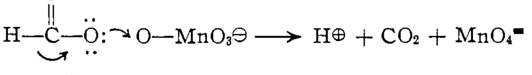
[5] J. L. Gay-Lussac, *Ann. chim. phys.*, [2] **46**, 219 (1831); *cf.* R. C. Herman and V. Z. Williams, *J. Chem. Phys.*, **8**, 447 (1940).

ion with manganate was determined. The rate constant, 0.18 l. mole^{-1} sec.$^{-1}$ in 0.2 *M* phosphate buffer at *p*H 12.3, 25.0°, was about one-seventh the rate of oxidation by permanganate at the same ionic strength in a less basic solution. Thus the decrease in rate is strongly indicative of the formation of the less reactive manganate as the reaction proceeded in the strongly basic solution. This result also indicates that step 3 in Tompkins' mechanism is not important, and that the intermediate Mn(V) is converted by disproportionation to permanganate as the reactive species.

The reaction would appear to involve either a transfer of a hydride ion or a pair of electrons from the formate ion to permanganate.



$$^{\ominus}O-\overset{O}{\overset{\|}{C}}-H \quad O-MnO_3^{\ominus} \longrightarrow CO_2 + HMnO_4^{-} \qquad (A)$$



$$H-\overset{O}{\overset{\|}{C}}-\ddot{O}{:}\quad O-MnO_3^{\ominus} \longrightarrow H^{\oplus} + CO_2 + MnO_4^{=} \qquad (B)$$

In either case, a deuterium isotope effect would be expected since the cleavage of the carbon–hydrogen bond is involved in the rate-determining step. In order to test this feature of the mechanism, the rate of oxidation of deuterioformic acid was determined. At both *p*H 7.8 and 10.0, the protioformic acid reacted 7.4 times as fast as the deuterioformic acid (Table I).

TABLE I

RATE OF OXIDATION OF FORMATE ION AND DEUTERIOFORMATE ION AT 25° IN A 0.2 *M* PHOSPHATE BUFFER

*p*H	k_H, l. mole^{-1} sec.$^{-1}$	k_D, l. mole^{-1} sec.$^{-1}$	k_H/k_D
7.8	0.927 ± 0.015[a]	0.126 ± 0.002[a]	7.4 ± 0.2[c]
10.0	.946 ± .014[b]	.128 ± .003[b]	7.4 ± .2[c]

[a] This is the average of three determinations. [b] This is the average of two determinations. The change in rate with *p*H is due to a small change in ionic strength. [c] Not corrected for the small amount (3%) of formic acid in the deuterioformic acid.

If one of the above mechanisms is correct, the carbonate formed by the reaction of the product carbon dioxide with hydroxyl ion in the solution would be devoid of O^{18} if potassium permanganate-O^{18} were used as the oxidizing agent. Since carbonate will not exchange oxygens with water, whereas carbon dioxide does,[6] the solutions were quenched with hypophosphite after a certain time interval, and the solution was immediately made basic. The carbonate was precipitated as barium carbonate, and the carbon dioxide was then liberated by treatment with concentrated sulfuric acid under conditions which would minimize exchange. The carbon dioxide was analyzed with a mass spectrometer giving the data in Table II.

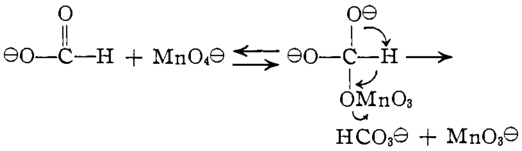
TABLE II

TRANSFER OF OXYGEN FROM PERMANGANATE TO FORMATE ION

*p*H	Reaction, %	O from permanganate, %
5.2	50	18
9.0	50	31
9.0	95	19
10.7	50	28

The low value at *p*H 5.2 can be attributed to exchange with the solvent of the carbon dioxide present in equilibrium. The lower value at *p*H 9.0 after 95% reaction is probably caused by exchange of the intermediate valence states of manganese with water before disproportionating and regenerating permanganate. This is similar to the previous observations in the case of the oxidation of benzaldehyde to benzoic acid.[7] Considering the previous results, it would appear that between 0.4–0.5 of the oxygen atoms introduced into the formate during the reaction arose from the oxidizing agent. Since the reaction appeared to give a fractional degree of transfer, the possibility of exchange of carbonate ion with water was tested by adding an equivalent quantity of sodium carbonate-O^{18} at the beginning of the reaction, and isolating the carbonate as before. It was found to contain 0.68% O^{18} as compared to the calculated value of 0.70%. The good agreement between these values indicated the absence of exchange.

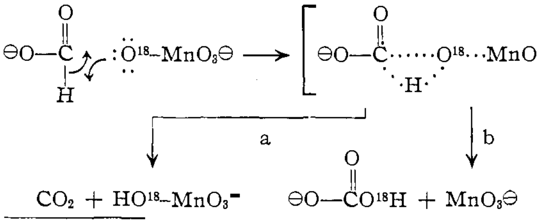
The oxygen transfer data show that mechanisms A and B cannot by themselves explain the nature of the reaction. The simplest hypothesis would then involve a competition between either A or B and mechanism C which would effect transfer of O^{18}.



$$^{\ominus}O-\overset{O}{\overset{\|}{C}}-H + MnO_4^{\ominus} \rightleftarrows {}^{\ominus}O-\underset{OMnO_3}{\overset{O^{\ominus}}{C}}-H \longrightarrow HCO_3^{\ominus} + MnO_3^{\ominus} \qquad (C)$$

However, there are objections to such a proposal. First, it is difficult to see why the permanganate ion would attack the carbonyl group of the negatively charged formate ion whereas it apparently does not react with formic acid. This type of reaction would certainly be expected to be more favorable with the uncharged acid, although the subsequent loss of a proton would be facilitated by the double negative charge arising from attack on formate ion. Second, the two reactions would have to proceed at almost exactly the same rate, which would be an unusual coincidence. One cannot rule out the proposal on the basis of the above arguments, but they raise sufficient question to merit consideration for some less conventional formulations.

One possibility is mechanism D, leading to the formation of an intermediate in which both the carbon and hydrogen of the formate may be bonded to the oxygen of the permanganate. This intermediate could lead to both labeled and unlabeled carbonate depending on which bonds were broken. The driving force for this reaction would be, presumably, the



$$^{\ominus}O-\underset{H}{\overset{O}{\overset{\|}{C}}}\;:\ddot{O}^{18}-MnO_3^{\ominus} \longrightarrow \left[{}^{\ominus}O-\overset{O}{\overset{\|}{C}}\cdots O^{18}\cdots MnO_3^{\ominus}\;\;\cdot\cdot H\cdot\cdot\right] \begin{cases} \xrightarrow{a} CO_2 + HO^{18}-MnO_3^{-} \\ \xrightarrow{b} {}^{\ominus}O-\overset{O}{\overset{\|}{C}}O^{18}H + MnO_3^{\ominus} \end{cases} \qquad (D)$$

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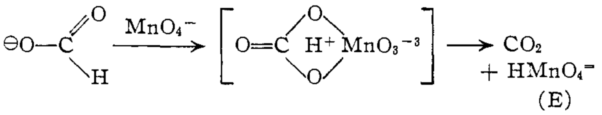
[6] G. A. Mills and H. C. Urey, THIS JOURNAL, **62**, 1019 (1940).

[7] The oxidation of benzaldehyde in neutral solution resulted in 76% transfer after 54% reaction and 54% transfer after 90% reaction (ref. 3). At *p*H 9, 54% transfer was noted after 65% reaction.

electrophilic nature of the permanganate oxygen and the electron donor character of the charged oxygen atom of the formate. This mechanism is in a sense analogous to the mechanism proposed by Denney[8] for the rearrangement of 9-decalyl hydroperoxide benzoate.

Since approximately one-half of the oxygen introduced into the formate came from the permanganate, mechanism E may be considered, in which one of the oxygens of the formate and one from the permanganate become equivalent in the intermediate. Cleavage of the intermediate would then lead to carbon dioxide in which one oxygen would have one-half the O^{18} content of the permanganate. An equivalent result would be obtained if the intermediate in mechanism C would permit an exchange of the MnO_3 group from one oxygen to the other. It unfortunately does not appear possible to obtain direct evidence concerning these possible mechanisms at the present time.



(E)

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[8] D. B. Denney, THIS JOURNAL, **77**, 1706 (1955).

[CONTRIBUTION FROM THE ROLLIN H. STEVENS MEMORIAL LABORATORY OF THE DETROIT INSTITUTE OF CANCER RESEARCH]

The Rearrangement of Some Substituted Allyl Alcohols to their Isomeric Ketones[1]

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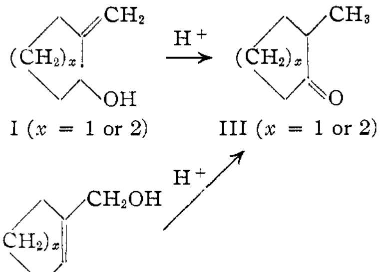
The allylic pair 2-methylenecyclohexanol and 1-cyclohexenemethanol rearrange to the isomeric 2-methylcyclohexanone in the presence of sulfuric acid. Similar results are obtained in the homologous five-membered ring series.

It has been shown that the enolic forms of some β-dicarbonyl compounds are reduced by an excess of lithium aluminum hydride to give one or a pair of substituted allyl alcohols, the number being dependent on the symmetry of β-dicarbonyl compound.[3]

A pair of allyl alcohols obtained by such a procedure is usually characterized by their susceptibility to the acid-catalyzed oxotropic rearrangement which results in the more stable isomer. However, complete conversion is often not realized in the absence of some stabilizing factor such as conjugation and, at elevated temperatures, etherification and/or dehydration may compete with rearrangement.[4]

The isolation of the 2-methylenecycloalkanols (I) ($x = 1$ and 2) and the 1-cycloalkenemethanols (II) ($x = 1$ and 2) has furnished two pairs of isomeric allyl alcohols which should be capable of undergoing at least a partial rearrangement on treatment with acid.[3] A projection of the work of Brown[5] on the stabilities of double bonds, *exo vs. endo*, in five- and six-membered rings has been attempted on these two pairs of alcohols in the absence of experimental evidence. It has been predicted that in the six-membered ring series the primary alcohol II ($x = 2$) should be more stable in a potential anionotropic system and, conversely, the secondary alcohol I ($x = 1$) should be favored in the five-membered ring series.[6]

We wish to report that in a given series both alcohols were unstable to acid and were converted to their isomeric 2-methylcycloalkanone (III).



I ($x = 1$ or 2)

III ($x = 1$ or 2)

II ($x = 1$ or 2)

In early experiments, in the formation of I and II, the alcoholate complexes from the lithium aluminum hydride reductions were worked up with dilute sulfuric acid. The isolated products gave small yields of a semicarbazone. This was in contrast to a high yield of the 2,4-dinitrophenylhydrazone (DNPH) of III which formed immediately with a 5% solution of the reagent in 50% sulfuric acid at room temperature. The formation of a semicarbazone could not be observed when the lithium aluminum–alcohol complex was decomposed by the weakly alkaline Rochelle salt.[7] However, the alcohols (I and II) retained the property of precipitation with the acid 2,4-dinitrophenylhydrazine solution. The secondary alcohols (I) reacted more rapidly than the primary (II) and gave slightly higher yields, both giving the same DNPH of III.[8]

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[1] This work was supported by institutional grants from The American Cancer Society, Inc., The American Cancer Society, Southeastern Michigan Division and the Kresge Foundation.

[2] To whom inquiries should be addressed.

[3] A. S. Dreiding and J. A. Hartman, THIS JOURNAL, **75**, 939, 3723 (1953).

[4] E. A. Braude, *Quart. Rev.*, **4**, 404 (1950).

[5] H. C. Brown, J. H. Brewster and H. Schecter, THIS JOURNAL, **76**, 467 (1954).

[6] O. H. Wheeler, Abstracts of the 125th Meeting of the American Chemical Society, Kansas City, Mo., April 1954, p. 25-N. See also *Chem. and Ind.*, 900 (1954).

[7] R. E. Lutz and J. S. Gillespie, THIS JOURNAL, **72**, 2002 (1950). The reported reduction of dibenzoylethylene with lithium aluminum hydride and sulfuric acid hydrolysis gave 1,4-diphenyl-2-butene-1,4-diol and 1,4-diphenylbutan-1-ol-4-one. The latter was presumably derived from a stable enolate of a 1,4-reduction. Using Rochelle salt hydrolysis we obtained similar results. Acid treatment of the unsaturated diol gave a spectrum typical of a styrene chromophore (λ_{max}^{alc} 252 mμ) and not that of the hydroxy ketone (λ_{max}^{alc} 243 mμ).

[8] A partial oxidation of some substituted allyl alchols has been observed by a less strongly acidic solution of 2,4-dinitrophenylhydrazine, the products being the DNPH's of the unrearranged unsaturated conjugated carbonyl compound. See E. A. Braude, *et al.*, *J. Chem. Soc.*, 1762 (1951); and 2202 (1953).