ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA]

The Mechanisms of Permanganate Oxidation. III. The Oxidation of Benzhydrol

BY ROSS STEWART

RECEIVED NOVEMBER 23, 1956

The permanganate oxidation of benzhydrol has been studied in an attempt to elucidate the reaction mechanism. The reaction kinetics, the existence of hydroxyl ion catalysis, the presence of a positive salt effect and the sign and magnitude of the entropy of activation all indicate that the rate-controlling step consists of a reaction between benzhydrylate ion and permanganate ion. The existence of an isotope effect (6.6:1) obtained for the oxidation of benzhydrol-α-d, and the fact that when potassium permanganate-O^{18} is used as the oxidant no excess oxygen-18 appears in the product, suggest that the reaction occurs by hydride ion transfer from benzhydrylate ion to permanganate ion.

Introduction

The previous papers in this series dealt with the permanganate oxidations of aromatic aldehydes[1] and formate ion[2] and demonstrated further the manifold character of permanganate ion as an oxidant.

The presently available evidence indicates that permanganate oxidizes each of the following groups or compounds by a distinctive reaction path: C=C,[3,4] ArCHO,[1] RCHO and R_2CO,[5] $-CH_3$,[6] $-HCO_2^{-}$[2] and $(CO_2H)_2$.[7]

Such versatility[8] is even more impressive when one considers that a change in reaction conditions can cause a change in mechanism as has been shown in the case of the permanganate oxidation of benzaldehyde.[1] The present study was undertaken to determine the mechanism of the reaction of this reagent with alcohols. It deals with the behavior of permanganate toward a typical secondary alcohol, benzhydrol, $(C_6H_5)_2CHOH$, which was chosen because of the stability of its oxidation product, benzophenone, to further attack.

Previous work on the reaction of alcohols with permanganate in acid media has been reported. Merz, Stafford and Waters showed that isopropyl alcohol in acid solution is oxidized by an induced process which probably involves Mn^{+4}.[9] Cullis and Ladbury have made a comprehensive study of reaction conditions for the acid permanganate oxidation of aromatic compounds including benzyl alcohol and 1-phenylethanol,[10] but the reaction mechanism remains obscure.

Experimental

Reagents.—Benzhydrol was crystallized from carbon tetrachloride to constant m.p. 64–65°. Benzhydrol-α-d was prepared as follows. Benzophenone (3.6 g., 0.02 mole) was dissolved in 30 ml. of dry ether and added dropwise to lithium aluminum deuteride (0.44 g., 0.01 mole) dissolved in 20 ml. of ether. The mixture was refluxed for ten minutes, cooled and poured on to a mixture of one ml. of concentrated sulfuric acid and about 20 g. of crushed ice. The ether layer was separated, washed, dried and evaporated to give 2.7 g. of white crystals, m.p. 63–64°. The benzhydrol-α-d used in the rate experiments was recrystallized from carbon tetrachloride to constant m.p. 64–65°. The infrared spectrum of the labeled alcohol showed a shift in the carbon–hydrogen stretching peak from 3.52 to 4.71 μ. The isotopic purity was shown to be high by the complete absence of a band at 3.52 μ in the benzhydrol-α-d.

Potassium permanganate-O^{18} and potassium manganate were obtained as previously described.[1]

Kinetic Method.—Two procedures, titration and measurement of light absorption, were used to follow the disappearance of permanganate and hence to determine the reaction rate.

In the first method an aqueous solution of benzhydrol, approximately 0.002 M, was obtained by dissolving a weighed amount of benzhydrol in hot distilled water which had been boiled to remove dissolved gases and making the solution up to the mark in a volumetric flask. In a typical experiment, 20 ml. of this solution, 10 ml. of 0.2 M carbonate-free potassium hydroxide and 18 ml. of boiled distilled water were brought to reaction temperature in a vessel immersed in a constant temperature bath controlled to ±0.04°. Two ml. of a standard solution of potassium permanganate was added to start the reaction, the progress of which was followed by titrating five-ml. aliquots iodometrically, essentially as described previously.[1] A slow flow of nitrogen through the system was maintained during the reaction.

Since most of the investigation dealt with the basic pH region where the permanganate oxidation of benzhydrol was fast and the manganate oxidation was shown to be slow, the reaction studied involved a valence change for manganese from +7 to +6. A very accurate titration is required if the points on the rate plot are to be precise since the titration measures the total oxidizing power of all manganese species above valence two. Reasonably good precision was obtained on most of the rate plots; nevertheless, there is a considerable scatter of points in Fig. 3, for example.

As a check on the titration method the disappearance of permanganate was also followed spectrophotometrically. The reaction mixture was made up essentially as in the previous method. After addition of the permanganate the solution was shaken and a portion of it transferred quickly to an absorption cell and placed in the cell compartment of a Beckmann spectrophotometer, model DU. Thermospacers kept the sample at a constant temperature and even when measurements were made at temperatures ten degrees above room temperature, no difficulty was experienced. In this case a drop in temperature of about one fifth of a degree in transferring the sample to the cell was observed. The temperature rose to that of the thermostat within a short time, however, and the rate constants were calculated from those points obtained after thermal equilibrium had been attained. Measurements of the light absorption were made at 522 and 426 mμ, the former wave length corresponding mainly to absorption by permanganate and the latter mainly to absorption by manganate. From the known values of the extinction coefficients of the two ions at these two wave lengths[11] the following equation was derived, where D stands for optical density.

---

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

[2] K. B. Wiberg and R. Stewart, *ibid.*, **78**, 1214 (1956).

[3] W. A. Waters in H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 1211, 1214.

[4] J. Boeseken, *Rec. trav. chim.*, **47**, 683 (1928).

[5] A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 497 (1955).

[6] W. Griehl, *Ber.*, **80**, 410 (1947).

[7] J. M. Malcolm and R. M. Noyes, THIS JOURNAL, **74**, 2769 (1952).

[8] For a simpler view of organic oxidations see L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955), and L. S. Levitt and E. R. Walinowski, THIS JOURNAL, **77**, 4517 (1955).

[9] J. H. Merz, G. Stafford and W. A. Waters, *J. Chem. Soc.*, 638 (1951).

[10] C. F. Cullis and J. W. Ladbury, *ibid.*, 2850 (1955).

[11] G. L. Zimmerman, Thesis, University of Chicago, 1949.

$$[\mathrm{MnO_4^-}] = D_{522} - 0.282D_{426}$$

In most of the rate experiments which were followed using this method, benzhydrol was present in considerable excess and the concentration of $\mathrm{MnO_4^-}$ need not be obtained in any specific units since only log $[\mathrm{MnO_4^-}]$ is used in the calculations. The values of $[\mathrm{MnO_4^-}]$ obtained by the use of the above equation are quite arbitrary.

The light absorption method for determining the rate is subject to the following disadvantages. For very slow permanganate oxidations some manganate is likely to be reduced to $\mathrm{MnO_2}$ which can cause light scattering and may introduce errors in the estimate of the permanganate concentration. It is assumed, too, that no other light absorbing species are formed as the reaction proceeds (see Results and Discussion). The fact that the two methods gave rate constants in good agreement with each other indicates that the results obtained are reliable.

Oxidation with Potassium Permanganate-$\mathrm{O^{18}}$.—A typical experiment was conducted as follows. Benzhydrol (0.45 g.) was dissolved in 860 ml. of hot, previously boiled, distilled water and, when the solution had cooled to 30°, 45 ml. of 0.2 *N* potassium hydroxide was added. Labeled potassium permanganate (1.55 g., onefold excess) was dissolved in 30 ml. of water and added to the reaction solution. After four minutes 30 ml. of 10% sodium bisulfite and one ml. of concentrated sulfuric acid were added to quench the reaction. The solution was immediately extracted with 30 ml. of petroleum ether which was washed, dried over anhydrous sodium sulfate and poured through a column of 3 g. of alumina. The column was eluted with three 15-ml. samples of petroleum ether and one sample of ether. The first two petroleum ether fractions yielded 0.25 g. of pure benzophenone, m.p. 49°. The third and fourth fractions contained small amounts of benzophenone, and the ether eluate contained about 0.06 g. of unreacted benzhydrol. The original reaction solution after the petroleum ether extraction was further extracted with 100 ml. of benzene and this, in turn, yielded about 0.11 g. of a mixture of benzophenone and benzhydrol, m.p. 46–54°.

Benzhydrol-$\mathrm{O^{18}}$.—Benzhydryl chloride readily was prepared by shaking 14 g. of benzhydrol with 80 ml. of concentrated hydrochloric acid for 0.5 hr. Extraction with ligroin followed by distillation at reduced pressure yielded 12 g. of benzhydryl chloride, m.p. 18–19°, b.p. 100–102° at 0.3 mm. A solution of 5 g. of benzhydryl chloride, 6 ml. of dry pyridine and 1 ml. of $\mathrm{H_2O^{18}}$ (about 1.4 atom % $\mathrm{O^{18}}$) was allowed to stand overnight and then heated for 2 hr. on the steam-bath. The liquid was distilled off under reduced pressure and the residual white solid was extracted with ether. Evaporation of the ether yielded 3.0 g. of white crystals which were recrystallized from carbon tetrachloride–ligroin. Repeated recrystallizations from this solvent did not raise the m.p. above 62–63°. One gram of ordinary benzhydrol was added to 2.5 g. of the labeled material and the whole dissolved in hot ether. Addition of petroleum ether produced 2.1 g. of crystals of benzhydrol which melted at 64–65° and gave no m.p. depression when mixed with an authentic sample.

Oxidation of Benzhydrol-$\mathrm{O^{18}}$.—The same general procedure was used here as for the oxidation with potassium permanganate-$\mathrm{O^{18}}$ except that in one experiment the reaction was quenched with sodium bisulfite only. The unreacted benzhydrol which was recovered in this experiment was submitted to oxygen-18 analysis to determine whether or not any exchange of oxygen with solvent had occurred prior to reaction.

Results and Discussion

Kinetics.—The benzhydrol–permanganate reaction is strongly base catalyzed as can be seen from the results shown in Fig. 1.[12]

In all rate experiments in which equivalent quantities of benzhydrol and permanganate were used and in which hydroxyl ion was in excess the reaction was found to be second order in agreement with the rate law

$$\frac{-\mathrm{d}\,[\mathrm{MnO_4^-}]}{\mathrm{d}t} = k_2[\mathrm{MnO_4^-}][(\mathrm{C_6H_5})_2\mathrm{CHOH}]$$

For those points in Fig. 1 below *p*H 12 the benzhydrol–permanganate ratio was kept at 3:2 since any manganate or hypomanganate formed in the process undergoes disproportionation to $\mathrm{MnO_2}$ and $\mathrm{MnO_4^-}$. This initial ratio of 3:2 ensures a constant ratio of the two reactants as the oxidation proceeds. The second-order rate constants were obtained using the expression

$$k_2 = \frac{1}{t[\text{benzhydrol}]_0} \times \frac{V_0 - V_t}{V_t - 2/5V_0} \qquad (1)$$

where V is the volume of thiosulfate required in the iodometric titration.[1] In sufficiently basic solution, however, the manganate formed does not disproportionate. Since it was shown that manganate reacts with benzhydrol at about one fortieth of the rate of permanganate in 0.1 *M* KOH solution, the manganate accumulates as the reaction proceeds and the reaction in basic solution, which was the one studied in detail, becomes

$$(\mathrm{C_6H_5})_2\mathrm{CHOH} + 2\mathrm{MnO_4^-} + 2\mathrm{OH^-} \longrightarrow (\mathrm{C_6H_5})_2\mathrm{C{=}O} + 2\mathrm{MnO_4^{=}} + \mathrm{H_2O}$$

To preserve a constant benzhydrol–permanganate ratio as the reaction proceeds a 1:2 initial ratio is required. It can be shown that in this case the rate constant is given by the expression

$$k_2 = \frac{1}{t[\text{benzhydrol}]_0} \times \frac{V_0 - V_t}{V_t - 4/5V_0} \qquad (2)$$

Linear relations were obtained when t was plotted against $V_0 - V_t/V_t - 4/5V_0$ showing the reaction to be second order but not proving it to be first order in each reactant. For this reason experiments were performed in which there was an initial benzhydrol–permanganate molar ratio of 1:1 and 1:4. It can be shown that when the initial molar concentrations of benzhydrol and permanganate are the same (two equivalents of benzhydrol to one of permanganate) relation (3) holds

$$k_2 = \frac{4.61}{y_0t} \log \frac{V_t - 3/5V_0}{V_t - 4/5V_0} \qquad (3)$$

and that when the ratio of the initial concentration of benzhydrol to permanganate is 1:4 this expression holds

$$k_2 = \frac{-2.30}{y_0t} \log \frac{V_t - 9/10V_0}{V_t - 4/5V_0} \qquad (4)$$

Equation 3 can be derived as (let $x = [\mathrm{MnO_4^-}]$ and $y = [\text{benzhydrol}]$)

$$\frac{-\mathrm{d}x}{\mathrm{d}t} = k_2xy$$

if $x_0 = y_0$, $y = 1/2y_0 + 1/2x$

$$-1/2k_2t = \int \frac{\mathrm{d}x}{(y_0x + x^2)} = -\frac{1}{y_0} \ln\left(\frac{y_0 + x}{x}\right)$$

now $x = A[V_t - 4(V_0 - V_t)]$, where A is a con-

---

(12) Except for the few experiments required to establish the fact that the reaction is slow in neutral or acid solution, the only work done in these regions was an experiment to determine the effect of added manganous ion on the rate, a device which has been used to determine whether or not the oxidizing agent is some manganese species of intermediate valence. Addition of enough manganous sulfate to make the solution 0.00024 *M* in $\mathrm{Mn^{++}}$ compared to a permanganate concentration of 0.0013 *M*, caused a drop in the bimolecular rate constant k_2 from 0.48 to 0.32 in 0.18 *M* $\mathrm{H_2SO_4}$, indicating that ions of intermediate valence produced by the manganous–permanganate reaction are not the active oxidizing species even in acid solution.

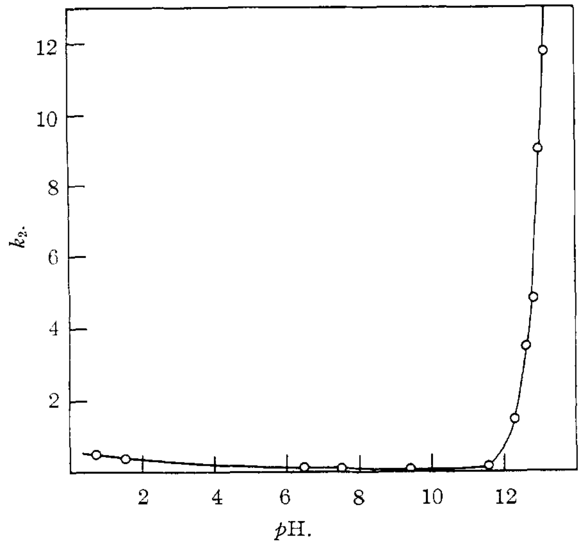


Fig. 1.—Effect of variation in pH on the bimolecular rate constant, k_2, for the permanganate–benzhydrol reaction; $T = 25°$.

stant, provided the only oxidizing species of manganese in solution are MnO_4^- and $MnO_4^=$.

$$\therefore\ 1/2k_2t = \frac{1}{y_0} \ln \frac{V_t - 3/5V_0}{V_t - 4/5V_0}$$

and

$$k_2 = \frac{4.61}{y_0t} \log \frac{V_t - 3/5V_0}{V_t - 4/5V_0}$$

Equation 4 follows from a similar argument.

Good straight line relations were obtained for these two cases when t was plotted against the logarithmic function and the rate constants listed in Table I show that the reaction is indeed first order in MnO_4^- and first order in benzhydrol. Also listed in Table I are values for the rate constant obtained using benzhydrol in excess. These values were obtained from spectrophotometric experiments and the kinetics were, as expected, pseudo unimolecular.

TABLE I

RATE CONSTANTS FOR THE BENZHYDROL–PERMANGANATE REACTION FOR VARIOUS INITIAL CONCENTRATION OF REACTANTS

$(C_6H_5)_2$ CHOH $\times 10^4$, mole l.$^{-1}$	MnO_4^- $\times 10^4$, mole l.$^{-1}$	OH^-, mole l.$^{-1}$	Ionic strength	k_2, l. mole^{-1} sec.$^{-1}$	Method
15.6	15.6	0.020	0.040	1.52[a]	Titration
7.80	15.6	.020	.040	1.54[b]	Titration
3.90	15.6	.020	.040	1.55[c]	Titration
7.80	15.6	.022	.040	1.79[b]	Titration
13.0	2.1	.022	.024	1.75[d]	Spectral
6.50	2.1	.022	.024	1.84[d]	Spectral

[a] Calculated using equation 3. [b] Calculated using equation 2. [c] Calculated using equation 4. [d] Calculated using the relation $k_2 = (2.30 \log x)/y_0't$ where $x = [MnO_4^-]$ and y_0' = mean concentration of benzhydrol over range studied.

Hydroxyl Ion Catalysis and Salt Effect.—The reaction rate was shown, too, to be directly proportional to the hydroxyl ion concentration (Fig. 2). A likely role for hydroxyl ion in the reaction would be to produce the anion of benzhydrol which, in turn, might undergo a rate-determining reaction with permanganate. This possibility can be further investigated by determining the effect of a change in ionic strength on the rate, since two anions would be reacting in the slow step. Unfortunately, a certain minimum hydroxyl ion concentration is required to ensure that the reaction one is studying is, indeed, the hydroxyl ion catalyzed one. This places the ionic strength in a region where the Brönsted–Debye–Hückel relation is not expected to hold. Harty and Rollefson[13] have recently had some success with a treatment for ionic reactions in more concentrated solution which involves plotting log k against a parameter which depends on both the ionic strength and the particular salt added. Using their value for the parameter when potassium sulfate is the added salt, as in the present case, one obtains the curve shown in Fig. 3. Although the precision of the results shown in this plot is not impressive (for reasons discussed in the Experimental section) the results do support the idea that the slow step is between two ions of like, single, charge. The over-all reaction may then be expressed as

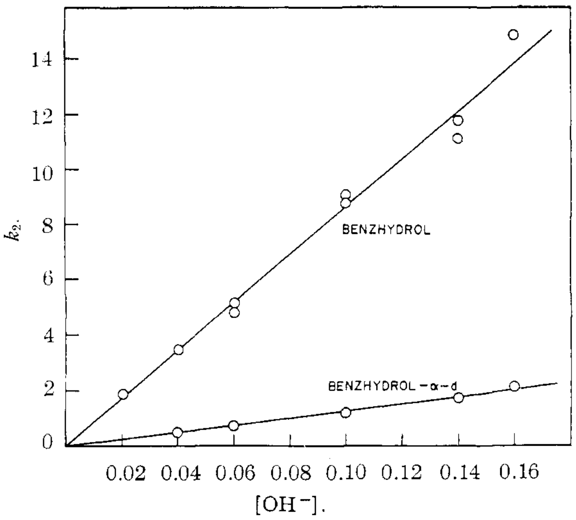


Fig. 2.—The bimolecular rate constant, k_2, as a function of the hydroxyl ion concentration for the permanganate oxidation of benzhydrol and benzhydrol-α-d; $T = 25.0°$.

$$(C_6H_5)_2CHOH + OH^- \overset{K}{\rightleftharpoons} (C_6H_5)_2CHO^- + H_2O$$

$$MnO_4^- + (C_6H_5)_2CHO^- \xrightarrow{k} \text{products}$$

The rate law which corresponds to this mechanism is

$$\frac{-d[MnO_4^-]}{dt} = k[MnO_4^-][(C_6H_5)_2CHO^-]$$
$$= kK[MnO_4^-][(C_6H_5)_2CHOH][OH^-]/[H_2O]$$
$$\therefore\ k_2 = kK[OH^-]/[H_2O]$$

These equations are in agreement with the observed kinetics.

Thermodynamic Functions.—A plot of log k/T against $1/T$ shows a satisfactory linear relation but leads to the rather low value for $\Delta H^{\ddagger}$ of 5.7 kcal. mole^{-1} and the rather high negative value for $\Delta S^{\ddagger}$

---

[13] W. E. Harty and G. K. Rollefson, THIS JOURNAL, **76**, 4811 (1954).

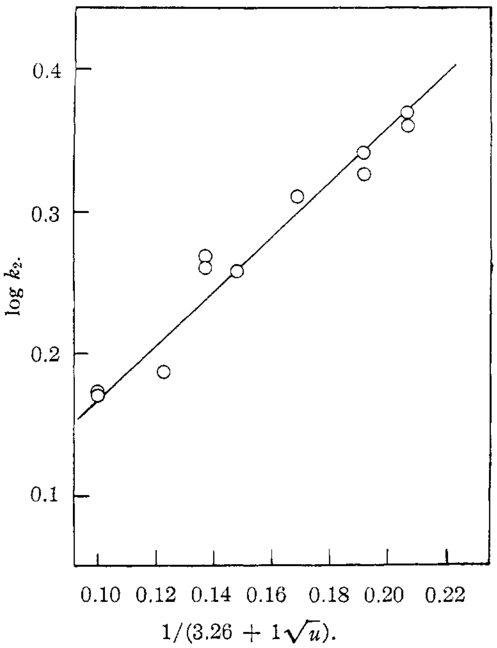


Fig. 3.—Log k_2 plotted against the parameter, $1/(3.26 + 1/\sqrt{u})$ for the permanganate–benzhydrol reaction; $T = 25.0°$.

of −38.4 e.u. It should be pointed out that these are composite values which include the thermodynamic parameters for the ionization step as well as for the rate-controlling step. The entropy of activation for the rate-controlling step must, in fact, be a much smaller negative quantity than the value of −38.4 e.u. calculated here since the equilibrium concentration of benzhydrylate ion is probably quite small in the solutions used in this work. In view of this the measured entropy of activation is not unreasonable since reactions between univalent anions in aqueous solution normally have activation entropies of the order of −20 e.u.[14]

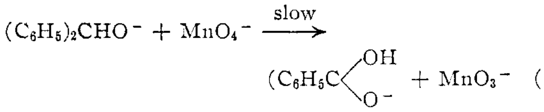
Mechanism of the Rate-controlling Step.—If it is assumed that the first step in the reaction is the ionization of benzhydrol, then the following mechanisms for the rate-controlling step can be considered, each of which agrees with the observed kinetics.[15]

$$(C_6H_5)_2CHO^- + MnO_4^- \xrightarrow{\text{slow}} (C_6H_5)_2CHO\cdot + MnO_4^= \quad (5a)$$

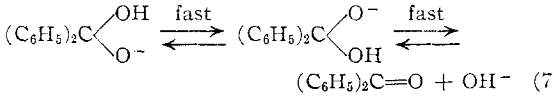
$$(C_6H_5)_2CHO\cdot + MnO_4^- \xrightarrow{\text{fast}} (C_6H_5)_2C{=}O + MnO_4^= + H^+ \quad (5b)$$

$$(C_6H_5)_2CHO^- + MnO_4^- \xrightarrow{\text{slow}} (C_6H_5)_2C{=}O + HMnO_4^= \quad (6a)$$

$$HMnO_4^= + MnO_4^- \xrightarrow{\text{fast}} 2MnO_4^= + H^+ \quad (6b)$$



$$(C_6H_5)_2CHO^- + MnO_4^- \xrightarrow{\text{slow}} (C_6H_5)_2C\begin{smallmatrix}OH\\O^-\end{smallmatrix} + MnO_3^- \quad (7a)$$



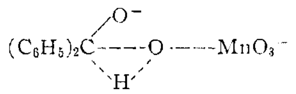
$$(C_6H_5)_2C\begin{smallmatrix}OH\\O^-\end{smallmatrix} \overset{\text{fast}}{\rightleftharpoons} (C_6H_5)_2C\begin{smallmatrix}O^-\\OH\end{smallmatrix} \overset{\text{fast}}{\rightleftharpoons} (C_6H_5)_2C{=}O + OH^- \quad (7b)$$

$$MnO_4^- + MnO_3^- + 2OH^- \xrightarrow{\text{fast}} 2MnO_4^= + H_2O \quad (7c)$$

In eq. 5 the permanganate is acting as an electron abstractor, a role which it plays in the rapid manganate–permanganate exchange reaction.[16] Symons has suggested, with reference to permanganate oxidations, that direct electron exchange between negative oxy-ions may be facilitated by their size and ease of polarization.[17] This mechanism was shown to be incorrect by establishing the fact there is an isotope effect when the hydrogen on the α-carbon atom is replaced by deuterium. The ratio, k_H/k_D, the ratio of the slopes of the lines in Fig. 2, is 6.6:1 showing clearly that the rate controlling step involves the scission of the carbon–hydrogen bond.[18]

Reaction 6a is simply a transfer of hydride ion from benzhydrylate ion to permanganate producing Mn(V).[19] A species of this valence is believed to be the intermediate in the benzaldehyde–permanganate reaction,[1] and it has recently been shown that hypomanganate ion, Mn(V), is very rapidly oxidized by permanganate in basic solution.[20] Further, the kinetics of the homogeneous reaction between permanganate and molecular hydrogen have been interpreted in terms of a two electron or hydride transfer to permanganate to form Mn(V).[21]

A possible route involving the same over-all valence changes and also requiring an isotope effect is shown in reactions 7a-c. In this mechanism the carbon–hydrogen bond is broken by the two atoms simultaneously bonding to an oxygen atom donated by the permanganate.



This mechanism warrants consideration since the oxidation of formate ion which resembles the reac-

---

[14] The Arrhenius activation energy reported by L. M. Hill and F. C. Tompkins, *Trans. Roy. Soc. S. Africa*, **30**, 59 (1943), for the permanganate–formate reaction is 11.8 kcal. mole^{-1}. The value of $\Delta S^\ddagger$ which corresponds to this value is −22.7 e.u.

[15] A reaction such as the following involving hydroxyl radicals would require the rate to decrease with time because of the accumulation of manganate in the system.

$$MnO_4^- + OH^- \rightleftharpoons MnO_4^= + \cdot OH$$
$$(C_6H_5)_2CHOH + \cdot OH \longrightarrow (C_6H_5)_2\dot{C}OH + H_2O$$
$$(C_6H_5)_2\dot{C}OH + MnO_4^- \longrightarrow \text{products}$$

If the hydroxyl radicals were involved in a chain reaction or if the first step above was irreversible, one would not expect the kinetics to be first order in each of benzhydrol, permanganate and hydroxyl ion as was observed here.

[16] J. C. Sheppard and A. C. Wahl, This Journal, **75**, 5133 (1953).

[17] M. C. R. Symons, *J. Chem. Soc.*, 3956 (1953).

[18] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[19] An equivalent reaction can be written in which the benzhydrylate ion gives up two electrons to MnO_4^- to produce $MnO_4^≡$ and simultaneously gives up a proton to a water molecule present in the solvation sphere. Since $MnO_4^≡$ is probably a fairly basic species, it does not seem unreasonable to picture the electron pair plus proton being transferred simultaneously to the same site, *i.e.*, a hydride ion transfer.

[20] J. S. F. Pode and W. A. Waters, *J. Chem. Soc.*, 717 (1956).

[21] A. H. Webster and J. Halpern, *Trans. Faraday Soc.*, in press (private communication).

tion studied here in many respects[22] may occur partly by just such a process since it has been shown that a considerable fraction of the oxygen found in the product, carbonate, is derived from the permanganate. In addition, the reaction of carbene, CH_2, with carbon–hydrogen bonds is believed to go through a similar transition state since the methylene group is found to be inserted between the previously bonded carbon and hydrogen atoms.[23]

To determine whether the hydride transfer *to* permanganate or the oxygen transfer *from* permanganate is occurring, benzhydrol was oxidized with $KMnO_4{}^{18}$ under conditions resembling as closely as possible those for the kinetic experiments. It was anticipated that the product, benzophenone, would exchange oxygen with the water in basic solution since ketones are known to do this,[24] but it was hoped that complete equilibration would not take place in the short reaction times used. The results of the oxidation of both benzhydrol with $KMnO_4{}^{18}$ and benzhydrol-O^{18} with $KMnO_4$ are shown in Table II.

TABLE II

OXYGEN-18 ANALYSIS OF BENZOPHENONE AND BENZHYDROL[a]

Sample	Source	Atom % O^{18} in CO_2 from sample[b]	Atom % O^{18} in excess in sample[b]
Tank CO_2		0.204	. . .
$(C_6H_5)_2C{=}O$	$(C_6H_5)_2CHOH$ +	.200	. . .
	$KMnO_4{}^{18}$	.206	. . .
		.205	. . .
$(C_6H_5)_2CHOH$	$(C_6H_5)_2CHCl$ +	.558	0.708
	H_2O^{18}	.557	.706
		.557	.706
$(C_6H_5)_2C{=}O$	$(C_6H_5)_2CHO^{18}H$ +	.249	.090
	$KMnO_4$	.254	.100
$(C_6H_5)_2CHOH$[c]	$(C_6H_5)_2CHO^{18}H$ +	.552	.696
	$KMnO_4$	.552	.696

[a] See Acknowledgment. [b] CO from sample was oxidized to CO_2 and the O^{18} content determined mass-spectrometrically. If $y = \%O^{18}$ in CO_2, the atom $\%O^{18}$ in excess in the sample $= 2(y - 0.204)$. [c] Recovered after the reaction.

It is apparent that none of the permanganate oxygen appears in the product when $KMnO_4{}^{18}$ is used as the oxidant. It is also apparent that considerable exchange has occurred between the product and water, since the excess O^{18} content of the benzophenone obtained by the oxidation of benzhydrol -O^{18} is reduced to one-seventh of its initial value. That the exchange occurs after the oxidation is shown by the fact that the benzhydrol recovered after partial reaction shows no loss of O^{18}. Since there is still a quite definite concentration of O^{18} in excess in the benzophenone formed when benzhydrol-O^{18} is oxidized and since there is no excess at all when $KMnO_4{}^{18}$ is used, one can conclude that the reaction probably does not involve oxygen transfer.[25] This conclusion is warranted only because of the high precision of the O^{18} analytical data. Thus, the route shown in reactions 6a and 6b is the probable mechanism for the base-catalyzed permanganate oxidation of benzhydrol and may, indeed, be the general course of permanganate–alcohol reactions in basic media.

Acknowledgments.—The author is grateful to Drs. K. B. Wiberg and J. Halpern for helpful discussions and to Mr. Klaus Saegebarth of the University of Washington for the O^{18} analytical data which appear in Table II. Certain of the experimental results reported herein were obtained by the author in the Chemistry Laboratories of the Canadian Services College, Royal Roads, B. C.

VANCOUVER 8, CANADA

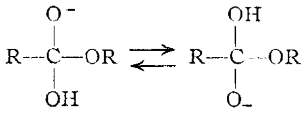
---

[22] The permanganate oxidations of benzhydrol and formate ion resemble one another in the following respects: the size of the isotope effect, the sign and magnitude of the entropy of activation, the fact that the reaction in each case involves an anion, benzhydrylate ion and formate ion. In addition, the reaction of manganate with both formate ion and benzhydrol is slow.

[23] P. S. Skell and R. C. Woodworth, THIS JOURNAL, **78**, 4496 (1956).

[24] M. Cole, *Chem. Revs.*, **51**, 286 (1952).

[25] Two other factors should be mentioned which might conceivably account for the absence of an excess of O^{18} in the benzophenone even though the mechanism shown in eq. 7a be correct. First, although permanganate by itself exchanges oxygen only slowly with water in neutral and basic solution, the exchange is more rapid in the presence of manganate (M. C. R. Symons, *J. Chem. Soc.*, 3676 (1954).) Since a onefold excess of permanganate was used in the tracer experiments and since the reaction time was short, this effect is not believed to be serious. Second, if the reaction shown on the left in eq. 7c is not a rapid equilibrium, the hydroxyl ion lost would be the one containing the excess of O^{18}. Since the equilibrium involves proton addition to an oxygen anion, it is believed that this would be a much faster reaction than the splitting of the oxygen–carbon bond to produce the products. An analogous situation exists for the case of ester hydrolysis where Bender has shown that rapid equilibration of the following type takes place



$$R{-}\overset{\displaystyle O^-}{\underset{\displaystyle OH}{C}}{-}OR \rightleftharpoons R{-}\overset{\displaystyle OH}{\underset{\displaystyle O^-}{C}}{-}OR$$

before the OR group is eliminated (M. L. Bender, THIS JOURNAL, **73**, 1626 (1951)).