NOTES

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Kinetics of the Oxidation of Benzyl Alcohol by Acid Permanganate

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The observed kinetic isotope effect[1] in the oxidation of cyclohexanol by acid permanganate has indicated that probably oxidation involves a hydride ion transfer from alcohol to the oxidant. Recently Barter and Littler[2] suggested that oxidation of alcohols and ethers involves transfer of a hydride ion from the carbon atom carrying the functional group to the oxidant. Littler[1] indicated permanganic acid as the important oxidising species, however, Banerjee and SenGupta[3] have postulated manganese(III) as the active species in the acid permanganate oxidation of methanol and ethanol. No information is available on the acid permanganate oxidation of benzyl alcohol except a preliminary work reported by Cullis and Ladbury.[4] It was, therefore, considered fruitful to investigate the kinetics of the oxidation of benzyl alcohol by acid permanganate.

Experimental

Materials. Perchloric acid (60% E. Merck) was used as a source of hydrogen ions; sodium perchlorate (Reidel) was used to adjust ionic strength; permanganate solutions were prepared by dissolving 'AnalaR' potassium permanganate and acetic acid (99.5% B.D.H.) was used for preparing the solvent mixture. Benzyl alcohol (B.D.H.) was purified by fractionation. All other chemicals used were chemically pure.

Kinetic Measurement. The reactions were studied at constant temperature (±0.02°C). Unless otherwise stated, the solvent was 20% acetic acid. The concentration of benzyl alcohol was kept in excess to that of $KMnO_4$. Reaction mixtures containing requisite amounts of perchloric acid, acetic acid and benzyl alcohol were placed in thermostat for sufficient time. Reactions were started by adding permanganate solution rapidly through a pipette. Aliquots were withdrawn at known intervals of time and concentration of permanganate was estimated iodometrically.

Results

Product Study. Oxidation of benzyl alcohol by acid permanganate gives benzaldehyde as the main product. The amount of benzaldehyde formed was estimated by gravimetric method as 2,4-dinitrophenylhydrazone.[5] The recovery of benzaldehyde is about 85% based on the following reaction:

$$2MnO_4^- + 5C_6H_5CH_2OH + 6H^+ \rightarrow$$
$$2Mn^{2+} + 5C_6H_5CHO + 8H_2O$$

This shows that the further oxidation of benzaldehyde is not significant under the conditions

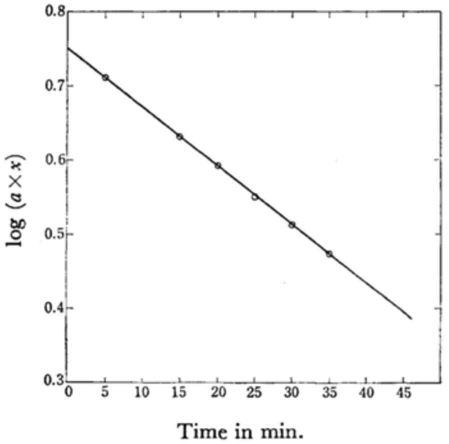

Fig. 1. Typical run.
[$PhCH_2OH$]: 2.0×10^{-3}M, [MnO_4^-]: 4.0×10^{-4}M, [H^+]: 0.61M, Temp. : 35°C, K_1 : 18.4×10^{-3}min^{-1}

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1) J. S. Littler, *J. Chem. Soc.*, **1962**, 2190.

2) R. N. Barter and J. S. Littler, *J. Chem. Soc.*, (*B*), **1967**, 205.

3) J. Banerjee and K. K. SenGupta, *Curr. Sci.* (*India*), **34**, 14 (1965).

4) C. F. Cullis and J. W. Ladbury, *J. Chem. Soc.*, **1955**, 555.

5) J. Mitchell, Jr., "Organic Analysis," Vol. I Interscience Publishers, Inc., New York (1953), p. 279.

of the reaction.

Rate Laws. When benzyl alcohol and hydrogen ions are in excess the rate at which permanganate disappears follows the first order rate law. A typical kinetic run is illustrated in Fig. 1. In all cases the values of first order constants were determined graphically, for first 30—40 percent of the reaction.

Further the value of first order rate constant does not vary with the initial concentration of permanganate (Table 1).

TABLE 1. VARIATION OF RATE WITH CONCENTRATION OF MANGANESE(VII)

[$PhCH_2OH$]: 2.0×10^{-3}M; [H^+]: 0.61M; Temp. 35°C

$[MnO_4^-]\times10^4$ mol l^{-1}	4.0	6.0	8.0	10.0	12.0
$k_1\times10^3$ min^{-1}	18.4	18.4	18.6	17.3	18.0

Thus the order with respect to manganese (VII) is one.

The reaction is also of first order with respect to benzyl alcohol (Table 2).

TABLE 2. VARIATION OF RATE WITH CONCENTRATION OF *BENZYL ALCOHOL*

[MnO_4^-]: 4.0×10^{-4}M; [H^+]: 0.61M; Temp. 35°C.

$[PhCH_2OH]\times10^3$ mol l^{-1}	1.0	2.0	3.0	4.0	5.0
$k_1\times10^3$ min^{-1}	9.1	18.4	27.7	36.8	46.1
$k_1/[PhCH_2OH]$	9.1	9.2	9.2	9.2	9.2

Under the conditions of constant ionic strength the rate varies linearly with concentration of hydrogen ions (Table 3).

TABLE 3. VARIATION OF RATE WITH CONCENTRATION OF HYDROGEN IONS

[MnO_4^-]: 4×10^{-4}M; [$PhCH_2OH$]: 1×10^{-3}M;
Temp. 35°C. Ionic strength (μ): 1.92M

[H^+] mol l^{-1}	0.48	0.72	0.96	1.44	1.68	1.92
$k_1\times10^3$ min^{-1}	10.0	13.8	17.5	26.5	30.9	26.8
$10^2\,k_1/[H^+]$	2.08	1.92	1.82	1.84	1.84	1.92

This indicates that increase in acidity brings about an increase in the rate of the oxidation. This may well be due to protonation of permanganate anion to give permanganic acid, a more powerful oxidant.

$$H^+ + MnO_4^- \rightleftarrows HMnO_4$$

This accords well with the suggestion of Littler[1] that acid catalysed path in the oxidation of cyclohexanol by permanganate involves a protonation in the pre-equilibrium. Stewart and Mocek also observed such an effect in the acid permanganate oxidation of formic acid.[6]

Effect of Manganese(II). Addition of manganous sulphate does not appreciably affect the rate of the oxidation (Table 4).

TABLE 4. EFFECT OF MANGANESE(II) ON THE RATE OF OXIDATION

[MnO_4^-]: 4×10^{-4}M; [$PhCH_2OH$]: 1×10^{-3}; [H^+]: 1.23M; Temp. 35°C

$[Mn(II)]\times10^4$ mol l^{-1}	0.0	4.0	8.0	10.0	12.0
$k_1\times10^3$ min^{-1}	21.0	23.0	22.2	22.7	23.0

These results are contrary to that observed by Banerjee and SenGupta[3] in the acid permanganate oxidation of methanol and ethanol. They observed that the rate of oxidation is decreased by addition of manganese(II). The fact that the rate of the oxidation is unaffected by manganese(II) indicates that intermediate valency states of manganese are not important in this reaction.

Effect of Fluoride Ions. Addition of sodium fluoride also does not cause any change in the first order rate constant.

This also supports the view that intermediate valency states of manganese are not important in this oxidation, as fluoride ions are known to suppress the oxidation by manganese(III) and manganese(IV) by complexation.

Effect of Temperature. Data on the effect of temperature on the rate of oxidation are summarized in Table 5.

TABLE 5. VARIATION OF RATE WITH TEMPERATURE

[$PhCH_2OH$]: 2.0×10^{-3}M; [MnO_4^-]: 4.0×10^{-4}M; [H^+]: 0.61M

Temp. °K	$k_1\times10^2$ min^{-1}	$k\times10^2$ l^2 m^{-2} sec^{-1}	$\Delta S^{\neq}$
303	1.38	18.9	−27.2 e.u.
308	1.84	25.1	
313	2.46	33.6	$\Delta H^{\neq}$
318	3.24	44.3	10.8 kcal mol^{-1}

It is found that a plot of log k against inverse of temperature is straight line. Arrhenius equation is therefore, valid for this reaction. The specific rate constant, k defined as

$$k = \frac{k_1\ (\text{min}^{-1})}{60\cdot[PhCH_2OH][H^+]}$$

Discussion

Absence of any effect of manganese(II) and

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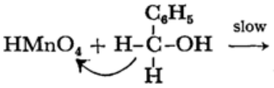
[6] R. Stewart and M. M. Mocek, "Oxidation in Organic Chemistry," ed. by K. B. Wiberg, Academic Press, New York (1965), p. 56.

of fluoride ions on the rate of oxidation suggests that benzyl alcohol is mainly oxidzed by manganese-(VII). The linear increase in the rate of oxidation with increase in acidity accords well with the suggestion that probably permanganic acid is the active species.

$$H^+ + MnO_4^- \rightleftarrows HMnO_4$$

The entropy of activation and heat of activation data suggest that a C–H bond is ruptured in the rate-determining step (*cf.* Bakore and Narain[7,8]). The hydrogen may be removed by the oxidant either as a hydrogen atom or a hydride ion. It has been pointed out that known cases of hydride-ion transfer reactions seems to have a low isotope effect.[9] The value of 2.42 for the kinetic isotope effect in the oxidation of cyclohexanol by acid permanganate, observed by Littler,[1] suggests hydride transfer in the oxidation. This is, however, not conclusive and permanganate is known to function as a one-electron oxidant also, abstracting a hydrogen atom. Recently Barter and Littler[2] have shown that acid permanganate oxidation of alcohols involve a two-electron mechanism, with transfer of a hydride-ion from the carbon atom bearing the functional group to the oxidant. The values of heat of activation and entropy of activation for the oxidation of benzyl alcohol are of the same order as those of methanol and ethanol. This indicates that probably same mechanism operates in these oxidations.

If one accepts the hydride-transfer mechanism, the oxidation of benzyl alcohol by acid permanganate may be visualized as



$$HMnO_4 + H\!-\!\underset{\displaystyle H}{\overset{\displaystyle C_6H_5}{C}}\!-\!OH \xrightarrow{\text{slow}}$$

$$\underset{(Mn(V))}{H_2MnO_4^-} + C_6H_5\overset{+}{C}HOH$$

$$C_6H_5\overset{+}{C}HOH \xrightarrow{\text{fast}} C_6H_5CHO + H^+$$

$$5Mn(V) \xrightarrow{\text{fast}} 2Mn(II) + 3Mn(VII)$$

The existance of manganese(V) as a reaction intermediate is well established.

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[7] G. V. Bakore and S. Narain, *J. Chem. Soc.*, **1963**, 3419.

[8] G. V. Bakore and S. Narain, *Z. Physik. Chem.*, **227**, 8 (1964).

[9] C. G. Swain, R. F. W. Bader, R. M. Esteve, Jr., and R. N. Griffin, *J. Am. Chem. Soc.*, **83**, 1951 (1961).