Kinetics and Mechanism of the Oxidation of Benzyl Alcohol to Benzaldehyde by Acid Permanganate

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The kinetics of the oxidation of benzyl alcohol to benzaldehyde by acid permanganate in the presence of fluoride ions have been studied. The reaction constant ρ for the oxidation of benzyl alcohol and nine substituted benzyl alcohols has a value of $-1{\cdot}76 \pm 0{\cdot}05$ at 30 °C. The activation enthalpies and entropies for the ten compounds are linearly related. The oxidation of αα-dideuteriobenzyl alcohol indicated a kinetic isotope effect; $k_H/k_D = 2{\cdot}70$ at 30 °C. The reaction does not show any solvent isotope effect. A mechanism involving transfer of a hydride ion from the alcohol carbon to the oxidant is suggested.

BARTER and LITTLER [1] have suggested that oxidation of alcohols by bromine and by acid permanganate follows a similar mechanistic pathway. The oxidation of alcohols by bromine is shown to involve removal of a hydride ion in the rate-determining step.[2] Stewart [3] has, however, maintained that there is nothing to distinguish between hydride ion and hydrogen transfer in the permanganate oxidation of alcohols under base conditions.

If a hydride ion is removed in the rate-determining step, then an unequivocal demonstration of the electron flow leading to the transition state can be obtained by studying the effect of polar substituents upon the oxidation rate of a suitable alcohol.

This communication reports the oxidation of monosubstituted benzyl alcohols by acid permanganate and evaluates the reaction constant. Some kinetic data on the oxidation of benzyl alcohol only were reported earlier.[4]

RESULTS

The oxidations of all the alcohols are autocatalytic. Such a phenomenon is well known in permanganate oxidations and is attributed to the reactions of Mn^{III} and/or Mn^{IV}.[3] To suppress these reactions, the oxidations were carried out in the presence of a large excess of sodium fluoride (*ca.* 0·02M). The addition of fluoride ions does not affect the initial rate,[4] but it suppresses the autocatalysis and good first-order plots were obtained for at least two half-lives.

In 1 : 4 (v/v) acetic acid–water, benzyl alcohol (0·02M) reacts with potassium permanganate (0·002M), in the presence of perchloric acid (1·0M), and sodium fluoride (0·02M), to give benzaldehyde which is isolable in 90% yield. The rate constant for the oxidation under these conditions, at 30 °C, is 0·19 $l^2\ mol^{-2}\ s^{-1}$, whereas the rate constant for the oxidation of benzaldehyde, under similar conditions is 0·16 $l^2\ mol^{-2}\ s^{-1}$. Although the rate of the oxidation of benzaldehyde is of the same order as that of benzyl alcohol, the kinetic importance of this may be reduced to an acceptable level by using a concentration of alcohol many times that of permanganate.

As has been shown earlier [4] the oxidation is of the first order with respect to the oxidant, the alcohol, and hydrogen ion in the presence of fluoride ions.

The rate constants for the oxidations of benzyl alcohol and αα-dideuteriobenzyl alcohol in 20% acetic acid (v/v) solution, at 30 °C are $10^2k = 18{\cdot}9$ and 7·0 $l^2\ mol^{-2}\ s^{-1}$, respectively. The kinetic isotope effect, $k_H/k_D = 2{\cdot}70$.

Benzyl alcohol (*ca.* 0·01M) was oxidised in 95% deuterium oxide, and rate constant obtained was 0·179 $l^2\ mol^{-2}\ s^{-1}$, at 30 °C. The rate constant, under similar conditions in ordinary water is 0·188 $l^2\ mol^{-2}\ s^{-1}$. The solvent isotope effect, $k(H_2O)/k(D_2O) = 1{\cdot}05$, does not differ significantly from unity. In this set of experiments, no acetic acid was present in solution.

The oxidation of benzyl alcohol under nitrogen failed to induce polymerisation of acrylonitrile. Thus a hydrogen abstraction mechanism giving rise to free radicals is unlikely. In control experiments, with the alcohol absent, the concentration of permanganate does not show any change during the period in which it is reduced to one-fourth in the presence of benzyl alcohol.

The rate constants for the oxidation of nine monosubstituted benzyl alcohols were determined at different temperatures and activation parameters were evaluated (Tables 1 and 2).

The rate of the oxidation of benzyl alcohol is not affected by changing the proportion of acetic acid in the solvent

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[1] R. M. Barter and J. S. Littler, *J. Chem. Soc.* (*B*), 1967, 205.

[2] P. Aukett and I. R. L. Barker, *J.C.S. Perkin II*, 1972, 568.

[3] R. Stewart in 'Oxidation in Organic Chemistry, Part A,' ed. K. B. Wiberg, Academic Press, New York, 1965, p. 30.

[4] K. K. Banerji and P. Nath, *Bull. Chem. Soc. Japan*, 1969, **42**, 2038.

from 0 to 80% (v/v). This is rather puzzling and no satisfactory explanation is available at present.

TABLE 1

Rate constants for the oxidation of substituted benzyl alcohols (0·01—0·03M) by permanganate (*ca.* 0·001M), in 20% acetic acid (v/v) solution in the presence of fluoride ions (0·02M) and perchloric acid (0·5—1·0M)

	10^3k/l^2 mol^{-2} s^{-1}			
Substituents	30 °C	35 °C	40 °C	45 °C
H	189	251	336	443
m-Me	250	330	437	575
p-Et	340	445	575	740
p-Me	363	495	616	760
p-OMe	603	775	980	1260
p-Cl	70·8	99·0	138	193
m-Br	37·2	53·5	76·0	106
p-CN	13·2	19·5	29·0	42·5
m-NO_2	10·0	15·0	22·1	32·4
p-NO_2	7·9	11·9	17·8	26·5

TABLE 2

Activation parameters for the oxidation of benzyl alcohols

Substituents	H	*m*-Me	*p*-Et	*p*-Me	*p*-OMe
$\Delta H^\ddagger$/kcal mol^{-1} [a]	10·8	10·5	10·0	9·9	9·2
$-\Delta S^\ddagger$/cal mol^{-1} K^{-1} [b]	27·2	27·7	2·84	28·6	30·0
Substituents	*p*-Cl	*m*-Br	*p*-CN	*m*-NO_2	*p*-NO_2
$\Delta H^\ddagger$/kcal mol^{-1} [a]	12·6	13·5	14·8	15·0	15·3
$-\Delta S^\ddagger$/cal mol^{-1} K^{-1} [b]	23·0	21·6	19·1	18·8	18·5

[a] ±0·5 kcal mol^{-1}. [b] ±1·5 cal mol^{-1} K^{-1}.

DISCUSSION

The kinetic isotope effect, $k_H/k_D = 2{\cdot}70$, is very close to the value obtained by Littler in the oxidation of cyclohexanol.[5] Aukett and Barker [2] recently reported a kinetic isotope effect of 4·1 for the oxidation of benzyl alcohol by bromine. The mechanistic conclusion is that the rate-determining step involves a C–H bond cleavage from the alcohol carbon.

The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are linearly related ($r = 0{\cdot}983$). The correlation was tested and found genuine by applying Exner's criterion.[6] The isokinetic temperature obtained from the slope of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ plot is 490 K. Current views do not attach much physical meaning to the isokinetic temperature,[7] though a linear correlation is usually a necessary condition for the validity of the Hammett equation.

No systematic study of the effect of substituents on the oxidation of alcohols by acid permanganate has been reported, though some studies are available for base conditions.[3] Limited studies with aliphatic alcohols by Barter and Littler,[1] in 1M-sulphuric acid, indicated that methanol reacts *ca.* 12 times slower than ethanol and propan-2-ol reacts *ca.* 1·5 times faster than ethanol in aqueous solution. No reaction constant could be evaluated with these limited data, though they show that introduction of electron-donating groups increases the rate. The rates of the oxidation of monosubstituted benzyl alcohols are well correlated ($r = 0{\cdot}996$) by a Hammett plot with a reaction constant $\rho = -1{\cdot}76 \pm 0{\cdot}05$ at 30 °C. The negative value of ρ points to an electron-deficient carbon centre in the transition state. The magnitude of the reaction constant decreases with temperature, as expected (Table 3).

TABLE 3

Temperature dependence of the reaction constant for the oxidation of benzyl alcohols with acid permanganate

Temp. (°C)	30	35	40	45
$-\rho$	1·76 ± 0·05	1·68 ± 0·05	1·62 ± 0·04	1·51 ± 0·1

Wiberg and Stewart [8] interpreted a reaction constant of −1·8, observed in the permanganate oxidation of aromatic aldehydes under base conditions, in terms of a permanganate ester formation followed by the loss of a proton. However, ester formation is unlikely in acid solutions in view of the equal ease of the oxidation of alcohols and ethers.[1] The simplest explanation seems to be a rate-determining loss of a hydride ion from the alcohol carbon. Permanganate ester formation is not likely to be susceptible to any considerable structural influence as in other alcohol–inorganic acid esterification.[9,10] The large negative reaction constant can thus arise only from the differential effects of the substituents in the rate-determining step. There is no evidence that the removal of the hydroxylic proton is synchronous with the hydride transfer and is unlikely in view of the absence of a solvent isotope effect and the magnitude of the reaction constant. The polar requirement, on the alcohol carbon, for hydride release from C–H is opposite to that for proton release from O–H and in a fully concerted process the reaction constant is likely to be nearer zero.

It is of interest to compare the reaction constant $\rho = -2{\cdot}3$ obtained for the oxidation of substituted benzyl alcohols by bromine [2] which also involves removal of a hydride ion in the rate-determining step. On the other hand, in the reduction of 2- and 4-substituted fluorenones by sodium borohydride, which probably involves rate-determining addition of a hydride ion, the reported values of the reaction constants ρ are +2·95 and +2·56 respectively.[11,12]

EXPERIMENTAL

Materials. Halogeno-, alkyl-, *p*-methoxy-, and *m*-nitrobenzyl alcohols were prepared by the reduction of the corresponding benzaldehydes with sodium borohydride.[13] Benzyl and *p*-nitrobenzyl alcohols were commercial pro-

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[6] O. Exner, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1094.

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[9] N. C. Deno and M. S. Newman, *J. Amer. Chem. Soc.*, 1950, **72**, 3852.

[10] U. Klanning and M. C. R. Symons, *J. Chem. Soc.*, 1961, 3204, and references therein.

[11] J. A. Parry and K. D. Warren, *J. Chem. Soc.*, 1965, 4049.

[12] K. D. Warren and J. R. Yandle, *J. Chem. Soc.*, 1965, 5518.

[13] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1962.

ducts. The alcohols were purified by repeated crystallization or by distillation under reduced pressure.

αα-Dideuteriobenzyl alcohol was prepared by the reduction of ethyl benzoate with lithium aluminium deuteride.[14] The isotopic purity was ascertained from its n.m.r. spectrum.

Perchloric acid was used as a source of hydrogen ions. All reagents were of analytical grade.

Kinetic Measurements.—The reactions were carried out at a constant temperature (±0·1 °C) and were followed by determining the permanganate concentration spectrophotometrically at 532 nm at suitable intervals. The rate constants were evaluated from the plots of log[oxidant] against time. All runs were arranged to be under pseudo-first-order conditions by keeping a large excess (× 10 or greater) of the alcohol over permanganate. The rate constants reported are mean values of duplicate runs and are reproducible within ±4%. The usual initial concentrations of the reactants were alcohol 0·01—0·03M, potassium permanganate *ca.* 0·001M, perchloric acid 0·4—1·0M, and sodium fluoride 0·02M. The solvent was always 20% acetic acid–80% water (v/v) unless mentioned otherwise.

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