Kinetics and Mechanism of Oxidation of Primary Alcohols by Pyridinium Hydrobromide Perbromide

Dipti Mathur, Pradeep K. Sharma and Kalyan K. Banerji *
Department of Chemistry, J.N.V. University, Jodhpur 342 005, India

Oxidation of nine primary aliphatic alcohols by pyridinium hydrobromide perbromide (PHPB) in aqueous acetic acid leads to the formation of the corresponding aldehydes. The reaction is first order with respect to PHPB. Michaelis–Menten-type kinetics are observed with respect to the alcohol. The oxidation of [1,1-$^2H_2$]ethanol ($MeCD_2OH$) exhibits a substantial kinetic isotopic effect. The effect of solvent composition indicates that the transition state is more polar than the reactants. The reaction is susceptible to both polar and steric effects of the substituents. A mechanism involving transfer of a hydride ion from the alcohol to the oxidant has been proposed.

Pyridinium hydrobromide perbromide (PHPB) has been extensively used in synthetic organic chemistry as a brominating reagent and as an oxidant.[1,2] There are not many reports on the mechanistic aspects of reactions of PHPB.[3,4] Gnanadoss and Vijayalaxmi[4] reported the kinetics of the oxidation of some primary aliphatic alcohols and attempted a correlation of reactivity with Charton's steric parameter, V.[5] However, they did not determine the order of reaction with respect to the alcohol and, in its absence, the correlation analysis is of doubtful significance. We have been interested in the study of kinetics and mechanism of oxidations by oxidants containing halogens. In this article, we report the kinetics of oxidation of nine aliphatic primary alcohols in aqueous acetic acid. Attempts have been made to correlate structure and reactivity in the reaction. Mechanistic aspects are discussed.

Table 1 Rate constants for the oxidation of ethanol by PHPB at 303 K

[PHPB]/10^{-3} mol dm^{-3}	[EtOH]/mol dm^{-3}	$k_{obs}/10^{-5}$ s^{-1}
1.0	0.01	2.15
1.0	0.03	5.85
1.0	0.05	8.84
1.0	0.08	12.6
1.0	0.13	17.0
1.0	0.16	19.2
1.0	0.20	21.7
1.0	0.25	23.5
1.0	0.30	25.6
2.0	0.20	20.9
4.0	0.20	21.6
6.0	0.20	22.1
8.0	0.20	21.9

Experimental

Materials.—All the alcohols were commercial products. Methanol, ethanol, and propan-1-ol were purified by the magnesium alkoxide method.[6] 2-Methoxyethanol and 2-chloroethanol were dried over anhydrous magnesium sulfate and then fractionated. Other alcohols were dried over anhydrous potassium carbonate and fractionated. PHPB was prepared by the reported method[7] and its purity checked by an iodometric method. [1,1-$^2H_2$]Ethanol was prepared by Kaplan's method.[8] Its isotopic purity, as ascertained by its NMR spectra, was 92 ± 5%. Acetic acid was refluxed with chromic oxide and acetic anhydride for 3 h and then fractionated. All other reagents were commercial products and were purified by the usual methods.[9]

Product Analysis.—The product analysis was carried out under kinetic conditions. In a typical experiment, ethanol (2.30 g, 0.05 mol) and PHPB (3.20 g, 0.01 mol) were made up to 50 cm^3 in 1 : 1 (v/v) acetic acid–water and kept in the dark for *ca.* 10 h to ensure completion of the reaction. The solution was then treated with an excess (200 cm^3) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The yields of DNP before and after recrystallization were 1.97 g (88%) and 1.62 g (72%) respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of acetaldehyde. Similar experiments were performed with other alcohols.

Kinetic Measurements.—Reactions were carried out under pseudo-first-order conditions by keeping an excess (× 15 or greater) of the alcohol over PHPB. The solvent was 1 : 1 (v/v) acetic acid–water, unless otherwise stated. All reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions. The reactions were followed up to *ca.* 80% reaction, by monitoring the decrease in [PHPB] at 358 nm. The pseudo-first-order rate constant, k_{obs}, was computed from the linear least-squares plot of log [PHPB] *versus* time. Duplicate runs showed that the rate constants were reproducible to within ±3%.

Results

The rate and other experimental data were obtained for all the alcohols. Since the results are similar, only representative data are reproduced here.

The oxidation of alcohols results in the formation of the corresponding aldehydes. The overall reaction may be represented as eqn. (1).

$$RCH_2OH + PyH^+Br_3^- \longrightarrow RCHO + 2\,HBr + PyH^+Br^- \quad (1)$$

Rate Laws.—The reactions are of first order with respect to PHPB. Further, the values of k_{obs} are independent of the initial concentration of PHPB. The reaction rate increases with an increase in the concentration of the alcohol but not linearly (Table 1). A plot (Fig. 1) of $1/k_{obs}$ against 1/[alcohol] is linear (r^2 0.9997) with an intercept on the rate ordinate. Thus Michaelis–Menten type kinetics are observed with respect to the alcohols. This leads to the postulation of the following

Table 2 Formation constants of the PHPB–RCH_2OH complexes and thermodynamic parameters

	K/dm^3 mol^{-1}						
Subst. (R)	293 K	303 K	308 K	323 K	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}	ΔG/kJ mol^{-1}
H	7.30	5.10	3.40	2.31	−32.8 ± 0.7	−87 ± 2	−7.0 ± 0.5
Me	8.37	5.55	3.70	2.52	−34.0 ± 0.2	−90 ± 1	−7.2 ± 0.2
Et	9.20	5.63	3.81	2.60	−33.5 ± 0.2	−89 ± 1	−7.3 ± 0.1
Pr	9.20	6.20	4.22	2.85	−33.2 ± 0.4	−87 ± 1	−7.5 ± 0.3
Bu	8.73	6.00	4.12	2.72	−32.9 ± 0.8	−86 ± 2	−7.4 ± 0.6
Pr^i	9.80	6.52	4.63	3.02	−32.9 ± 0.8	−85 ± 2	−7.7 ± 0.6
$ClCH_2$	7.93	5.21	3.47	2.40	−33.9 ± 0.1	−90 ± 1	−7.1 ± 0.1
$MeOCH_2$	10.2	6.75	4.80	3.22	−32.4 ± 0.6	−83 ± 2	−7.7 ± 0.4
Bu^t	9.77	6.60	4.58	3.00	−33.2 ± 0.7	−86 ± 2	−7.6 ± 0.6
$MeCD_2OH$	8.43	5.42	3.70	2.48	−34.4 ± 0.3	−92 ± 1	−7.2 ± 0.2

Table 3 Rate constants for the decomposition of PHPB–RCH_2OH complexes, and activation parameters

	$k_2/10^{-5}$ s^{-1}						
Subst. (R)	293 K	303 K	308 K	323 K	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J mol^{-1} K^{-1}	$\Delta G^‡$/kJ mol^{-1}
H	0.42	1.31	3.27	9.43	78.1 ± 1.5	−82 ± 4	102 ± 1
Me	17.0	40.9	94.2	222	64.6 ± 0.8	−97 ± 3	93.4 ± 0.6
Et	29.7	70.2	164	394	65.1 ± 1.1	−91 ± 4	92.1 ± 0.8
Pr	44.2	94.3	200	462	58.7 ± 1.5	−110 ± 5	91.2 ± 1.2
Bu	59.4	120	265	605	58.4 ± 1.9	−108 ± 6	90.5 ± 1.5
Pr^i	70.5	156	334	721	58.3 ± 0.6	−107 ± 2	90.0 ± 0.5
$ClCH_2$	0.40	1.10	2.80	7.47	73.9 ± 0.9	−97 ± 3	103 ± 1
$MeOCH_2$	3.44	8.82	20.6	50.0	67.3 ± 0.7	−101 ± 2	97.3 ± 0.6
Bu^t	472	803	1580	3030	46.6 ± 1.8	−131 ± 6	85.6 ± 1.4
$MeCD_2OH$	4.71	11.5	26.9	65.3	66.1 ± 1.0	−103 ± 3	96.6 ± 0.8

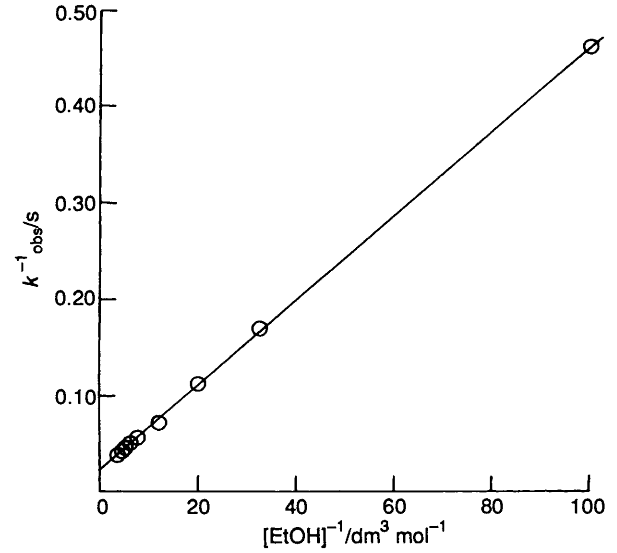


Fig. 1 Michaelis–Menten plot for the oxidation of ethanol by PHPB. The reaction conditions are given in Table 1.

overall mechanism [eqns. (2) and (3)] and rate law [eqn. (4)].

$$\text{Alcohol} + \text{PHPB} \overset{K}{\rightleftharpoons} [\text{complex}] \quad (2)$$

$$\text{Complex} \xrightarrow{k_2} \text{Products} \quad (3)$$

$$\text{Rate} = k_2K[\text{alcohol}][\text{PHPB}]/(1 + K[\text{alcohol}]) \quad (4)$$

The dependence of k_{obs} on the alcohol concentration was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic parameters of the complex formation and activation parameters of the decomposition of the complexes were calculated from the values of K and k_2 respectively at different temperatures (Tables 2 and 3).

Kinetic Isotope Effect.—To ascertain the importance of the cleavage of the α-C–H bond in the rate-determining step, the oxidation of [1,1-$^2H_2$]ethanol was studied. Results, recorded in Tables 2 and 3, showed that the formation constants of the complexes of ordinary and deuteriated ethanol have similar values but the rate of decomposition of the complexes shows a considerable primary kinetic isotope effect ($k_H/k_D = 3.56$ at 303 K). The rate for deuteriated alcohol was corrected for the amount of protio alcohol present.

Solvent Effect.—The rates of oxidation of alcohols were determined in solvents containing different amounts of water and acetic acid. The value of k_{obs} increases as the water content of the solvent increases.

To determine whether the changes in solvent composition are affecting the formation constant, K, and/or the rate of decomposition, k_2, the dependence on alcohol concentration was studied in solvents of different composition. Results showed that the effect of solvent is primarily on the rate constant for decomposition of the complex, k_2. The formation constant, K, is practically independent of solvent composition (Table 4).

Effect of Pyridinium Bromide.—Addition of pyridinium bromide has no effect on the rate of oxidation (Table 5).

Discussion

A linear correlation (r^2 0.9976) between the log k_2 values at 293 K and at 323 K for the nine alcohols indicates that all the alcohols are oxidized by the same mechanism.[10] The value of the isokinetic temperature is 784 ± 21 K.

Table 4 Dependence of k_{obs} on alcohol concentration in solvents of different composition[a]

[EtOH]/ mol dm^{-3}	$k_{obs}/10^{-5}$ s^{-1} [at % AcOH (v/v)]				
	25	40	50	60	72
0.01	6.75	3.11	2.15	1.30	0.71
0.03	18.4	8.46	5.65	3.60	1.86
0.08	39.0	18.3	12.6	7.62	4.10
0.16	60.0	27.5	19.2	11.7	6.22
0.20	66.7	31.0	21.7	13.4	6.88
0.25	73.9	34.4	23.5	14.6	7.64
K/dm^3 mol^{-1}	5.66	5.56	5.55	5.29	6.02
$k_2/10^{-4}$ s^{-1}	12.5	5.91	4.09	2.59	1.25

[a] [PHPB] = 0.001 mol dm^{-3}; T = 303 K.

Table 5 Effect of pyridinium bromide on the oxidation of ethanol[a]

[PyH$^+$Br$^-$]/mol dm^{-3}	$k_{obs}/10^{-4}$ s^{-1}
0.00	4.09
0.01	4.02
0.04	4.21
0.08	4.13
0.12	3.96

[a] [PHPB] = 0.001 mol dm^{-3}; [EtOH] = 0.20 mol dm^{-3}; T = 303 K.

In solution, PHPB may undergo the following reactions [eqns. (5) and (6)].

$$PyH^+Br_3^- \rightleftharpoons Br_2 + PyH^+Br^- \qquad (5)$$

$$PyH^+Br_3^- \rightleftharpoons Br_3^- + PyH^+ \qquad (6)$$

The possible oxidizing species in a solution of PHPB are, therefore, PHPB itself, tribromide ion and molecular bromine. However, strict first-order dependence on PHPB and the absence of any effect of pyridinium bromide rule out both bromine and tribromide ion as the reactive oxidizing species. Hence PHPB itself must be the reactive oxidizing species in this reaction.

The increase in the value of k_2 with an increase in the polarity of the medium suggests that, in the rate-determining step, the transition state is more polar than the reactant. A plot of $\log k_2$ against the inverse of relative permittivity is non-linear. The solvent effect was analysed using the Grunwald–Winstein[11] equation (7).

$$\log k_2 = \log k_0 + mY \qquad (7)$$

The plot of $\log k_2$ against Y was linear (r^2 0.9964) with m = 0.53 ± 0.02. The positive value of m points to a transition state which is more polar than the reactant. Thus considerable charge separation takes place in the transition state of the decomposition of the PHPB–alcohol complex.

A perusal of the data in Table 2 revealed that the formation constants of the alcohol–PHPB complexes are not very sensitive to the nature of the substituent in the alcohol molecule. Similar observations have earlier been recorded in the oxidation of benzyl alcohols[12] and of mandelic acids[13] by ammonium cerium(IV) nitrate and of aliphatic primary alcohols by pyridinium fluorochromate.[14] The rates of decomposition of the complexes (*cf.* Table 3), however, showed considerable variation.

The rates of decomposition of the complexes failed to yield any significant correlations separately with Taft's[15] σ^* and E_s [eqns. (8) and (9)].

Table 6 Temperature dependence of the reaction constants

T/K	ρ^*	δ	r^2	s.d.
293	−1.69 ± 0.04	−0.62 ± 0.02	0.9988	0.04
303	−1.61 ± 0.04	−0.55 ± 0.02	0.9987	0.04
313	−1.56 ± 0.04	−0.52 ± 0.03	0.9981	0.05
323	−1.51 ± 0.04	−0.47 ± 0.03	0.9978	0.05

$$\log k_2 = -2.15\,(\pm 0.33)\,\sigma^* - 3.35$$
$$r^2 = 0.8576;\ \text{s.d.} = 0.42;\ n = 9 \qquad (8)$$

$$\log k_2 = -1.11\,(\pm 0.36)\,E_s - 4.09$$
$$r^2 = 0.7534;\ \text{s.d.} = 0.58;\ n = 9 \qquad (9)$$

The rates were, therefore, correlated in terms of the Pavelich–Taft[16] dual substituent-parameter equation (10).

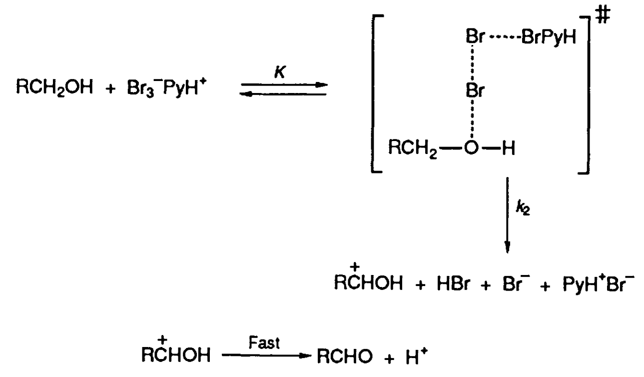
$$\log k = \rho^*\sigma^* + \delta E_s + \log k_0 \qquad (10)$$

The values of the substituents constants were obtained from the compilation by Wiberg.[15] The correlations are excellent; reaction constants being negative (Table 6). There is no significant collinearity (r^2 0.2136) between σ^* and E_s of the nine substituents.

The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step. The negative steric reaction constant shows a steric acceleration of the reaction. This may be explained on the basis of the high ground-state energy of the sterically crowded alcohols. Since the crowding is relieved in the product aldehyde, as well as in the transition state leading to it, the transition state energies of the crowded and uncrowded alcohols do not differ much and steric acceleration, therefore, results.

Mechanism.—The presence of a substantial kinetic isotope effect confirms the cleavage of the α-C–H bond in the rate-determining step.

From the rate law [eqn. (4)], it is apparent that an intermediate complex is formed in a rapid pre-equilibrium (Scheme 1). With the present data, it is not possible to state definitely the nature of the intermediate complex. Formation of a hypobromite ester [eqn. (11)] as an intermediate is unlikely in view of the absence of any effect of pyridinium bromide.



Scheme 1

$$ROH + PyH^+Br_3^- \rightleftharpoons$$
$$R{-}O{-}Br + HBr + PyH^+Br^- \qquad (11)$$

Heasley *et al.*[2] have postulated the formation of an intermediate π-complex in the reaction of alkenes with PHPB. A similar complex may be formed by the interaction between the non-bonded pairs of electrons of the alcohol oxygen and PHPB. The formation of a moderately stable intermediate is supported by the observed values of thermodynamic parameters (*cf.* Table 2). The complex formation is favoured by the enthalpy term but there is a loss of entropy indicating the formation of a rigid structure.

The correlation analysis of the substituent effect indicated the presence of a highly electron-deficient carbon centre in the transition state. Therefore, a hydride ion transfer in the rate-determining step is postulated. A moderate degree of charge separation in the transition state of the rate-determining step is supported by the observed value of m. A non-linear transition state, implied in a hydride-ion transfer *via* an intermediate complex, is supported by the relatively low magnitude of kinetic isotope effect. In the oxidation of ethanol by bromine,[17] the value of the kinetic isotope effect is 4.3.

The observed negative entropy of activation also supports a polar transition state. As the charge separation takes place, the two charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy.

Acknowledgements

Thanks are due to the University Grants Commission (India) for financial assistance.

References

1 C. Djerassi and C. R. Schloz, *J. Am. Chem. Soc.*, 1948, **70**, 417.
2 V. L. Heasley, T. J. Louie, D. K. Luttrull, M. D. Miller, H. B. Moore, D. F. Nogales, A. M. Sauerbrey, A. B. Shevel, T. Y. Shibuya, M. S. Stanley, D. F. Shellhamer and G. E. Heasley, *J. Org. Chem.*, 1988, **53**, 2199.
3 S. Rajan, J. Rajaram and J. C. Kuriacose, *Indian J. Chem.*, 1973, **11**, 1152.
4 L. Gnanadoss and A. Vijayalaxmi, *Indian J. Chem. Sect. B*, 1980, **19**, 725.
5 M. Charton, *J. Am. Chem. Soc.*, 1975, **97**, 1552, 3691.
6 A. I. Vogel, *A Text Book of Practical Organic Chemistry*, Longmans, London, 1967, p. 167.
7 L. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Wiley, New York, 1967, vol. 1, p. 967.
8 L. Kaplan, *J. Am. Chem. Soc.*, 1958, **80**, 2639.
9 D. D. Perrin, W. L. Armarego and D. R. Perrin, *Purification of Organic Compounds*, Pergamon, Oxford, 1980.
10 O. Exner, *Prog. Phys. Org. Chem.*, 1973, **10**, 411.
11 A. H. Falnberg and S. Winstein, *J. Am. Chem. Soc.*, 1956, **78**, 2770.
12 L. B. Young and W. S. Trahanovsky, *J. Am. Chem. Soc.*, 1969, **91**, 5060.
13 K. K. Banerji, *J. Indian Chem. Soc.*, 1975, **52**, 573.
14 K. K. Banerji, *J. Chem. Soc., Perkin Trans. 2*, 1988, 547.
15 K. B. Wiberg, *Physical Organic Chemistry*, Wiley, New York, 1963, p. 416.
16 W. A. Pavelich and R. W. Taft, *J. Am. Chem. Soc.*, 1957, **79**, 4935.
17 K. K. Banerji, *Indian J. Chem.*, 1973, **11**, 244.

Paper 2/04417J
Received 14*th August* 1992
Accepted 15*th October* 1992