

Kinetics and mechanism of the oxidation of diols by pyridinium hydrobromide perbromide

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Abstract. Kinetics of oxidation of five vicinal, four non-vicinal diols, and one of their monoethers by pyridinium hydrobromide perbromide (PHPB) have been studied. The vicinal diols yield products arising out of the glycol bond fission while the other diols yield hydroxycarbonyl compounds. The reaction is first order with respect to PHPB. Michaelis-Menten type kinetics are observed with respect to the diol. There is no effect of added pyridinium bromide on the reaction. The oxidation of [1, 1, 2, 2- $^2\text{H}_4$]ethanediol shows the absence of a primary kinetic isotope effect. The values of solvent isotope effect, $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$, at 313 K, for the oxidation of ethanediol, propane-1, 3-diol and 3-methoxybutan-1-ol are 4.71, 2.17 and 2.23 respectively. A mechanism involving glycol-bond fission has been proposed for the oxidation of the vicinal diols. The other diols are oxidised by a hydride-transfer mechanism as they are monohydric alcohols.

Keywords. Diols; pyridinium hydrobromide perbromide; kinetics; mechanism; oxidation.

1. Introduction

Pyridinium hydrobromide perbromide (PHPB) is a well-known brominating and dehydrogenating agent and its use in synthetic organic chemistry is well documented (Fieser and Fieser 1967; Heasley *et al* 1988). We have been interested in the kinetics and mechanism of the oxidation by PHPB and have reported the oxidation of alcohols (Mathur *et al* 1993), lower oxyacids of phosphorus (Varshney *et al* 1992), and aliphatic aldehydes (Devi *et al* 1993) by PHPB. However, several oxidations of monohydric and polyhydric alcohols are known to follow different mechanistic pathways, e.g. oxidations by lead (IV) (Bunton 1966), periodic acid (Duke 1947), acid permanganate (Bhatia and Banerji 1983) and bromamine-B (Mathur and Banerji 1987). Therefore, we have studied the oxidation of several diols by PHPB in aqueous acetic acid solution. The mechanistic aspects are discussed.

2. Experimental

2.1 Materials

The diols were commercial products and were distilled under reduced pressure before use. [1, 1, 2, 2- $^2\text{H}_4$]ethanediol was prepared by the reduction of diethyl oxalate with

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lithium aluminium deuteride (Kemp and Waters 1963). Its isotopic purity, determined by its NMR spectrum, was $90 \pm 4\%$. PHPB was prepared by the reported method (Fieser and Fieser 1967) and its purity checked by an iodometric method.

2.2 Product analysis

The product analyses were carried under kinetic conditions. In a typical experiment ethanediol (6.2 g, 0.1 mol) and PHPB (6.3 g, 0.02 mol) were dissolved in 100 ml of 1:1 (v/v) acetic acid–water and was kept in the dark for about 12 h to ensure completion of the reaction. The solution was then treated with an excess (200 cm³) of a saturated solution of 2, 4–dinitrophenylhydrazine in 2 mol dm⁻³ HCl and kept in a refrigerator for about 15 h. The precipitated 2, 4–dinitrophenylhydrazone (DNP) was filtered off, weighed, recrystallized from ethanol, and weighed again. The product was identical (m.p. and mixed m.p.) with an authentic sample of the DNP of formaldehyde. The yield of DNP before and after recrystallization was 7.4 g (88%) and 6.8 g (81%). A similar experiment with propane–1, 3–diol yielded DNP of 3–hydroxypropanal in 73% yield after recrystallization.

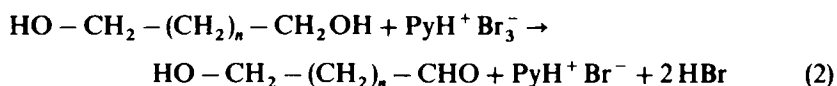
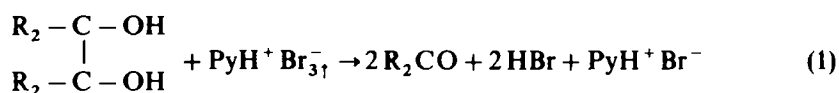
2.3 Kinetic measurements

The pseudo-first-order conditions were attained by keeping an excess ($\times 15$ or greater) of the diol over PHPB. The solvent was 1:1 (v/v) acetic acid–water, unless mentioned otherwise. The reactions were carried out in flasks blackened from the outside to avoid any photochemical reactions and were followed by monitoring the decrease in the [PHPB] at 358 nm for up to 70% reaction. The pseudo-first-order rate constants, k_{obs} , were evaluated from the linear least-squares plots of $\log[\text{PHPB}]$ against time. Duplicate kinetic runs showed that the rate constants are reproducible to within $\pm 3\%$. Simple and multivariate linear regression analyses were carried out by the least-squares method.

3. Results

3.1 Stoichiometry

The oxidation of vicinal diols by PHPB yields products arising from the glycol-bond fission, i.e. rupture of the bond between the carbon atoms bearing the hydroxy groups, while the other diols give products of simple oxidation of one of the hydroxy groups. Analyses of products indicate the overall reactions below.



3.2 Rate laws

The reactions were found to be first-order with respect to PHPB. Individual kinetic runs were strictly first-order in PHPB. Further, the first-order rate coefficients did not vary with the initial concentration of PHPB. The order with respect to the diol is less than one (table 1). A plot of $1/k_{\text{obs}}$ versus $1/[\text{diol}]$ is linear with an intercept on

Table 1. Rate constants for the oxidation of ethanediol and propane-1,3-diol at 313 K.

10^3 [PHPB] (mol dm ⁻³)	[Diol] (mol dm ⁻³)		$10^5 k_{\text{obs}}$ (S ⁻¹)	
	Ethanediol	Propane-1,3-diol	Ethanediol	Propane-1,3-diol
1.0	0.10	0.04	8.64	2.53
1.0	0.17	0.06	12.4	3.56
1.0	0.25	0.08	15.5	4.46
1.0	0.36	0.10	18.5	5.25
1.0	0.45	0.25	20.2	9.19
1.0	0.55	0.34	21.8	10.6
1.0	0.67	0.44	23.2	11.7
2.0	0.45	0.34	20.3	10.2
4.0	0.45	0.34	19.8	10.1
6.0	0.45	0.34	20.1	10.3
8.0	0.45	0.34	19.9	10.5

the rate ordinate. Thus Michaelis–Menten type kinetics are observed with respect to the diols. This leads to the postulation of the following overall mechanism (3) and (4) and rate law (5).



$$\text{Rate} = k_2 K [\text{diol}][\text{PHPB}]/(1 + K [\text{diol}]). \quad (5)$$

The dependence on the concentration of the diol was studied at different temperatures and the values of K and k_2 were calculated from the double reciprocal plots. The thermodynamic parameters of the complex formation and the 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).

3.3 Isotope effects

To ascertain the importance of the cleavage of the α -C–H bond in the rate-determining step, the oxidation of (1, 1, 2, 2-²H₄)ethanediol was studied. The results showed the absence of a primary kinetic isotope effect.

The rates of oxidation of ethanediol, propane-1, 3-diol, and 3-methoxybutan-1-ol were obtained in deuterium oxide (overall 95% D₂O). This set of experiments was carried out in aqueous solutions. The values of $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$, at 313 K, are 4.71, 2.17 and 2.23 respectively.

3.4 Effect of pyridinium bromide

The rates of oxidation were not affected by an addition of pyridinium bromide (up to 0.02 mol dm⁻³).

Table 2. Formation constants and thermodynamic parameters of the diol-PHPB complexes.

Diol	$K(\text{dm}^3 \text{mol}^{-1})$ at temp. (K) =				ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)
	293	303	313	323			
Ethane-diol	6.52	4.78	3.55	2.58	-24.1 ± 0.4	-67 ± 1	-4.3 ± 0.3
Propane-1,2-diol	7.21	5.48	4.20	3.12	-21.8 ± 0.5	-58 ± 2	-4.5 ± 0.4
Butane-2,3-diol	6.93	4.87	3.42	2.38	-28.0 ± 0.5	-80 ± 2	-4.3 ± 0.4
Butane-1,2-diol	6.41	4.50	3.30	2.30	-26.6 ± 0.5	-76 ± 2	-4.2 ± 0.3
Pinacol	7.03	5.11	3.82	2.79	-24.1 ± 0.4	-66 ± 1	-4.4 ± 0.3
Propane-1,3-diol	8.75	5.90	4.00	2.77	-30.2 ± 0.4	-85 ± 3	-4.9 ± 0.4
Butane-1,3-diol	9.21	6.00	3.89	2.60	-33.2 ± 0.3	-95 ± 2	-5.0 ± 0.5
Butane-1,4-diol	8.32	5.12	3.15	1.92	-38.4 ± 0.6	-114 ± 3	-4.6 ± 0.5
Pentane-1,5-diol	9.56	5.80	3.50	2.11	-39.6 ± 0.6	-117 ± 4	-5.0 ± 0.5
3-Methoxybutan-1-ol	10.4	7.31	5.20	3.50	-28.3 ± 0.8	-78 ± 3	-5.4 ± 0.6
2-Methoxyethanol ^a	10.2	6.75	4.80	3.22	-32.4 ± 0.6	-83 ± 2	-7.7 ± 0.4

^aData from Mathur *et al* (1993)

3.5 Effect of solvent composition

The rate of oxidation was determined in solvents containing different amounts of acetic acid and water. It was observed that the rate increased with an increase in the amount of water in the solvent.

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

4. Discussion

In solution, PHPB may undergo the following reactions (6) and (7).



Table 3. Rate constants and activation parameters of the decomposition of diol-PHPB complexes.

Diol	$10^5 k_2 (\text{s}^{-1})$ at temp. (K) =				ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔG^* (kJ mol ⁻¹)
	293	303	313	323			
Ethane- diol	0.93	1.75	3.30	6.20	47.2 ± 0.7	-181 ± 2	101 ± 0.5
Propane- 1,2-diol	1.36	2.44	4.52	8.12	44.5 ± 0.5	-187 ± 2	100 ± 0.6
Butane- 2,3-diol	1.88	3.33	5.88	10.5	42.5 ± 0.7	-191 ± 3	99.3 ± 0.6
Butane- 1,2-diol	3.60	6.16	10.5	18.0	39.6 ± 0.6	-195 ± 2	97.7 ± 0.5
Pinacol	3.82	6.36	10.8	18.6	39.0 ± 0.9	-197 ± 3	97.6 ± 0.7
Propane- 1,3-diol	2.95	7.40	18.4	46.4	70.0 ± 0.9	-93 ± 3	97.7 ± 0.7
Butane- 1,3-diol	4.90	11.6	25.2	63.5	64.0 ± 1.7	-110 ± 5	96.5 ± 1.3
Butane- 1,4-diol	4.20	10.5	23.6	56.8	65.3 ± 0.9	-106 ± 3	96.9 ± 0.7
Pentane- 1,5-diol	5.12	12.6	29.0	64.8	63.9 ± 0.9	-109 ± 4	96.4 ± 0.2
3-Methoxy- butan-1-ol	5.80	13.4	28.3	70.0	62.1 ± 1.7	-115 ± 3	96.2 ± 1.3
2-Methoxy- ethanol ^a	3.44	8.82	20.6	50.0	67.3 ± 0.7	-101 ± 2	97.3 ± 0.6

^aData from Mathur *et al* (1993)

The probable 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 on the rate of reaction ruled out both bromide and tribromide ion as the reactive oxidizing species. Thus the most probable oxidizing species is PHPB itself.

The increase in the values 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 nonlinear. The solvent effect was analysed using the Grunwald-Winstein (Falnberg and Winstein 1956) equation

$$\log k_2 = \log k_0 + mY. \quad (8)$$

The plot of $\log k_2$ against Y was linear ($r^2 = 0.9978$) with $m = 0.54 \pm 0.01$. The value of m points to a transition state which is more polar than the reactant.

The diverse nature of the products formed in the oxidation of vicinal diols and other diols suggests that these compounds follow different mechanistic pathways. This is further supported by the two linear plots obtained between $\log(\text{rate})$ at 293 K and at 323 K, one for the vicinal diols and another for the rest (figure 1).

Table 4. Dependence of k_{obs} on the concentration of ethane-
diol in solvents of different compositions.
[PHPB] = 0.001 mol dm⁻³, $T = 313$ K

[Diol] (mol dm ⁻³)	$10^6 k_{\text{obs}}$ (s ⁻¹) [at % AcOH (v/v)]				
	25	40	50	60	72
0.01	28.0	14.4	8.64	5.20	2.82
0.17	40.5	20.7	12.4	7.47	4.06
0.25	50.1	26.0	15.5	9.36	5.03
0.36	60.7	30.5	18.5	11.2	6.08
0.45	66.5	33.8	20.2	12.3	6.70
0.55	71.5	36.3	21.8	13.3	7.21
$K/\text{dm}^3 \text{mol}^{-1}$	3.46	3.60	3.55	3.52	3.40
$10^3 k_2/\text{s}^{-1}$	10.9	5.45	3.30	2.00	1.10

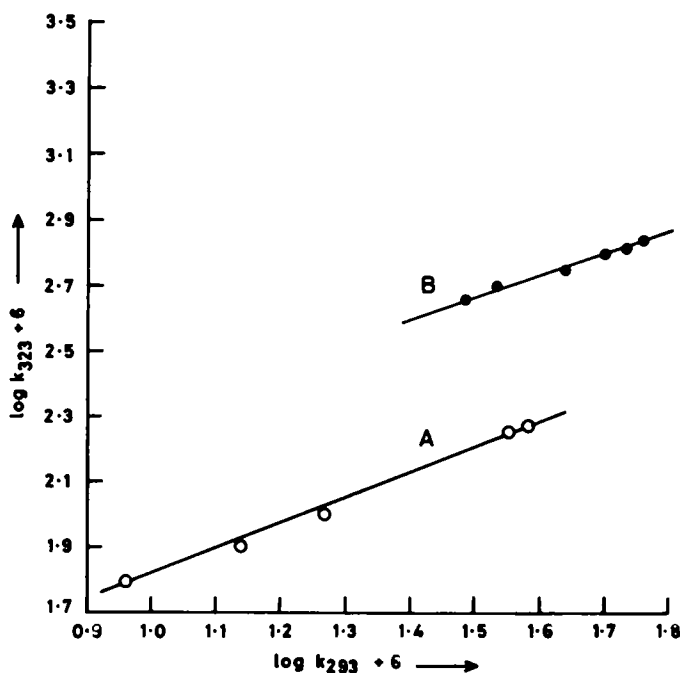


Figure 1. Isokinetic relationship in the oxidation of vicinal and other diols by PHPB. A-vicinal diols, B-other diols.

4.1 Oxidation of vicinal diols

The linear correlation between $\log(\text{rate})$ at 293 K and 323 K for the oxidation ($r = 0.9996$; slope = 0.7904 ± 0.0133) shows that an isokinetic relationship exists in the oxidation of vicinal diols by PHPB (Exner 1973). The value of the isokinetic temperature is 528 ± 26 K. An isokinetic relationship is a necessary condition for the validity of

linear-free energy relationships. It also implies that all the diols are oxidized by the similar mechanism.

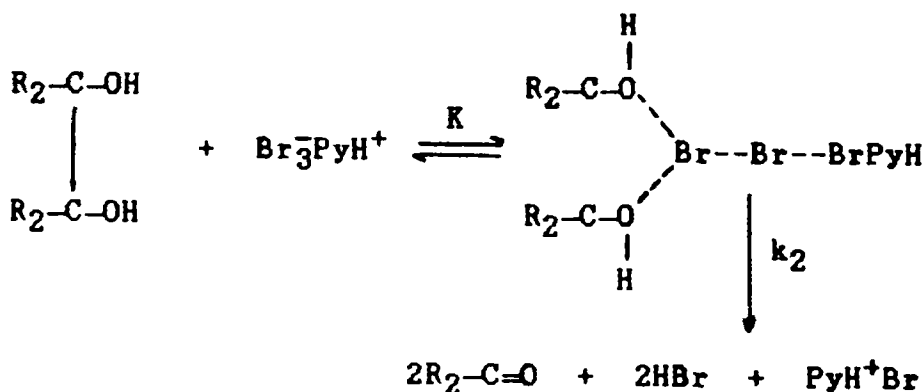
The absence of a primary kinetic isotope effect confirms that the α -C-H bond is not cleaved in the rate-determining step. In contrast, substantial primary kinetic isotope effect was observed in the oxidations of ethanol by PHPB (Mathur *et al* 1993). Thus it seems that the oxidation of monohydric alcohols and vicinal diols follows different mechanisms.

Active hydrogens like those present in hydroxyl and carboxyl groups undergo rapid exchange in deuterium oxide. If the cleavage of the O-H bond is involved in the rate-determining step, the O-H/O-D isotope effect comes into play. In view of the observed value of solvent isotope effect, an O-H bond cleavage in the rate-determining step is indicated. The large magnitude of solvent isotope effect, observed in the oxidation of ethanediol, suggests that both the hydroxy groups are involved in the rate-determining step. The magnitude of the negative entropy of activation is almost double in the oxidation of vicinal diols as compared to that of the other compounds (table 3). This points to a more rigid transition state in the oxidation of the vicinal diols. The only mode of oxidation available for pinacol is the fission of the bonds between carbinol carbon atoms. That the other vicinal diols follow this mechanism is confirmed by the isolation of products formed by the C-C bond fission and the isokinetic relationship.

From the rate-law (5), it is apparent that an intermediate complex is formed in a rapid pre-equilibrium. With the present data it is not possible to state definitely the nature of the intermediate complex. Formation of a hypobromite ester, as given below, as an intermediate is unlikely in view of the absence of any effect of pyridinium bromide.



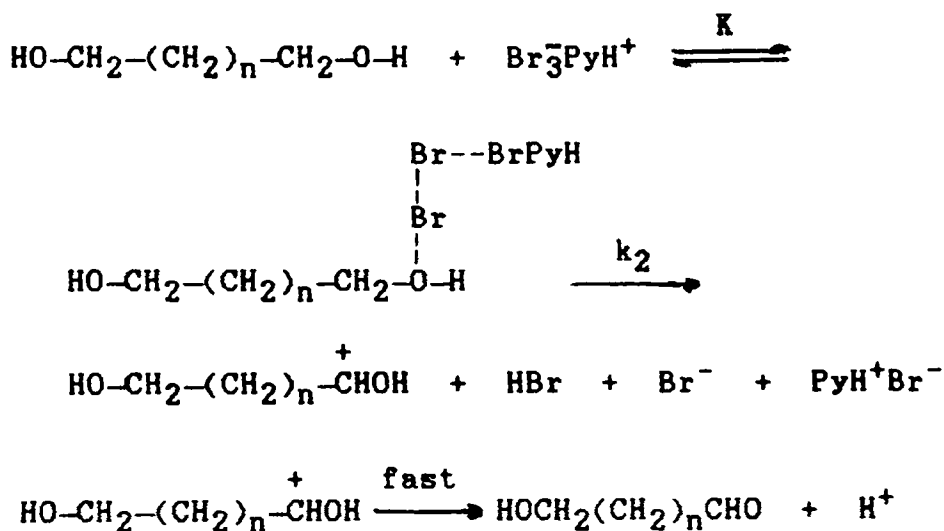
Heasley *et al* (1988) have postulated the formation of an intermediate π -complex in the reaction of alkenes with PHPB. A similar complex may be formed by the interaction between the non-bonded pairs of hydroxy oxygens and PHPB. The formation of a moderately stable intermediate is supported by the observed thermodynamic parameters (table 3). The complex formation is favoured by the enthalpy term but there is a loss of entropy indicating a rigid structure.



Scheme 1.

Table 5. Reaction constants of the oxidation of vicinal diols by PHPB.

T/K	ρ_1	δ	R^2	sd
293	-0.97 ± 0.05	-1.49 ± 0.03	0.9996	0.007
303	-0.84 ± 0.02	-1.40 ± 0.01	0.9999	0.003
313	-0.76 ± 0.05	-1.29 ± 0.03	0.9995	0.007
323	-0.71 ± 0.04	-1.19 ± 0.02	0.9996	0.006

**Scheme 2.**

The mechanism depicted in scheme 1 accounts for the experimental results.

4.1a Correlation of structure and reactivity: A perusal of the data in tables 2 and 3 showed that the formation constants of the PBPB-diol complexes are not sensitive to the structure of the diol. However, the rate constants of the decomposition show considerable variation. The rates of decomposition were, therefore, subjected to correlation analyses.

The rates of decomposition of the complexes failed to show satisfactory correlation with either the polar or steric substituent constants (Johnson 1987). Therefore, the rates were analysed in terms of the dual substituent-parameter (DSP) equation (9) of Pavelich and Taft (1957)

$$\log k = \rho_1 \Sigma \sigma_I + \delta \Sigma E_s + \log k_0 \quad (10)$$

The results recorded in table 5, show that the rates exhibited an excellent correlation with polar and steric substituent constants. Though the number of compounds (five) is rather small for a correlation analysis by a DSP equation, the correlations are excellent and the results can be used qualitatively.

The values of the reaction constants support the proposed mechanism. The small negative polar reaction constant accords with the net flow of electrons towards the oxidant. The negative steric reaction constant implies a steric acceleration of the reaction. This is probably due to increase in the steric relief on going from tetragonal (sp^3) carbon atoms to trigonal (sp^2) ones, with increasing substitution at the carbon atoms.

4.2 Oxidation of other diols

The linear correlation between $\log k$ at 293 K and 323 K ($r = 0.9986$, slope = 0.6235 ± 0.0167) for the oxidation of four non-vicinal diols, 3-methoxybutan-1-ol, and 2-methoxyethanol shows that all the compounds are oxidized by the same mechanism (Exner 1973). The value of the isokinetic temperature is 389 ± 5 K. 3-methoxybutan-1-ol and 2-methoxyethanol are typical monohydric alcohols and, therefore, it is highly likely that these diols are oxidized by a mechanism similar to that operative for monohydric alcohols. The oxidation of ethanol (Mathur *et al* 1993) exhibited a substantial kinetic isotope effect confirming the cleavage of the α -C-H bond in the rate-determining step. Therefore, a mechanism, similar to one proposed earlier (Mathur *et al* 1993) for monohydric alcohols, accounts for the experimental results obtained in the oxidation of non-vicinal diols (scheme 2).

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