Kinetics and Mechanism of the Oxidation of Diols by Acid Permanganate

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The kinetics of the oxidation of four vicinal diols, four other diols, and two of their monoethers by acid permanganate have been studied. The vicinal diols yielded products arising out of glycol bond fission while other diols yielded hydroxycarbonyl compounds. The reaction is first order with respect to the diol and permanganate. The rate increases with an increase in the acidity. Permanganic acid has been postulated as the reactive oxidising species. The oxidation of $[1,1,2,2-^2H_4]$ethane-1,2-diol showed the absence of a primary kinetic isotope effect. The values of solvent isotope effect, $k(H_2O)/k(D_2O)$, at 298 K for the oxidation of ethane-1,2-diol, propane-1,3-diol, and 2-ethoxyethanol were 3.30, 0.43, and 0.40, respectively. Plots of $(\log k_1 + H_0)$ against $\log a_{H_2O}$ are linear in the case of vicinal diols with the slope, ω, having values from 3.45 to 3.92. This suggested proton abstraction by water in the rate-determining step. An acyclic mechanism involving glycol bond fission has been proposed for the vicinal diols. The other diols are oxidised by a hydride-transfer mechanism as are monohydric alcohols.

Although the kinetics of the oxidation of various types of organic compounds by acid permanganate have been studied, there seems to be no report of a systematic study of the oxidation of diols by acid permanganate. The investigations already reported [1,2] were carried out under the conditions in which intermediate valence states of manganese are the reactive oxidising species. Therefore an investigation of the oxidation of diols by manganese(VII) in acid solutions was undertaken. We now report the oxidation of four vicinal diols, four other diols, and two of their monoethers. The mechanistic conclusions are discussed. Sodium fluoride (0.01 mol l^{-1}) was added to each reaction mixture to suppress the reactions of Mn^{III} and/or Mn^{IV}.[3]

Experimental

Materials.—All the diols and ethers were commercial products (B.D.H. or Fluka) and were distilled under reduced pressure before use. Perchloric acid (E. Merck) was used as a source of hydrogen ions. $[1,1,2,2-^2H_4]$Ethane-1,2-diol was prepared by the reduction of diethyl oxalate with lithium aluminium deuteride.[4] Deuterium oxide (purity 99.4%) was supplied by B.A.R.C., Bombay.

Product Analysis.—In a typical experiment ethanediol (6.2 g, 0.1 mol), potassium permanganate (1.58 g, 0.01 mol), and sodium fluoride (0.84 g, 0.02 mol) were made up to 100 ml in aqueous perchloric acid (the total solution was 1.0 mol l^{-1} in perchloric acid). The reaction mixture was allowed to stand for *ca.* 12 h to ensure completion of the reaction. It was then treated overnight with an excess (300 ml) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol l^{-1} HCl. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, 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 8.72 (83%) and 7.46 g (71%), respectively. A similar experiment with propane-

1,3-diol yielded the DNP of 3-hydroxypropanal in 74% yield after recrystallization.

The products of oxidation of other compounds were also isolated as their DNP but quantitative estimations were not done. The oxidation of 2-ethoxyethanol yielded ethoxyethanal, isolated as its phenylhydrazone (m.p. 160 °C).

Attempts were made to determine the stoicheiometry of the reaction by treating ethanediol with an excess of permanganate. That, however, led to a large consumption of permanganate. As no reproducible results were obtained, further experiments of this type were abandoned. The large consumption of permanganate may be due to eventual oxidation of ethanediol to carbon dioxide *via* formic acid.

Kinetic Measurements.—The reactions were studied under pseudo-first-order conditions by keeping an excess of the diol over permanganate. The reactions were carried out in flasks blackened from the outside to avoid any photochemical reactions and were followed iodometrically for at least two half-lives. Rate constants were computed from the linear ($r > 0.98$) plot of log $[MnO_4^-]$ against time. Duplicate kinetic runs showed that the rates were reproducible to within $\pm 4\%$. Preliminary experiments showed that the oxidation is not sensitive to ionic strength, therefore, no attempt was made to keep it constant. The second-order rate constant, k_2, was obtained from the relation $k_2 = k_1/[diol]$, where k_1 is the pseudo-first-order rate constant.

Table 1. Dependence of the reaction rate on permanganate concentration. [Ethanediol] 0.05M, [propane-1,3-diol] 0.01M, [H⁺] 1.0M, T 298 K

$10^3[MnO_4^-]$/M	0.5	1.0	1.5	2.0	2.5
$10^4 k_1$/s⁻¹					
Ethanediol	6.92	6.75	6.84	6.75	6.58
Propane-1,3-diol	4.48	4.57	4.45	4.45	4.57

$$5 \begin{array}{c} R_2C-OH \\ | \\ R_2C-OH \end{array} + 2MnO_4^- + 6H^+ \longrightarrow 10\ R_2CO + 2Mn^{2+} + 8H_2O \qquad (1)$$

$$5 HOCH_2-(CH_2)_n-CH_2OH + 2MnO_4^- + 6H^+ \longrightarrow$$
$$5 HOCH_2-(CH_2)_n-CHO + 2Mn^{2+} + 8H_2O \qquad (2)$$
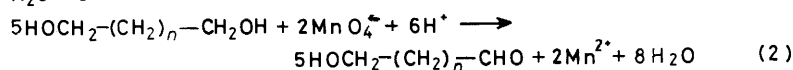
Table 2. Dependence of reaction rate on the concentration of diol. [MnO_4^-] 0.001M, [H^+] 1.0M, T 298 K

	$10^4 k_1/s^{-1}$					
10^2[Diol]/M	1.0	2.0	3.0	5.0	7.0	10.0
Ethanediol	1.38	2.70	4.08	6.75	9.60	13.6
Propane-1,3-diol	4.57	9.20	13.5	26.8	32.3	

Table 3. Effect of acidity on the rate of oxidation of diols by permanganate. [MnO_4^-] 0.001M, T 298 K

Compound	$10^2 k_2/l\ mol^{-1}\ s^{-1}$						
[$HClO_4$]/M	1.0	2.0	2.5	3.0	4.0	5.0	6.0
Ethanediol	1.37	4.00	6.10	8.75	16.6	30.2	46.8
Propane-1,2-diol	1.83	5.27	8.00	10.8	22.0	35.0	51.7
Butane-2,3-diol	2.45	7.02	10.6	16.2	28.0	54.2	80.5
Pinacol	4.27	11.9	18.4	25.1	43.2	73.2	96.4
Propane-1,3-diol	4.60	9.10	11.6	13.5	18.3	23.0	28.1
Butane-1,3-diol	16.0	31.5	40.3	49.0	65.0	81.5	97.0
Butane-1,4-diol	7.0	13.8	17.7	21.1	27.7	35.0	41.6
Pentane-1,5-diol	13.8	27.3	34.5	42.0	55.7	71.0	83.8
3-Methoxybutan-1-ol	27.5	54.5	68.0	82.0	110	137	
2-Ethoxyethanol	0.98	2.00	2.50	2.88	3.85	4.96	6.00

Table 4. Kinetic isotope effect in the oxidation of ethanediol by acid permanganate. [MnO_4^-] 0.001M, [H^+] 1.0M, T 298 K

Compound	$10^{-3} k_2/$ $l\ mol^{-1}\ s^{-1}$	k_H/k_D
Ethanediol	13.7	
		1.02
[1,1,2,2-^{2}H$_4$]Ethanediol	13.4	

Table 5. Solvent isotope effect in the oxidation of ethanediol, propane-1,3-diol, and 2-ethoxyethanol. [MnO_4^-] 0.001M, [H^+] 1.0M, T 298 K

Compound	$10^3 k_2(H_2O)/$ $l\ mol^{-1}\ s^{-1}$	$10^3 k_2(D_2O)/$ $l\ mol^{-1}\ s^{-1}$	$\dfrac{k_2(H_2O)}{k_2(D_2O)}$
Ethanediol	13.7	4.15	3.30
Propane-1,3-diol	45.7	106	0.43
2-Ethoxyethanol	9.75	24.4	0.40

Table 6. Rate constants for the oxidation of diols by permanganate in the presence of 1.0M perchloric acid

Compound	$10^3 k_2/l\ mol^{-1}\ s^{-1}$			
	298 K	303 K	308 K	313 K
Ethanediol	13.7	23.0	35.2	58.0
Propane-1,2-diol	18.3	28.2	43.6	67.0
Butane-2,3-diol	24.4	38.8	53.7	80.0
Pinacol	42.7	52.5	85.0	105
Propane-1,3-diol	45.7	63.2	79.5	110
Butane-1,3-diol	158	209	270	345
Butane-1,4-diol	69.2	93.1	125	167
Pentane-1,5-diol	138	182	240	310
3-Methoxybutan-1-ol	275	360	470	590
2-Ethoxyethanol	9.75	14.2	20.0	28.3

Table 7. Activation parameters for the oxidation of diols by acid permanganate

Compound	$\Delta H^*/$ $kJ\ mol^{-1}$	$\Delta S^*/$ $J\ mol^{-1}\ K^{-1}$	$\Delta G^*/$ $kJ\ mol^{-1}$
Ethanediol	73.6	−36	84.3
Propane-1,2-diol	67.1	−56	83.7
Butane-2,3-diol	61.6	−72	83.0
Pinacol	49.2	−109	81.6
Propane-1,3-diol	45.5	−120	81.2
Butane-1,3-diol	39.9	−129	78.3
Butane-1,4-diol	45.4	−118	80.5
Pentane-1,5-diol	41.9	−123	78.5
3-Methoxybutan-1-ol	38.3	−130	77.0
2-Ethoxyethanol	54.6	−103	85.3

Results

The oxidation of vicinal diols by acid permanganate yields products arising out of glycol bond fission while the other diols gave products by simple oxidation of the hydroxy-group. Analysis of products indicates the overall reactions (1) and (2). The reaction mixtures become colourless at the end showing that Mn^{VII} is reduced eventually to Mn^{II}.

Rate Laws.—The reaction was found to be first order with respect to the oxidant. Individual kinetic runs were strictly first order with respect to permanganate. Further the first-order rate coefficients did not vary with the initial concentration of permanganate (Table 1). The order with respect to the diol is also one (Table 2). The rate increases with an increase in the hydrogen ion concentration (Table 3).

Isotope Effect.—To ascertain the importance of the C–H bond cleavage in the rate-determining step, the oxidation of [1,1,2,2-^{2}H$_4$] ethane-1,2-diol was studied. The results show the absence of a primary kinetic isotope effect (Table 4).

The rate of oxidation of ethanediol, propane-1,3-diol, and 2-ethoxyethane were obtained in deuterium oxide (overall 90% D_2O). The results are summarised in Table 5.

Effect of Temperature.—The rates of oxidation of diols were obtained at different temperatures (Table 6) and the activation parameters were calculated (Table 7). The average error limits in the values of ΔH^*, ΔS^*, and ΔG^* (at 298 K) are ± 3 kJ mol^{-1}, ± 4 J mol^{-1} K^{-1}, and ± 5 kJ mol^{-1}, respectively.

Discussion

The diverse nature of the products formed and the different values of solvent isotope effect obtained in the oxidation of vicinal diols and other diols suggest that these compounds
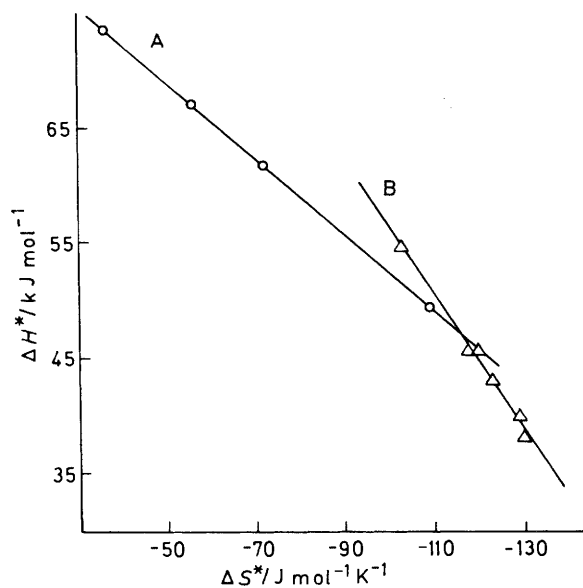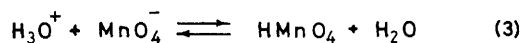
Figure 1. Isokinetic plot for the oxidation of diols by acid permanganate: A, vicinal diols; B, other diols and the monoethers

Figure 2. Bunnett's plot for the effect of acidity on the oxidation rate: A, ethanediol; B, pinacol; [ethanediol] 0.1M, [pinacol] 0.028M, [MnO_4^-] 0.001M; T 298 K

$$H_3O^+ + MnO_4^- \rightleftharpoons HMnO_4 + H_2O \qquad (3)$$

follow different mechanistic pathways. This is further supported by the two separate linear plots obtained between the activation enthalpies and entropies, one for the vicinal diols and another for the rest (Figure 1).

Oxidation of Vicinal Diols.—The linear correlation between the activation enthalpies and entropies (r 0.9992, β 335 K) implies that all the vicinal diols are oxidised by the same mechanism and the changes in rates are governed by changes in both enthalpies and entropies of activation.

The sharp increase in the rate of oxidation with acidity suggests that the reactive oxidising species is permanganic acid [reaction (3)].

This is in accord with suggestions of Stewart and Mocek [5] that in strong acid solution, fluoral hydrate is oxidised by permanganic acid. Similarly, Verma *et al.*[6] also attributed the rate enhancement with acidity to the formation of permanganic acid in the oxidation of amino-acids.

However, the reaction does not observe any simple order with respect to acidity. A plot of log k_1 against H_0 is linear but the slope is far from the ideal unity.[7] To obtain a clearer picture of the role of hydrogen ions in the oxidation process, Bunnett's hypothesis was applied.[8] The plots of (log k_1 + H_0) against log a_{H_2O} gave fairly linear plots (r 0.9981—0.9996) with slopes varying from 3.46 to 3.93 (Figure 2). This suggests a rate-determining proton abstraction by water.

The absence of a primary kinetic isotope effect confirms that the α-C-H bond is not cleaved in the rate-determining step. The rate of an acid-catalysed reaction in D_2O is expected to be 2.0—3.0 times the rate in water.[9] In the present case, however, an ' inverse ' solvent isotope effect has been observed. Active hydrogens like those present in hydroxy- and carboxy-groups undergo rapid exchange in D_2O, and the O-H/O-D isotope effect may neutralize the rate-enhancing effect of D_2O or even result in an ' inverse ' solvent isotope effect. Thus O-H bond rupture is indicated in the rate-determining step. The relatively large magnitude of the solvent isotope effect suggests that both the hydroxy-groups are thus
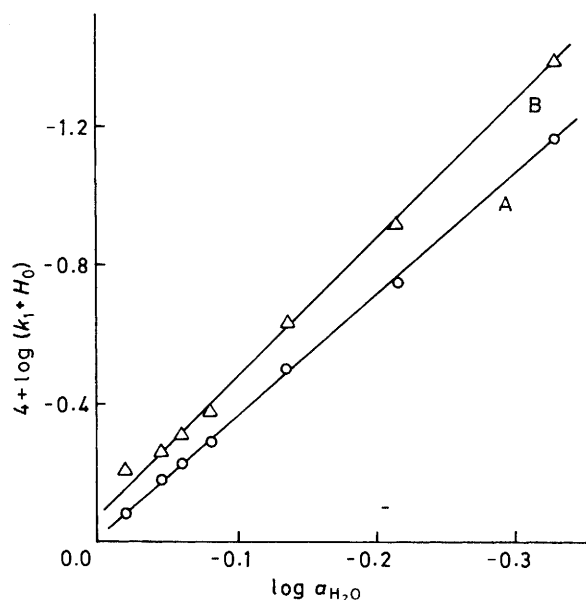
involved. The only mode of oxidation available for pinacol is by the rupture of the bond between the carbinol carbon atoms. That other vicinal diols follow this mechanism is confirmed by the isolation of products formed by the C-C bond fission and the isokinetic relationship. Littler [10] has theoretically analysed and concluded that though the formation of a cyclic ester in the oxidation of diols by Mn^{VII} is an allowed process, the ring formed will involve much strain and an acyclic pathway may be preferred. This accords with the observation that water plays the role of proton abstractor in the present case. Mechanism (4) accounts for the results obtained in the present investigation.

The negative entropy of activation supports a reaction in which charge separation takes place in the transition state. The progressive lowering of the entropy of activation with increasing substitution indicates a crowded transition state in which freedom of motion of the substituents is hindered. The four methyl groups in pinacol obviously add to the crowding in the transition state.[11]

The rate of oxidation increases sharply with progressive substitution of hydrogen atoms of ethanediol by methyl groups because of the increase in strain relief on going from tetragonal (sp^3) carbon atoms to trigonal (sp^2) ones, with increasing substitution at the carbon atoms.

Oxidation of Other Diols.—The activation enthalpies and entropies of the oxidation of non-vicinal diols correlate with those of the oxidation of 3-methoxybutan-1-ol and 2-ethoxyethanol, typical monohydric alcohols (r 0.9932, β 600 K). The value of the isokinetic temperature is quite close to one obtained in the oxidation of aliphatic alcohols.[12] Therefore, it is highly likely that these diols are oxidised by a mechanism similar to that operative for the oxidation of monohydric alcohols. The observed solvent isotope effect suggests that the hydroxy-group is not involved either in the rate-determining step or in the pre-equilibria. The effect of acidity is also of different order as compared to that obtained for vicinal diols. In fact it is parallel to that recorded earlier for ethanol.[12] The formation of hydroxycarbonyl compounds further confirms that these diols behave like alcohols towards permanganate.

$$H-O\cdots\overset{R^2}{\underset{R^1}{\overset{|}{\underset{|}{C}}}}-\overset{R^2}{\underset{R^1}{\overset{|}{\underset{|}{C}}}}-O-H + HMnO_4 \xrightarrow{\text{slow}} \quad (4)$$

$$H_2O \qquad\qquad 2R^1COR^2 + H_3O^+ + H_2MnO_4^- \quad (Mn)$$

$$HOCH_2-(CH_2)_n-\overset{OH}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H + HMnO_4 \xrightarrow{\text{slow}} HOCH_2-(CH_2)_n-\overset{+}{C}HOH \quad (5)$$

$$+ H_2MnO_4^-$$

$$HOCH_2-(CH_2)_n-\overset{+}{C}HOH \xrightarrow{\text{fast}} HOCH_2-(CH_2)_n-CHO + H^+ \quad (6)$$

Therefore, it is proposed that the rate-determining step in the oxidation of non-vicinal diols involves transfer of a hydride ion to permanganic acid as has been suggested earlier for alcohols.[12,13]

The formation of an Mn^V species as a short-lived intermediate in the reduction of permanganate by *trans*-crotonic acid has been postulated by Simandi and Jáky.[14]

The observed negative entropy of activation also supports the above mechanism. Reaction of neutral molecules to yield ions invariably shows a negative entropy of activation. As the charge separation begins in the transition state, each end of the dipole becomes solvated by a sheath of solvent molecules, which must, however, be suitably oriented.[11] This increase in orientation means restricted freedom and results in a decrease in entropy.

Acknowledgements

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