

Kinetics and mechanism of the oxidation of diols by bromine in acid solution

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Abstract. Kinetics of oxidation of five vicinal diols, four non-vicinal diols, and two of their monoethers by bromine in strong acid solutions have been studied. The vicinal diols yielded the products arising out of glycol bond fission while the other diols yielded the hydroxycarbonyl compounds. The reaction is first order with respect to both bromine and the diol. The rate decreases with an increase in the acidity. The oxidation of [1,1,2,2- $^2\text{H}_4$]ethanediol showed the absence of a primary kinetic isotope effect. The value of solvent isotope effect, $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$, at 303 K for the oxidation of ethanediol, propane-1,3-diol and 3-methoxybutane-1-ol are 4.71, 1.04 and 1.07 respectively. A mechanism involving a glycol bond fission has been proposed for the oxidation of the vicinal diols. The other diols are oxidised by a hydride-transfer mechanism as are monohydric alcohols.

Keywords. Kinetics; mechanism; oxidation; diol; bromine; correlation analysis.

1. Introduction

A number of reports on the mechanism of the oxidations by bromine are available in the literature¹. However, most of the studies have been made in the pH range 2–11. There are very few studies of the mechanism of oxidation of hydroxy compounds by bromine in strongly acidic solution viz that of 2-propanol and α -hydroxy acids^{2,3}. The oxidation involves a hydride ion transfer instead of a proton transfer. The reaction path does not involve organic hypobromites and the reactive species is molecular bromine. It is known that with several oxidants like lead tetraacetate⁴, periodic acid⁵, acid permanganate⁶, bromamine-B⁷ etc., diols and monohydric alcohols follow different mechanistic pathways. We now report the oxidation of several vicinal and non-vicinal diols by bromine in the presence of perchloric acid. The mechanistic aspects are discussed.

2. Experimental

2.1 Materials

The diols and the monoethers (BDH or Fluka) were distilled under reduced pressure before use. [1,1,2,2- $^2\text{H}_4$]Ethanediol (DED) was prepared by the reduction of diethyl oxalate with lithium aluminium deuteride⁸. Its isotopic purity, determined by its NMR spectrum was $90 \pm 4\%$.

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2.2 Product analysis

Product analysis was carried out under kinetic conditions i.e. with an excess of the reductant over bromine. However, the concentration of the reactants used were of preparative scale. In a typical experiment, the diol (0.1 mol) and bromine (3.2 g, 0.02 mol) were taken in a 2.0 mol dm⁻³ solution of perchloric acid (100 ml) and the mixture was allowed to stand in the dark for ≈ 10 h to ensure completion of the reaction. It was then treated overnight with an excess (250 cm³) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm⁻³ HCl. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, recrystallized from ethanol and weighed. The DNP derivatives were found to be homogenous by TLC except in the oxidation of propane-1,2- and butane-1,2-diols. In these cases the mixtures were separated by fractional crystallization. The identity of the products were established by comparing the m.p. of the DNP derivatives with the literature values. In the oxidation of ethanediol and butane-1,3-diol, the identity of the products were confirmed by determining the m.m.p. with the authentic samples of DNP of formaldehyde and 3-hydroxybutanal respectively. The melting points were obtained in open capillaries and are uncorrected. The results are summarized in table 1.

2.3 Kinetic measurements

The pseudo-first-order conditions were attained by keeping a large excess ($\times 15$ or greater) of the diols over bromine. The reactions were followed by monitoring the decrease in the concentration of bromine in the reaction mixture spectrophotometrically at 398 nm for up to 80% reaction. The pseudo-first-order rate constants, k_{obs} , were evaluated from the linear ($r = 0.990 - 0.999$) plots of $\log [\text{bromine}]$ 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. Preliminary experiments showed that the reaction is not sensitive to changes in the ionic strength. Hence no attempt was made to keep the ionic strength constant.

Table 1. Analysis of products in the oxidation of diols by bromine.

Compound	Product	m.p. of DNP, °C	Yield ^a
Ethanediol	HCHO	166	96
Propane-1, 2-diol	HCHO &	165	83
	MeCHO	147	85
Butane-2, 3-diol	MeCHO	144	89
Butane-1, 2-diol	HCHO &	166	88
	EtCHO	144	89
Pinacol	MeCOMe	126	97
Propane-1, 3-diol	HOCH ₂ CH ₂ CHO	132	89
Butane-1, 3-diol	MeCH(OH)CH ₂ CHO	93	87
Butane-1, 4-diol	HOCH ₂ CH ₂ CH ₂ CHO	116	93
Pentane-1, 5-diol	HOCH ₂ (CH ₂) ₃ CHO	80	91
3-Methoxybutane-1-ol	MeCH(OMe)CH ₂ CHO	105	85
2-Methoxyethanol	MeOCH ₂ CHO	117 ^b	84

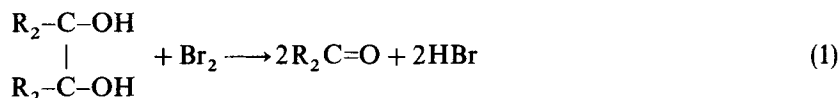
^aThe yield is of DNP derivative after recrystallization in percentage

^bInstead of DNP, 4-nitrophenylhydrazone derivative was prepared

3. Results

3.1 Stoichiometry

In 2.0 mol dm⁻³ perchloric acid, the oxidation of vicinal diols by bromine yields products arising out of glycol bond fission, i.e. rupture of the bond between the carbon atoms bearing the hydroxy groups, while the other diols give products by simple oxidation of one of the hydroxy-groups. Analyses of products indicate the overall reactions (1) and (2).



3.2 Rate laws

The rate laws and other experimental data were obtained for all the diols investigated. As the results were similar, only representative data are produced here.

The reaction was found to be first order with respect to the bromine. The individual kinetic runs were strictly first order in bromine. Further, the first order rate coefficients did not vary with the initial concentration bromine. The reaction was of first order with respect to the diol also (table 2).

3.3 Induced polymerisation of acrylonitrile

The oxidation of diols by bromine, in an atmosphere of nitrogen, failed to induce the polymerisation of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation (table 2).

Table 2. Rate constants for the oxidation of ethanediol and propane-1, 3-diol at 298 K.

$10^3[\text{Br}_2]$ (mol dm ⁻³)	[Diol] (mol dm ⁻³)	$[\text{H}^+]$ (mol dm ⁻³)	$10^5 k_{\text{obs}}(\text{s}^{-1})$	
			Ethanediol	Propane-1,3-diol
1.0	0.10	1.0	1.90	7.90
1.0	0.20	1.0	3.82	16.1
1.0	0.40	1.0	7.64	31.8
1.0	0.60	1.0	11.6	47.5
1.0	1.00	1.0	19.2	78.8
1.0	1.50	1.0	28.8	120
1.0	2.00	1.0	39.0	161
2.0	1.00	1.0	18.8	79.5
4.0	1.00	1.0	19.5	79.1
12.0	1.00	1.0	19.0	79.8
1.0	0.40	1.0	7.71 ^a	32.2 ^a
1.0	1.0	0.5	21.7	82.5
1.0	1.0	1.5	18.2	74.6
1.0	1.0	2.0	16.7	72.0
1.0	1.0	3.0	14.3	68.4
1.0	1.0	4.0	12.5	64.0
1.0	1.0	5.0	10.4	59.9

^a contained 0.05 mol dm⁻³ acrylonitrile

Table 3. Kinetic isotopic effect in the oxidation of ethanediol by bromine

Substrate	$10^5 k_2/\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	k_H/k_D
Ethanediol	19.2	1.04
DED	18.5	

[diol] = 1.00 mol dm^{-3} ; $[\text{Br}_2] = 0.001 \text{ mol dm}^{-3}$;
 $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$; $T = 298 \text{ K}$.

Table 4. Solvent isotope effect in the oxidation of ethanediol, propane-1,3-diol and 3-methoxybutane-1-ol at 298 K, $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$.

Substrate	$10^5 k_2 (\text{H}_2\text{O})$	$10^5 k_2 (\text{D}_2\text{O})$	$k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$
	$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	
Ethanediol	19.2	4.24	4.53
Propane-1,3-diol	78.8	75.6	1.04
3-Methoxybutane-1-ol	112	105	1.07

Table 5. Dependence of the rate of oxidation of ethanediol on bromide ion concentration^a

$10^2 [\text{Br}^-]$	0.00	2.00	4.00	8.00	15.0	30.0
mol dm^{-3}						
$10^5 k_{\text{obs}}/\text{s}^{-1}$	7.70	5.64	4.21	3.10	2.14	1.22

^a[diol] = 0.40 mol dm^{-3} ; $[\text{Br}_2] = 0.001 \text{ mol dm}^{-3}$;
 $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$;
 $T = 298 \text{ K}$

3.4 Effect of acidity

The rate decreases slightly with an increase in the acidity (table 2).

3.5 Isotope effects

To ascertain the importance of the cleavage of the $\alpha\text{-C-H}$ bond in the rate-determining step, the oxidation of $[1,1,2,2\text{-}^2\text{H}_4]$ ethanediol was studied. The results showed the absence of a primary kinetic isotope effect (table 3).

The rate of oxidation of ethanediol, propane-1,3-diol, and 3-methoxybutane-1-ol were obtained in deuterium oxide (overall 95% D_2O). The results are summarised in table 4.

3.6 Effect of bromide ion

The reaction rate decreases with an increase in the concentration of bromide ions (table 5). This accords with the earlier observations in the oxidation of 2-propanol² and mandelic acid³. This led us to suggest that the active oxidizing species is molecular

Table 6. Rate constants and activation parameters for the oxidation of diols by bromine at $[H^+] = 1.0 \text{ mol dm}^{-3}$.

Diol	$10^4 k_2 / \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$				ΔH^*	ΔS^*	ΔG^*
	298 K	303 K	308 K	313 K	kJ mol^{-1}	$\text{J mol}^{-1} \text{ K}^{-1}$	kJ mol^{-1}
Ethane-1,2-diol	1.92	2.60	3.55	4.80	44.9 ± 0.5	-166 ± 2	94.2 ± 0.4
Propane-1,2-diol	2.70	3.60	4.75	6.21	40.5 ± 0.1	-178 ± 1	93.4 ± 0.1
Butane-2,3-diol	4.00	5.20	6.81	8.82	38.4 ± 0.2	-182 ± 1	92.4 ± 0.2
Butane-1,2-diol	6.45	8.30	10.6	13.4	35.3 ± 0.2	-188 ± 1	91.2 ± 0.2
Pinacol	7.40	9.85	12.7	17.0	40.1 ± 0.7	-171 ± 2	90.9 ± 0.5
Propane-1,3-diol	7.88	11.8	17.5	26.2	59.5 ± 0.5	-105 ± 2	90.7 ± 0.4
Butane-1,3-diol	10.2	15.3	22.8	33.9	59.5 ± 0.4	-103 ± 1	90.1 ± 0.3
Butane-1,3-diol	9.15	14.2	20.9	31.3	60.6 ± 0.6	-100 ± 1	90.3 ± 0.2
Pantane-1,5-diol	10.6	16.0	23.9	35.2	59.5 ± 0.3	-103 ± 1	89.9 ± 0.2
3-Methoxybutane-1-ol	11.2	16.8	25.0	37.5	59.8 ± 0.6	-101 ± 2	89.9 ± 0.4
2-Methoxy-ethanol	6.84	10.0	14.1	20.1	53.0 ± 0.5	-128 ± 2	91.1 ± 0.4

bromine. The decrease in the rate be attributed to the formation of Br_3^- ion which is kinetically either inactive or much less reactive.

3.7 Effect of temperature

The rates of oxidation of diols were obtained at different temperatures and the activation parameters were calculated (table 6).

4. Discussion

The decrease in the oxidation rate with an increase in the acidity can be either due to protonation of the diol, assuming that protonated diol is not easily oxidised or due to the effect of change in the medium on the activity coefficient of bromine. Mason and Baird² concluded that in the oxidation of 2-propanol, there seems to be no need for the postulation of protonated substrate and the effect observed can be adequately explained by an activity coefficient effect. Similar results were observed in the oxidation of mandelic acids³.

The diverse nature of the products formed and the different values of the solvent isotope effect obtained in the oxidation of vicinal diols and other compounds suggest that these classes of compounds follow different mechanistic pathways. This is further supported by the two linear plots obtained between $\log(\text{rate})$ at 298 K and at 313 K, one for the vicinal diols and another for the rest (figure 1).

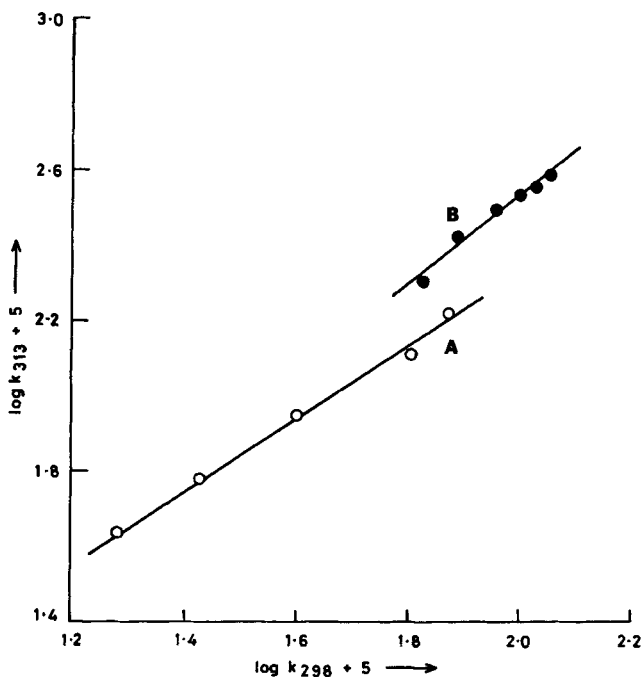


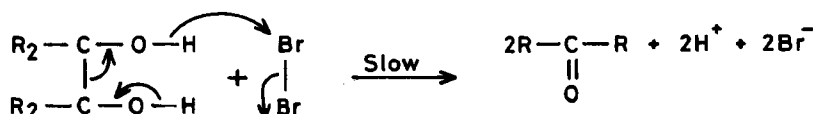
Figure 1. Isokinetic relationship in the oxidation of vicinal and other diols by bromine, **A**-vicinal diols, **B**-other diols

4.1 Oxidation of vicinal diols

The linear correlation between $\log(\text{rate})$ at 298 K and 313 K for the oxidation ($r = 0.9960$) shows that an isokinetic relationship exists in the oxidation of vicinal diols by bromine⁹. The value of the isokinetic temperature is 972 ± 14 K. An isokinetic relationship is a necessary condition for the validity of linear free energy relationships. It also implies that all the vicinal diols are oxidized by a similar mechanism.

The absence of a primary kinetic isotopic effect confirms that the α -C-H bond is not cleaved in the rate-determining step.

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 come 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 (cf. table 6). This points to a more rigid transition state in the oxidation of the vicinal diols. Thus an involvement of both the hydroxyl groups in the rate-determining step is indicated. 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 the products formed by the C-C bond fission and the isokinetic



Scheme 1.

Table 7. Reaction constants of the oxidation of vicinal diols by bromine

T/K	ρ_I	δ	R^2	sd
298	-2.13 ± 0.18	-1.18 ± 0.13	0.9891	0.04
303	-2.10 ± 0.19	-1.10 ± 0.14	0.9861	0.04
308	-2.02 ± 0.20	-1.06 ± 0.15	0.9840	0.04
313	-2.02 ± 0.22	-0.98 ± 0.18	0.9790	0.05

relationship. The following mechanism (scheme 1) accounts for the observed data. The negative entropy of activation also supports a mechanism in which charge separation takes place in the transition state.

4.1a *Correlation of structure and reactivity* The rate of oxidation of the vicinal diols failed to show satisfactory correlation with either the polar or steric substituent constants¹⁰. Therefore, the rates were analysed in terms of dual substituent-parameter (DSP) (3)¹¹,

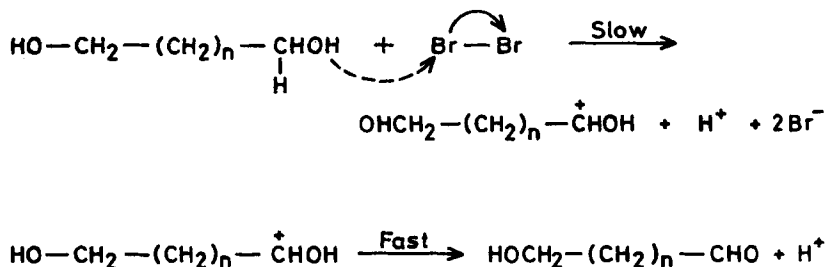
$$\log k_2 = \rho_I \Sigma \sigma_i + \delta \Sigma E_s + \log k_0. \quad (3)$$

The results recorded in table 7, 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 negative polar reaction constants 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 tetrahedral (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 298 K and 313 K ($r = 0.9869$) for the oxidation of four non-vicinal diols, 3-methoxybutane-1-ol, and 2-methoxyethanol shows that all the compounds are oxidized by the same mechanism⁹. The value of the isokinetic temperature is 801 ± 45 K. 3-Methoxybutane-1-ol and 2-methoxyethanol are typical monohydric alcohols and therefore it is highly likely that the non-vicinal diols are oxidized by a mechanism similar to that operative for 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 formation of hydroxycarbonyl compounds further confirms that these diols behave like monohydric alcohols towards bromine. The oxidation of ethanol by bromine is reported to exhibit a kinetic isotope



Scheme 2.

effect, $k_H/k_D = 4.3^{12}$ confirming the cleavage of an α -C-H bond in the rate-determining step. Similarly the oxidation of an α -deuteriomandelic acid [$\text{PhCD}(\text{OH})\text{COOH}$] by bromine, in acid solution, exhibited a $k_H/k_D = 5.14$ at 298 K^3 . Therefore, it is proposed that the rate-determining step in the oxidation of non-vicinal diols involves transfer of a hydride ion (scheme 2) to bromine as has been suggested earlier for 2-propanol².

The observed negative entropy of activation also supports the above mechanism. Reaction of neutral molecules to yield ions invariably show a negative entropy of activation. As the charge separation begins in the transition state, each end of the dipole becomes solvated by a sheet of solvent molecules, which must, however, be suitably oriented¹³. This increase in the orientation means restricted freedom and results in a decrease in entropy.

It is of interest to compare here the activation parameters of the oxidation of the vicinal and non-vicinal diols. The values of enthalpies of activation of the oxidation of vicinal diols are $40 \pm 5\text{ kJ mol}^{-1}$, whereas the values for the non-vicinal diols are $55 \pm 5\text{ kJ mol}^{-1}$. This shows that a hydride-ion transfer involves a higher enthalpy of activation as compared to the concerted process. However, the entropy term is less favourable for the concerted process which is reflected in a higher magnitude of the negative entropy of activation. These two parameters compensate each other resulting in almost similar values of the free energy of activation for both the vicinal and non-vicinal diols ($92 \pm 2\text{ kJ mol}^{-1}$).

Acknowledgements

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