Kinetic Study of Oxidation of Diols by Sodium *N*-Bromobenzenesulphonamide

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The kinetics of the oxidation of five vicinal diols, four other diols, and one of their monoethers by sodium *N*-bromobenzenesulphonamide 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 the oxidant. The oxidation of vicinal diols follows two mechanistic pathways, one acid-independent and another acid-dependent. The oxidation of the other diols shows a first-order dependence on hydrogen ion. The oxidation of [1,1,2,2-$^2H_4$]ethanediol showed the absence of a primary kinetic isotope effect. The values of solvent isotope effect, $k(H_2O)/k(D_2O)$, at 303 K for the oxidation of ethanediol, propane-1,3-diol, and 3-methoxybutan-1-ol are 2.24, 0.42, and 0.42, respectively. An acyclic mechanism involving glycol bond fission has been proposed for the vicinal diols. The other diols are oxidized by a hydride-transfer mechanism as are monohydric alcohols.

We have recently reported [1,2] the kinetics and mechanism of the oxidation of alcohols by sodium *N*-bromobenzenesulphonamide (bromamine-B or BAB). It is known, however, that some oxidations of mono- and poly-hydric alcohols follow different mechanistic pathways, *e.g.* oxidations by lead(IV),[3] periodic acid,[4] and acid permanganate.[5] Therefore, an investigation of the oxidation of diols by BAB in acid solution was undertaken. The mechanistic aspects are discussed here.

Experimental

Materials.—All the diols were commercial products and were distilled under reduced pressure before use. Perchloric acid (E. Merck) was used as a source of hydrogen ions. [1,1,2,2-$^2H_4$]-Ethanediol was prepared by the reduction of diethyl oxalate with lithium aluminium deuteride.[6] BAB was prepared by the bromination of benzenesulphonamide (BSA) in alkaline solution.[7]

Product Analysis.—In a typical experiment ethanediol (6.2 g, 0.1 mol) and BAB (5.6 g, 0.02 mol) were made up to 100 ml in 1:1 (v/v) acetic acid–water, in the presence of perchloric acid (the total solution was 0.5 mol l^{-1} in perchloric acid). The mixture was allowed to stand for *ca.* 12 h to ensure completion of the reaction. It was then treated overnight with an excess (200 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 7.4 g (88%) and 6.6 g (79%). A similar experiment with propane-1,3-diol yielded the DNP of 3-hydroxypropanal in 76% yield after recrystallization.

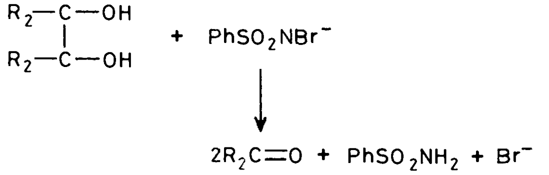
Attempts were made to determine the stoicheiometry of the reaction by treating ethanediol with an excess of BAB. That, however, led to a large consumption of BAB. As no reproducible results are obtained further experiments of this type were abandoned. The large consumption of BAB may be due to eventual 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 BAB. 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 iodometrically for up to 70% reaction. Pseudo-first-order rate constants were evaluated from the linear plots ($r > 0.98$) of log [BAB] against time. Duplicate kinetic runs showed that the rates are reproducible to within ±3%. Preliminary experiments indicated that the oxidation is not sensitive to ionic strength (0.1—2.0M) and, therefore, no attempt was made to keep it constant.

Simple and multivariate linear regressions were carried out by a least-squares method using an Apple IIe microcomputer.

Results

The oxidation of vicinal diols by BAB yields products arising from 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 the hydroxy group. Analysis of products indicates the overall reactions (1) and (2).



$$R_2C(OH){-}C(OH)R_2 + PhSO_2NBr^- \longrightarrow 2R_2C{=}O + PhSO_2NH_2 + Br^- \qquad (1)$$

$$HO{-}CH_2{-}(CH_2)_n{-}CH_2OH + PhSO_2NBr^- \longrightarrow HOCH_2{-}(CH_2)_n{-}CHO + PhSO_2NH_2 + Br^- \qquad (2)$$

Rate Laws.—The reactions were found to be first order with respect to BAB. Individual kinetic runs were strictly first order in BAB. Further, the first-order coefficients did not vary with the initial concentration of BAB. The order with respect to the diol is also one. The rate increases with an increase in the hydrogen ion concentration. The rate constants for the oxidation of ethanediol and propane-1,3-diol are recorded in Tables 1 and 2.

Isotope Effects.—To ascertain the importance of the C–H bond cleavage in the rate-determining step, the oxidation of

Table 1. Rate constants of the oxidation of ethanediol at 303 K

10^3[BAB]/M	[Diol]/M	[H$^+$]/M	10^5k_1/s^{-1}
5.0	0.36	0.2	1.00
5.0	0.72	0.2	1.98
5.0	1.08	0.2	2.98
5.0	1.80	0.2	4.94
5.0	2.52	0.2	7.03
5.0	3.60	0.2	9.90
2.0	1.80	0.2	5.03
3.5	1.80	0.2	4.94
10.0	1.80	0.2	4.87
15.0	1.80	0.2	5.00
5.0	1.80	0.5	5.32
5.0	1.80	0.8	5.81
5.0	1.80	1.0	6.08
5.0	1.80	1.3	6.50
5.0	1.80	1.5	6.84
5.0	1.80	1.7	7.20
5.0	1.80	2.0	7.60

Table 2. Rate constants of the oxidation of propane-1,3-diol by BAB at 303 K

10^3[BAB]/M	[Diol]/M	[H$^+$]/M	10^5k_1/s^{-1}
2.5	1.5	0.5	6.60
5.0	1.5	0.5	6.56
10.0	1.5	0.5	6.73
15.0	1.5	0.5	6.64
20.0	1.5	0.5	6.47
5.0	0.3	0.5	1.37
5.0	0.6	0.5	2.60
5.0	0.9	0.5	4.03
5.0	1.8	0.5	8.00
5.0	2.4	0.5	10.3
5.0	1.5	0.2	2.65
5.0	1.5	0.4	5.13
5.0	1.5	0.8	10.5
5.0	1.5	1.2	16.0
5.0	1.5	1.6	20.6
5.0	1.5	2.0	26.4

Table 3. Kinetic isotope effect in the oxidation of ethanediol by BAB. [BAB] 0.005M, [H$^+$] 0.2M, [Diol] 1.8M, *T* 303 K

Compound	10^5k_1/s^{-1}	k_H/k_D
Ethanediol	4.94	0.99
[1,1,2,2-$^2H_4$]Ethanediol	5.00	

[1,1,2,2-$^2H_4$]ethanediol was studied. The results show the absence of a primary kinetic isotope effect (Table 3).

The rates of oxidation of ethanediol, propane-1,3-diol, and 3-methoxybutan-1-ol were obtained in deuterium oxide (overall 90% D_2O). The results are summarized in Table 4. This set of experiments was carried out in aqueous solution.

Effect of BSA.—The rates of oxidation were obtained in the presence of initially added BSA. The results show the absence of any effect of BSA on the reaction rate (Table 5).

Effect of Temperature.—The rates of the oxidation of diols were obtained at different temperatures and the activation parameters were evaluated (Tables 6—8).

Discussion

Bromamine-B behaves like a strong electrolyte[8-10] in aqueous solution and dissociates into ions [reaction (3)].

Table 4. Solvent isotope effect in the oxidation of ethanediol, propane-1,3-diol, and 3-methoxybutan-1-ol. [BAB] 0.005M, [H$^+$] 0.2M, *T* 303 K

Compound	$10^6k'_2(H_2O)$/ l mol^{-1} s^{-1}	$10^6k'_2(D_2O)$/ l mol^{-1} s^{-1}	$\frac{k'_2(H_2O)}{k'_2(D_2O)}$
Ethanediol	18.7	8.35	2.24
Propane-1,3-diol	41.3	98.5	0.42
3-Methoxybutan-1-ol	141	354	0.42

$k'_2 = k_1/[\text{Diol}]$

Table 5. Effect of benzenesulphonamide (BSA) on the oxidation of ethanediol and propane-1,3-diol. [BAB] 0.005M, [H$^+$] 0.2M, *T* 303 K

10^3[BSA]/M	0.0	3.0	6.0	9.0	12.0
	$10^5k'_2$/l mol^{-1} s^{-1}				
Ethanediol	2.74	2.82	2.81	2.85	2.90
Propane-1,3-diol	1.79	1.73	1.85	1.89	1.80

$k'_2 = k_1/[\text{Diol}]$

$$\text{PhSO}_2\text{NBrNa} \longrightarrow \text{PhSO}_2\text{NBr}^- + \text{Na}^+ \quad (3)$$

$$\text{PhSO}_2\text{NBr}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{PhSO}_2\text{NHBr} + \text{H}_2\text{O} \quad (4)$$

$$2\text{PhSO}_2\text{NHBr} \rightleftharpoons \text{PhSO}_2\text{NH}_2 + \text{PhSO}_2\text{NBr}_2 \quad (5)$$

$$\text{PhSO}_2\text{NHBr} + \text{H}_2\text{O} \rightleftharpoons \text{PhSO}_2\text{NH}_2 + \text{HOBr} \quad (6)$$

$$\text{PhSO}_2\text{NBr}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{PhSO}_2\text{NH}_2 + 2\text{HOBr} \quad (7)$$

The anion picks up a proton in an acid solution to give the free acid *N*-bromobenzenesulphonamide [reaction (4)]. The free acid undergoes disproportionation and hydrolysis [reactions (5)—(7)].

The probable oxidizing species in an acidified solution of BAB are $PhSO_2NHBr$, $PhSO_2NBr^-$, $PhSO_2NBr_2$, and HOBr. The dibromamine species can be ruled out as an oxidizing species in view of the strict first-order dependence of the reaction rate on BAB. The absence of any effect of BSA on the rate of oxidation also precludes both HOBr and dibromamine-B. This leaves $PhSO_2NHBr$ and its anion as the probable oxidizing species. However, $PhSO_2NHBr$ is a weak acid[9] (p*K* 4.95) and in the acidity range used almost all of BAB will be in the form of the free acid. Thus the most probable oxidizing species is *N*-bromobenzenesulphonamide.

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 follow different mechanistic pathways.

Oxidation of Vicinal Diols.—The hydrogen-ion dependence of the rate of oxidation has the form (8). This suggests that (i) there

$$k_1 = a + b[\text{H}^+] \quad (8)$$

is a rapid equilibrium between the protonated and unprotonated form, (ii) the equilibrium constant has a small value, (iii) both the protonated and unprotonated forms are kinetically reactive, and (iv) the protonated form is more reactive.[11] It is proposed

$$\text{PhSO}_2\text{NHBr} + \text{H}_3\text{O}^+ \rightleftharpoons (\text{PhSO}_2\text{NH}_2\text{Br})^+ + \text{H}_2\text{O} \quad (9)$$

that $PhSO_2NHBr$ is being protonated to yield a stronger oxidant and electrophile, and both $PhSO_2NHBr$ and its protonated form are the reactive oxidizing species. The dependence of the reaction rate on acidity was studied at

Table 6. Temperature dependence and activation parameters for the acid-independent oxidation of vicinal diols by BAB

	10^5k_2/l mol^{-1} s^{-1}							
Compound	303 K	308 K	313 K	318 K	323 K	ΔH^*/ kJ mol^{-1}	ΔS^*/ J mol^{-1} k^{-1}	ΔG^*/ kJ mol^{-1}
Ethanediol	2.58	3.66	5.10	6.82	9.29	49.1 ± 0.5	−171 ± 1	99.8 ± 1.2
Propane-1,2-diol	3.40	4.92	6.52	9.02	12.1	48.8 ± 1.1	−169 ± 3	99.1 ± 1.8
Butane-2,3-diol	4.55	6.40	8.42	11.6	15.0	45.8 ± 0.9	−177 ± 2	98.4 ± 1.6
Butane-1,2-diol	7.59	10.0	14.9	18.8	25.2	46.6 ± 2.0	−170 ± 5	97.2 ± 3.0
Pinacol	8.10	11.0	15.3	19.5	24.6	42.8 ± 1.6	−182 ± 4	96.9 ± 2.4

Table 7. Temperature dependence and activation parameters for the acid-dependent oxidation of vicinal diols by BAB

	10^5k_3/l^2 mol^{-2} s^{-1}							
Compound	303 K	308 K	313 K	318 K	323 K	ΔH^*/ kJ mol^{-1}	ΔS^*/ J mol^{-1} k^{-1}	ΔG^*/ kJ mol^{-1}
Ethanediol	0.92	1.24	1.60	2.13	2.82	42.5 ± 0.7	−201 ± 2	102 ± 1.3
Propane-1,2-diol	1.24	1.65	2.05	2.72	3.45	38.7 ± 0.9	−211 ± 3	101 ± 2.0
Butane-2,3-diol	1.61	2.11	2.90	3.80	4.80	42.4 ± 1.0	−197 ± 2	101 ± 1.5
Butane-1,2-diol	2.75	3.55	4.90	6.25	7.92	41.0 ± 1.1	−197 ± 3	99.6 ± 1.8
Pinacol	3.00	3.94	5.00	6.28	7.53	34.9 ± 1.1	−216 ± 3	99.3 ± 2.0

Table 8. Temperature dependence and activation parameters of the oxidation of non-vicinal diols by BAB

	10^5k_3/l^2 mol^{-2} s^{-1}							
Compound	303 K	308 K	313 K	318 K	323 K	ΔH^*/ kJ mol^{-1}	ΔS^*/ J mol^{-1} k^{-1}	ΔG^*/ kJ mol^{-1}
Propane-1,3-diol	8.75	13.3	23.4	42.0	63.3	80.2 ± 3.1	−58 ± 1.5	97.3 ± 4.2
Butane-1,3-diol	29.2	46.8	69.0	118	170	69.6 ± 2.1	−83 ± 1.3	94.1 ± 3.1
Butane-1,4-diol	14.0	23.6	36.7	62.7	90.0	73.7 ± 2.0	−75 ± 1.0	95.9 ± 2.8
Pentane-1,5-diol	25.0	38.8	63.8	102	150	11.2 ± 1.4	−79 ± 1.0	94.5 ± 2.0
3-Methoxybutan-1-ol	32.0	50.0	77.7	123	190	69.8 ± 0.8	−81 ± 1.0	93.9 ± 1.7

$k_3 = k_1/[\text{diol}][\text{H}^+]$

Table 9. Reaction constants of the oxidation of vicinal diols by BAB

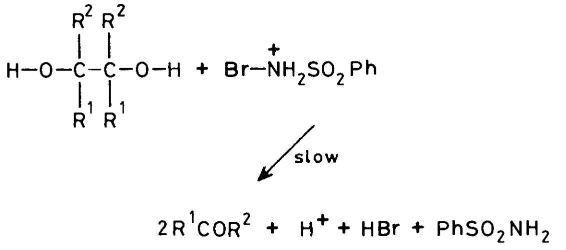
	Acid-independent				Acid-dependent			
T/K	ρ_I	δ	R	SD	ρ_I	δ	R	SD
303	−0.82	−1.19	0.9999	0.003	−0.86	−1.21	0.9995	0.01
313	−0.68	−1.22	0.9991	0.013	−0.74	−1.26	0.9993	0.01
323	−0.53	−1.12	0.9997	0.006	−0.51	−1.19	0.9982	0.02

R = Coefficient of multiple correlation. SD = Standard deviation. Substituent constants were taken from ref. 14.

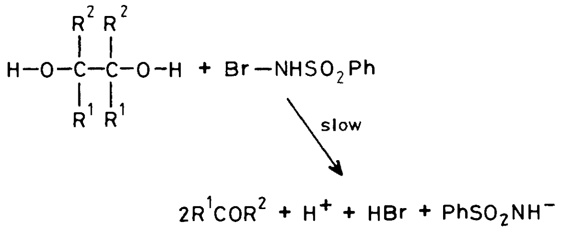
different temperatures and acid-independent and -dependent rate constants were evaluated from linear plots of k_1 against $[\text{H}^+]$. The specific rate constants k_2 and k_3 for the acid-independent and -dependent oxidations of the vicinal diols were obtained from the relations k_2 = a/[diol] and k_3 = b/[diol] respectively.

The linear correlations between log(rate) at 303 and 323 K for both the acid-independent and -dependent reactions (r 0.9974 and 0.9932, respectively) show that an isokinetic relationship exists in the oxidation of vicinal diols by BAB.[12] The values of isokinetic temperature are 581 and 684 K, respectively.[12] 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 same mechanism and the changes in the rates are governed by both entropy and enthalpy of activation.[12] The numerical value of the isokinetic temperature is not accorded much physical meaning.[12] But the fact that the isokinetic temperature is much higher than the experimental temperature range means that the selectivity decreases with an increase in temperature.

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 effects were observed in the oxidations of ethanol[1] and benzyl alcohol[2] by BAB. Thus it seems that the oxidations of monohydric and vicinal diols follow different mechanistic pathways. The rate of an acid-catalysed reaction is expected to be faster in D_2O than in H_2O[13] when a pre-equilibrium protonation is involved. In the present case 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 O–H–O–D exchange may neutralize the rate-enhancing effect of D_2O or even result in an 'inverse' solvent isotope effect. Thus O–H bond rupture in the rate-determining step is indicated. The only mode of oxidation available for pinacol is by 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. The mechanisms in equations (10)—(12) account for the results obtained in the present investigation.



$$H-O-CR^1R^2-CR^1R^2-O-H + Br-\overset{+}{N}H_2SO_2Ph \xrightarrow{slow} 2R^1COR^2 + H^+ + HBr + PhSO_2NH_2 \qquad (10)$$



$$H-O-CR^1R^2-CR^1R^2-O-H + Br-NHSO_2Ph \xrightarrow{slow} 2R^1COR^2 + H^+ + HBr + PhSO_2NH^- \qquad (11)$$

$$PhSO_2NH^- + H^+ \xrightarrow{fast} PhSO_2NH_2 \qquad (12)$$

Correlation of Structure and Reactivity.—The rates of oxidation of vicinal diols failed to show satisfactory correlation with either polar or steric substituent constants.[14] Therefore, the rates were analysed in terms of the dual substituent parameter equation (13).

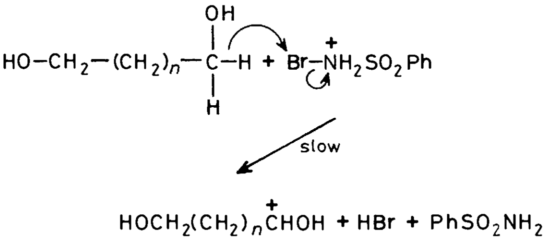
$$\log k/k_0 = \rho_I\Sigma\sigma_I + \delta\Sigma E_s \qquad (13)$$

The results, recorded in Table 9, show that the rates show excellent correlation with polar and steric substituent constants. There is no significant colinearity between $\Sigma\sigma_I$ and ΣE_s (r 0.5224).

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 steric acceleration of the reaction. This is probably due to the 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.

Oxidation of Other Diols.—The linear correlation between log k at 303 and 323 K (r 0.9984, slope 0.8430) for the oxidation of five non-vicinal diols and 3-methoxybutan-1-ol shows that all the compounds are oxidized by the same mechanism.[12] The isokinetic temperature is 500 K. 3-Methoxybutan-1-ol is a typical monohydric alcohol and, therefore, it is highly likely that these diols are oxidized by a mechanism similar to that operative for monohydric alcohols. This is further supported by the similar values of solvent isotope effect obtained in oxidations of propane-1,3-diol and 3-methoxybutan-1-ol.

The observed linear dependence of the reaction rate on the hydrogen ion concentration is parallel to that observed in oxidation of benzyl alcohol[2] and suggests that, in this case, only $(PhSO_2NH_2Br)^+$ is the reactive oxidizing species. The value of the 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 confirms that these diols behave like alcohols towards BAB. Therefore, it is proposed that the rate-determining step in the oxidation of non-vicinal diols involves transfer of a hydride ion to protonated *N*-bromobenzenesulphonamide as has been suggested for alcohols.[1,2]



$$HO-CH_2-(CH_2)_n-CH(OH)-H + Br-\overset{+}{N}H_2SO_2Ph \xrightarrow{slow} HOCH_2(CH_2)_n\overset{+}{C}HOH + HBr + PhSO_2NH_2 \qquad (14)$$

$$HOCH_2(CH_2)_n-\overset{+}{C}HOH \xrightarrow{fast} HOCH_2-(CH_2)_n-CHO + H^+ \qquad (15)$$

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