

Kinetics and mechanism of the oxidation of some vicinal and non-vicinal diols by tetrabutylammonium tribromide

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Abstract. Kinetics of oxidation of five vicinal and four non-vicinal diols, and two of their monoethers, by tetrabutylammonium tribromide (TBATB) has been studied. The vicinal diols yield products arising out of glycol-bond fission, while the non-vicinal diols produce the hydroxycarbonyl compounds. The reaction is first-order with respect to TBATB. Michaelis–Menten type kinetics is observed with respect to diols. The reaction fails to induce the polymerization of acrylonitrile. There is no effect of tetrabutylammonium chloride on the reaction rate. The proposed reactive oxidizing species is the tribromide ion. The effect of solvent composition indicates that the rate increases with increase in the polarity of the solvent. The oxidation of [1,1,2,2-²H₄] ethanediol shows the absence of any primary kinetic isotope effect. Values of solvent isotope effect, $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$, at 288 K for the oxidation of ethanediol, propane-1,3-diol and 3-methoxybutan-1-ol are 3.41, 0.98 and 1.02 respectively. A mechanism involving a glycol-bond fission has been proposed for the oxidation of vicinal diols. Non-vicinal diols are oxidised by a hydride-transfer mechanism, as they are monohydric alcohols.

Keywords. Correlation analysis; vicinal and non-vicinal diols; tetrabutylammonium tribromide.

1. Introduction

Tetraalkylammonium polyhalides are widely used as halogenating reagents in synthetic organic chemistry.^{1–3} Recently, tetrabutylammonium tribromide (TBATB) has been used for the bromination of some selected organic substrates.⁴ There are, however, only a few reports regarding their use as oxidizing and brominating agents in synthetic chemistry.^{5–7} These compounds are more suitable than molecular halogens because of their solid nature, ease of handling, stability, selectivity and excellent product yields. We have been interested in the kinetic and mechanistic studies of the reactions of polyhalides and many reports (including the use of TBATB for oxidation) have already been sent from our laboratory.^{8–10} There seems to be no report on the oxidation of diols by TBATB. However, several oxidations of monohydric alcohols and diols are known to follow different mechanistic pathways, e.g. oxidations by lead (IV),¹¹ periodic acid,¹² acid permanganate,¹³ bromamine-B,¹⁴ and by bromine¹⁵ in acid solutions. Therefore, we have studied the oxidation of several diols by TBATB in aqueous acetic acid solution. The mechanistic aspects are discussed.

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2. Experimental

2.1 Materials

The diols and monoethers used were commercial products (BDH or Fluka) and were distilled under reduced pressure before use. TBATB was prepared by the reported method¹ and its purity checked iodometrically. Acetic acid was purified by the usual methods. [1,1,2,2-²H₄]Ethanediol (DED) was prepared by reducing diethyl oxalate with lithium aluminium deuteride.¹⁶ Its isotopic purity, as determined by its NMR spectrum, was 93 ± 5%. Acetic acid was refluxed with chromic oxide and acetic anhydride for 6 h and then fractionally distilled. All other reagents were commercial products and were purified by the usual methods.¹⁷

2.2 Product analysis

Product analysis was carried out under kinetic conditions. In a typical experiment, the diol (0.1 mol) and TBATB (4.82 g, 0.01 mol) were taken in 100 ml of acetic acid-water (1 : 1 v/v) and the mixture was allowed to stand in the dark for ≈ 12 h to ensure complete reaction. It was then treated overnight with an excess (250 ml) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm⁻³ HCl and kept in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, recrystallized from ethanol and weighed. The DNP derivatives were found to be homogeneous by TLC except for the oxidation of propane-1,2- and butane-1,2-diols. In these cases the mixtures were separated by fractional crystallization. The identities of products were established by comparing the m.p. of the DNP derivatives with the literature values¹⁸. In the oxidation of ethanediol, propane-1,2-diol, and butane-1,2-, -2,3-, -1,3-, and -1,4-diols, the identity of the products was confirmed by taking mixed m.p. with authentic samples of DNP of formaldehyde, acetaldehyde, propionaldehyde, 3-hydroxybutanal and 4-hydroxybutanal respectively. The melting points were obtained in open capillaries and are uncorrected. The results are summarized in table 1.

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

Diol	Product	m.p. of DNP (°C)	Yield ^a
Ethanediol	HCHO	165	91
Propane-1,2-diol	MeCHO, HCHO	145, 165	95
Butane-2,3-diol	MeCHO	145	88
Butane-1,2-diol	EtCHO, HCHO	142, 165	92
Pinacol	MeCOMe	126	96
Propane-1,3-diol	HOCH ₂ CH ₂ CHO	131	93
Butane-1,3-diol	MeCH(OH)CH ₂ CHO	91	92
Butane-1,4-diol	HOCH ₂ CH ₂ CH ₂ CHO	116	89
Pentane-1,5-diol	HOCH ₂ (CH ₂) ₃ CHO	78	86
3-Methoxybutan-1-ol	MeCH(OMe)CH ₂ CHO	104	91
2-Methoxyethanol	MeOCH ₂ CHO	118 ^b	88

^a The yield is that of DNP derivative, after recrystallization, percent

^b Instead of DNP, the 4-nitrophenylhydrazone derivative was prepared

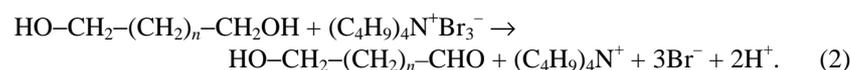
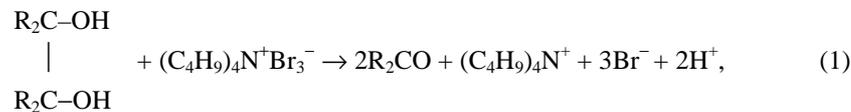
2.3 Kinetic measurements

The reactions were studied under pseudo-first-order conditions by maintaining an excess ($\times 15$ or greater) of the substrate over TBATB. The solvent used was 1:1 (v/v) acetic acid–water, unless mentioned otherwise. Tribromide ion is known to dissociate to a large extent to bromine and bromide ion. The value¹⁹ of the dissociation constant in 1:1 (v/v) acetic acid–water is $\approx 0.02 \text{ mol dm}^{-3}$. To suppress the dissociation, all kinetic runs were carried out in the presence of an excess (0.2 mol dm^{-3}) of potassium bromide. The reactions were studied at constant temperature ($\pm 0.1 \text{ K}$) and were followed by monitoring the decrease in the concentration of TBATB at 394 nm for up to 80% reaction. Pseudo-first-order rate constants, k_{obs} , were evaluated from linear plots ($r > 0.995$) of $\log [\text{TBATB}]$ against time. Duplicate kinetic runs showed that the rate constants are reproducible to within $\pm 3\%$. Simple and multivariate regression analyses were carried out by the least-squares method. The second order rate constant, k_2 , was determined from the relation: $k_2 = k_{\text{obs}}/[\text{diol}]$.

3. Results

3.1 Stoichiometry

The oxidation of vicinal diols by TBATB 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).



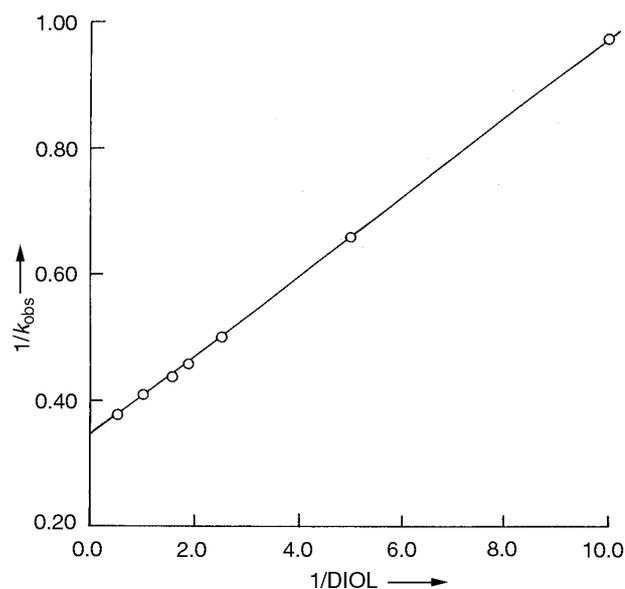
3.2 Rate laws

The reactions are first-order with respect to TBATB. Individual kinetic runs are strictly first-order in TBATB. Further, the first-order rate coefficients do not vary with the initial concentration of the TBATB. The order with respect to the diol is less than one (table 2). The rate increases relatively sharply at lower concentrations but becomes almost constant at higher concentrations. Further, a plot of $1/k_{\text{obs}}$ versus $1/[\text{diol}]$ is linear with an intercept at the rate ordinate (figure 1). Thus Michaelis–Menten type kinetics is observed with respect to the diols. The overall mechanism therefore involves the formation of an intermediate complex before equilibrium and slow disproportionation of the intermediate in the slow step. This leads to the postulation of the following overall mechanism and rate law.



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

10^3 [TBATB] (mol dm ⁻³)	[Diol] (mol dm ⁻³)	$10^4 k_{\text{obs}}$ (s ⁻¹)	
		Ethanediol	Propane-1,3-diol
1.0	0.10	1.03	7.02
1.0	0.20	1.51	10.1
1.0	0.40	1.97	13.1
1.0	0.60	2.18	14.4
1.0	0.80	2.31	15.2
1.0	1.00	2.40	15.7
1.0	2.00	2.59	16.5
2.0	0.20	1.66	10.4
4.0	0.20	1.44	11.2
6.0	0.20	1.65	10.6
8.0	0.20	1.45	10.2
1.0	0.20	1.56 ^a	11.1 ^a

^a Contained 0.05 mol dm⁻³ acrylonitrile**Figure 1.** Double reciprocal plot depicting the dependence of the reaction rate on the concentration of ethanediol. Conditions are given in table 2.

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

Dependence of the concentration of diol was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. 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 3 and 4).

Table 3. Formation constants and thermodynamic parameters of diols-TBATB complexes.

Diol	K (dm ³ mol ⁻¹ s ⁻¹) at (K)				ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)
	288	298	308	318			
Ethane-1,2-diol	6.55	5.83	5.11	4.40	-12.6 ± 0.4	-20 ± 1	-6.83 ± 0.3
Propane-1,2-diol	7.26	6.51	5.73	5.00	-12.0 ± 0.3	-17 ± 1	-7.11 ± 0.3
Butane-2,3-diol	7.01	6.23	5.44	4.71	-12.6 ± 0.4	-19 ± 1	-6.99 ± 0.3
Butane-1,2-diol	6.46	5.68	4.83	4.10	-14.1 ± 0.6	-25 ± 2	-6.75 ± 0.4
Pinacol	7.10	6.28	5.55	4.80	-12.4 ± 0.3	-18 ± 1	-7.03 ± 0.3
Propane-1,3-diol	6.90	6.22	5.51	4.80	-11.7 ± 0.4	-16 ± 1	-7.00 ± 0.3
Butane-1,3-diol	7.38	6.45	5.70	5.00	-12.3 ± 0.1	-18 ± 1	-7.11 ± 0.1
Butane-1,4-diol	6.41	5.61	4.80	4.05	-14.1 ± 0.5	-25 ± 2	-6.73 ± 0.4
Pentane-1,5-diol	7.65	6.88	6.15	5.33	-11.4 ± 0.4	-15 ± 1	-7.25 ± 0.3
3-Methoxybutan-1-ol	6.74	6.00	5.28	4.51	-12.6 ± 0.5	-20 ± 2	-6.91 ± 0.4
2-Methoxyethanol ^a	5.63	4.92	4.25	3.41	-15.0 ± 0.9	-29 ± 3	-6.41 ± 0.7

^aData from ref. 9**Table 4.** Rate constants for the decomposition of TBATB-diol complexes and the activation parameters.

Diol	$10^5 k_2$ (s ⁻¹) at (K)				ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔG^* (kJ mol ⁻¹)
	288	298	308	318			
Ethane-1,2-diol	1.47	2.81	5.33	9.95	47.7 ± 0.9	-159 ± 4	94.2 ± 0.9
Propane-1,2-diol	2.13	3.80	7.31	13.1	46.1 ± 0.9	-162 ± 2	94.2 ± 0.6
Butane-2,3-diol	3.10	5.62	10.2	17.7	44.0 ± 0.7	-166 ± 2	93.4 ± 0.6
Butane-1,2-diol	5.86	10.4	17.5	29.6	41.5 ± 0.9	-172 ± 3	92.6 ± 0.8
Pinacol	6.47	11.3	18.7	31.5	40.3 ± 0.9	-174 ± 3	91.9 ± 0.8
Propane-1,3-diol	7.81	18.3	42.2	101	62.5 ± 0.8	-89 ± 2	88.7 ± 0.6
Butane-1,3-diol	9.91	23.4	54.4	131	61.7 ± 0.7	-92 ± 2	88.1 ± 0.5
Butane-1,4-diol	8.60	20.6	47.0	111	61.6 ± 0.6	-90 ± 2	88.4 ± 0.6
Pentane-1,5-diol	10.8	26.2	61.1	141	60.7 ± 0.9	-92 ± 3	87.9 ± 0.7
3-Methoxy-butan-1-ol	8.41	20.2	46.6	110	62.2 ± 0.8	-88 ± 3	88.4 ± 0.8
2-Methoxy-ethanol ^a	12.8	29.9	68.7	154	61.9 ± 0.9	-87 ± 3	87.7 ± 0.8

^aData from ref. 9

3.3 Induced polymerization of acrylonitrile

Oxidation of diols by TBATB in nitrogen failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate (table 2) Therefore, occurrence of a one-electron oxidation, giving rise to free radicals, is unlikely.

3.4 Kinetic isotope effect

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

The rates of oxidation of ethanediol, propane-1,3-diol and 3-methoxybutane-1-ol were obtained in deuterium oxide (overall 95% D₂O). This set of experiments was carried out in aqueous solutions. The values of $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$ are recorded in table 5.

3.5 Effect of tetrabutylammonium chloride

Addition of tetrabutylammonium chloride (TBACl) had no effect on the rates of oxidation (table 6).

3.6 Effect of solvent composition

The rate of oxidation was determined in solvents containing different amounts of acetic acid and water. It is observed that the rate increases with increase in the amount of water in the solvent mixture. To determine whether the solvent composition affects the formation constant, K , and/or rate constant, k_2 , the variation of rate with the concentration of ethanediol was studied in solutions of different compositions. The results (table 7) show that rate constants, k_2 , vary considerably while the formation constant, K , remains practically independent of solvent composition.

4. Discussion

We have carried out some conductivity measurements to determine the nature of TBATB in aqueous acetic acid solution. It was observed that acetic acid has very low conductivity. Addition of TBATB increases this conductivity. We measured the conductivity of TBATB in solvents containing different proportions of acetic acid (10–30%) as well as in water. We found that the conductivity increases sharply as the water content is initially increased but reaches a limiting value in about 60% acetic acid–water mixture. Therefore, TBATB can be considered an ionic compound, which exists under our reaction conditions in the form of tetrabutylammonium and tribromide ions as in (6)

Table 5. Solvent isotope effect in the oxidation of ethanediol, propane-1,3-diol and 3-methoxy-butan-1-ol by TBATB at 288 K.

Substrate	$10^5 k_2(\text{H}_2\text{O})$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	$10^5 k_2(\text{D}_2\text{O})$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	$k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$
Ethanediol	70.3	20.6	3.41
Propane-1,2-diol	107	109	0.98
3-Methoxybutan-1-ol	176	172	1.02

Table 6. Effect of tetrabutylammonium chloride on the rate of oxidation of ethanol diol by TBATB.

[TBATB] = 0.001 mol dm⁻³; [ethanoldiol] = 1.0 mol dm⁻³; Temp. = 298 K

$10^3[\text{TBACl}]$ (mol dm ⁻³)	0.00	0.5	1.0	2.0	3.0	4.0
$10^5 k_{\text{obs}}(\text{s}^{-1})$	2.44	2.37	2.47	2.41	2.35	2.40

Table 7. Dependence of rate for the oxidation of ethane diol by TBATB on substrate concentration of different solvent composition.[TBATB] = 0.001 mol dm⁻³; Temp. = 298 K

Ethane diol (mol dm ⁻³)	% AcOH (v/v)				
	25	40	50	60	72
0.1	5.52	1.88	1.03	0.54	0.19
0.2	8.00	2.75	1.51	0.78	0.28
0.4	10.3	3.59	1.97	1.00	0.37
0.6	11.4	4.00	2.18	1.11	0.41
0.8	12.0	4.24	2.31	1.17	0.43
1.0	12.5	4.40	2.40	1.21	0.45
1.5	13.1	4.63	2.52	1.27	0.47
3.0	13.8	4.88	2.66	1.33	0.50
<i>K</i> (dm ³ mol ⁻¹)	6.14	5.70	5.83	6.25	5.66
(10 ⁵ <i>k</i> ₂ s ⁻¹)	14.5	5.17	2.81	1.40	0.53

below. The fact that there is no effect on adding more tetrabutylammonium ions also indicates that (6) lies far towards the right.



Tribromide ion is known to dissociate to bromine and bromide ion and the value of the dissociation constant has been reported.¹⁹ However, in the presence of the large excess of bromide ion, the reaction as below is suppressed. Thus, in the present reaction, the reactive oxidising species is the tribromide ion,



Oxidation of alcohols by bromine is reported to be much faster²⁰ as compared to this reaction. This also supports the view that bromine is not the reactive species in this oxidation.

4.1 Solvent composition effect

The increase in the rate of oxidation with increase in the polarity of the medium suggests that the transition state is more polar than the reactants. The plot of log*k*₂ against the inverse of the relative permittivity is nonlinear. The solvent effect was analysed using Grunwald–Winstein equation,²¹

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

The plot of log*k*₂ versus *Y* is linear (*r* = 0.9994) with *m* = 0.77 ± 0.02. The value of *m* suggests a transition state, which is more polar than the reactants. Thus considerable charge separation takes place in the transition state of the reaction.

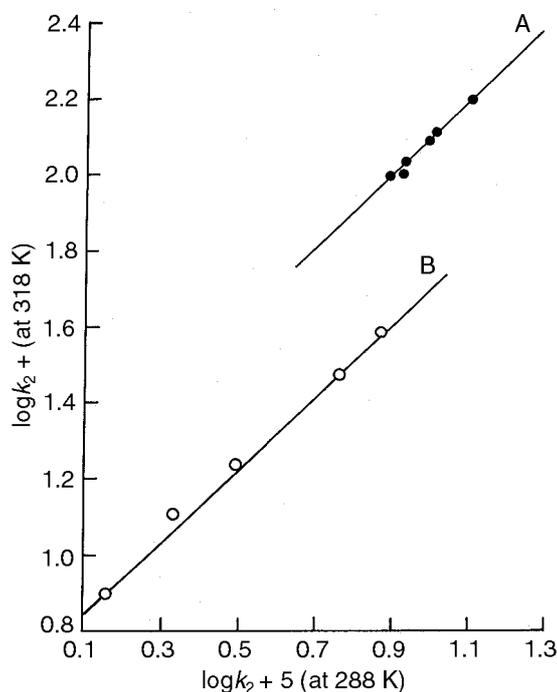


Figure 2. Exner's isokinetic plot. Isokinetic relationship in the oxidation of diols by TBATB: (A) vicinal diols; (B) non-vicinal diols.

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 $\log k_2$ at 288 and 318 K, one for the vicinal diols and another for the others (figure 2).

4.2 Oxidation of vicinal diols

The linear correlation between $\log k_2$ at 288 and 318 K for the oxidation ($r = 0.9998$; slope = 0.7866 ± 0.015) shows that an isokinetic relationship exists in the oxidation of vicinal diols by TBATB.²² The value of the isokinetic temperature is 516 ± 14 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 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. In contrast, substantial primary kinetic isotopic effect was observed in the oxidation of ethanol by TBATB.⁹ Thus it seems that the oxidation of monohydric alcohols and vicinal diols follow 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 come into play. In view of the observed value of solvent isotope effect, an O-H bond cleavage is indicated in the rate-determining step. 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 twice in the case of oxidation of vicinal diols as compared to that of the other compounds (cf. table 4). This points to a more rigid transition state in the oxidation of the vicinal diols. Thus the 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 relationship. The following mechanism (scheme 1) accounts for the observed data.

The observed negative entropy of activation also supports the above mechanism. As charge separation takes place, in the transition state of the rate-determining step, the charged ends become highly solvated. This results in immobilisation of a large number of solvent molecules, as reflected by the loss of entropy.²³

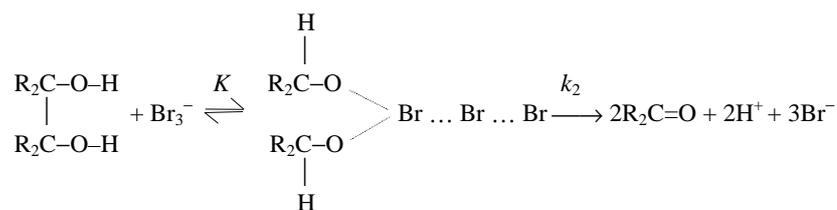
4.3 Correlation of structure and reactivity

The rate of oxidation of the vicinal diols failed to show satisfactory correlation with either the polar or the steric substituent constants.²⁴ Therefore, the rates were analysed in terms of dual substituent-parameter (DSP) equation of Pavelich and Taft²⁵ (table 8),

$$\log k = r_1 \sum s_1 + d \sum E_s + \log k_0. \quad (9)$$

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.

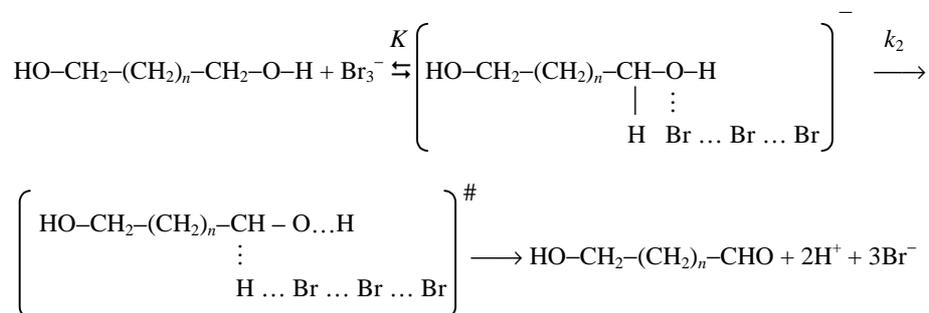
The values of the reaction constants support the proposed mechanism. The negative polar reaction constant accords with the net flow of electrons towards the oxidant. The negative steric reaction constant implies a steric acceleration of the reaction. This is probably due to increase in the steric relief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



Scheme 1.

Table 8. Reaction constants of the oxidation of vicinal diols by TBATB.

T/(K)	r_1	d	R^2	sd
288	-1.09 ± 0.01	-1.51 ± 0.01	0.9999	0.001
298	-1.00 ± 0.01	-1.46 ± 0.05	0.9991	0.012
308	-0.91 ± 0.04	-1.30 ± 0.02	0.9997	0.006
318	-0.82 ± 0.03	-1.21 ± 0.01	0.9998	0.003



Scheme 2.

4.4 Oxidation of other diols

The linear correlation between $\log k_2$ at 288 and 318 K ($r = 0.9937$, slope = 0.8804 ± 0.071) 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.²² 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 of monohydric alcohols. The observed solvent isotope effect suggests that the hydroxy group is not involved either in the rate-determining step or in pre-equilibria. The formation of a hydroxycabonyl compound further confirms that these diols behave like monohydric alcohols towards TBATB. The oxidation of ethanol⁹ by TBATB exhibits a substantial kinetic isotopic effect confirming the cleavage of the α -C-H bond in the rate-determining step. Therefore, a mechanism similar to one proposed earlier⁹ for monohydric alcohols, accounts for the experimental results obtained in the oxidation of non-vicinal diols (scheme 2).

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 charge separation begins in the transition stage, each end of the dipole becomes solvated by a sheath of solvent molecules, which must, however, be suitably oriented.²³ This increase in the orientation means restricted freedom results in a decrease in the entropy.

It is of interest to compare here the activation parameters of the oxidation of the vicinal and non-vicinal diols. The value of enthalpies of activation of the oxidation of vicinal diols are $44 \pm 4 \text{ kJ mol}^{-1}$ whereas those for the non-vicinal diols are in the range of $61 \pm 2 \text{ kJ mol}^{-1}$. 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, reflected in a higher magnitude of negative entropy of activation. These two parameters compensate for each other resulting in almost similar values of the free energy of activation for both vicinal and non-vicinal diols ($91 \pm 3 \text{ kJ mol}^{-1}$).

Acknowledgement

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