Kinetics and Mechanism of Oxidation of Diols by Hexamethylenetetramine–bromine

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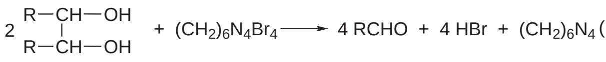
The oxidation of vicinal diols by hexamethylenetetramine–bromine (HABR) proceeds by a glycol-bond fission *via* an intermediate complex whereas non-vicinal diols behave like monohydric alcohols towards HABR.

Hexamethylenetetramine–bromine (HABR) has been reported as an oxidizing reagent in synthetic organic chemistry[1,2] and mechanistic aspects of the oxidation of alcohols by HABR have been reported.[3] However, there seems to be no report on the oxidation of diols by HABR. Here, we report the kinetics of the oxidation of several vicinal and non-vicinal diols, *viz.* ethanediol, propane-1,2-diol, butane-1,2-diol, butane-2,3-diol, pinacol, propane-1,3-diol, butane-1,3-diol, butane-1,4-diol, pentane-1,5-diol and the monoether 3-methoxybutan-1-ol by HABR in glacial acetic acid solution and mechanistic aspects are discussed.

HABR was prepared by the reported method[1] and its purity was checked by an iodometric method. [1,1,2,2-$^2H_4$]Ethanediol (DED) was prepared by reducing diethyl oxalate with lithium aluminium deuteride.[9] The reactions were studied under pseudo-first-order conditions by using a large excess (×15 or greater) of the diols over HABR. The solvent was glacial acetic acid. The reactions were followed by monitoring the decrease in [HABR] at 394 nm for up to 80% reaction. The pseudo-first-order rate constants, k_{obs}, were evaluated from linear least-squares plots of log[HABR] *vs.* time.

The oxidation of vicinal diols by HABR 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 by simple oxidation of one of the hydroxy groups. Analyses of products indicate the overall reactions (1) and (2).



$$2\ \begin{matrix}\mathrm{R{-}CH{-}OH}\\ |\\ \mathrm{R{-}CH{-}OH}\end{matrix} + (CH_2)_6N_4Br_4 \longrightarrow 4\,RCHO + 4\,HBr + (CH_2)_6N_4 \quad (1)$$

$$2\ HO{-}CH_2{-}(CH_2)_n{-}CH_2OH + (CH_2)_6N_4Br_4 \longrightarrow 2\ HO{-}CH_2{-}(CH_2)_n{-}CHO + 4\,HBr + (CH_2)_6N_4 \quad (2)$$

The reaction was found to be first order with respect to HABR. Michaelis–Menten type kinetics are observed with respect to the diols. This leads to the postulation of the following overall mechanism [eqns. (3) and (4)] and rate law (5). The rate constants for the decomposition of the intermediate and the activation parameters are listed in Table 4.

$$\text{Diol} + \text{HABr} \xrightarrow{K} [\text{intermediate}] \quad (3)$$

$$[\text{intermediate}] \xrightarrow{k_2} \text{Products} \quad (4)$$

$$\text{Rate} = k_2K\,[\text{diol}]\,[\text{HABR}]/(1 + K\,[\text{diol}]) \quad (5)$$

The rate of oxidation increased upon the addition of HXA. Oxidation of diols by HABR under a nitrogen atmosphere failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate, thus a one-electron oxidation giving rise to free radicals is unlikely.

In solution, HABR may dissociate to form molecular bromine [eqn. (6)].

$$(CH_2)_6N_4Br_4 \rightleftharpoons 2\,Br_2 + (CH_2)_6N_4 \quad (6)$$

The probable oxidizing species in a solution of HABR are, therefore, HABR itself, molecular bromine and its acetolysis product. Addition of HXA should result in the suppression of the decomposition of HABR. Therefore, the rate-enhancing effect of HXA and strict first order dependence on HABR rule out both bromine and its acetolysis product as the reactive oxidizing species.

A study of UV–VIS spectra of HABR (0.001 mol dm^{-3}) and an equivalent amount of bromine (0.002 mol dm^{-3}), in acetic acid at *ca.* 293 K, showed that the difference in the spectra of HABR and bromine was not very striking but

Table 4 Rate constants and activation parameters of the decomposition of diol–HABR complexes

	$10^5\,k_2/s^{-1}$						
Diol	288 K	298 K	308 K	318 K	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$\Delta G^‡$/kJ mol^{-1}
Ethane-1,2-diol	0.87	1.58	3.20	5.95	46.7 ± 1.1	−180 ± 4	100 ± 0.9
Propane-1,2-diol	1.23	2.25	4.21	7.80	44.4 ± 0.7	−185 ± 2	99.5 ± 0.6
Butane-2,3-diol	1.72	3.10	5.65	10.2	42.7 ± 0.7	−188 ± 2	98.7 ± 0.5
Butane-1,2-diol	2.53	4.21	7.73	13.3	40.0 ± 1.0	−195 ± 3	97.9 ± 0.8
Pinacol	3.45	5.51	10.1	16.6	37.9 ± 1.2	−199 ± 4	97.2 ± 0.9
Propane-1,3-diol	2.76	7.10	17.1	44.0	67.4 ± 1.1	−99 ± 4	97.6 ± 0.9
Butane-1,3-diol	4.65	11.8	29.8	73.9	67.6 ± 0.8	−93 ± 3	95.4 ± 0.6
Butane-1,4-diol	3.98	10.1	24.5	62.8	67.2 ± 1.1	−96 ± 4	95.8 ± 0.9
Pentane-1,5-diol	4.81	13.1	31.2	79.6	68.2 ± 0.9	−91 ± 3	95.2 ± 0.7
3-Methoxybutane-1-ol	5.43	15.2	35.6	90.2	68.1 ± 0.9	−90 ± 3	94.9 ± 0.7
2-Methoxyethanol[a]	8.00	20.1	49.3	120	66.1 ± 0.7	−94 ± 2	94.1 ± 0.6

[a] Data from ref. 3.

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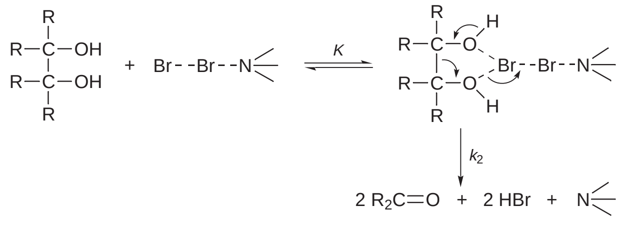
their optical densities showed variations while HXA showed no appreciable absorption in this range. Further the spectrum of HABR did not show any change over the experimental time period (*ca.* 2 h). When a solution of HABR in acetic acid was evaporated to dryness under reduced pressure, HABR was recovered unchanged. This confirmed that HABR retained its identity in acetic acid.

The diverse nature of the products formed in the oxidation of vicinal and non-vicinal diols suggests that these compounds follow different mechanistic pathways. This is further supported by the two linear plots obtained for log k_2 at 288 and 318 K, one for the vicinal diols and another for the non-vicinal diols.

Oxidation of the vicinal diol [1,1,2,2–$^2H_4$]ethanediol showed an absence of a primary kinetic isotope effect. This confirms that the α-C–H bond is not cleaved in the rate-determining step.

The magnitude of the negative entropy of activation is almost doubled in the oxidation of vicinal diols compared to that of non-vicinal diols. This points to a more rigid transition state in the oxidation of the vicinal diols and 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 bonds between carbinol carbon atoms. That the other vicinal diols follow this mechanism is confirmed by the isolation of the products formed by C–C bond fission and the isokinetic relationship.

The observed Michaelis–Menten kinetics with respect to the diol lead us to suggest that an intermediate complex may be formed by the interaction between non-bonded pairs of electrons of diol-oxygen and HABR in a rapid pre-equilibrium. Thus on the basis of all the above experimental facts, the mechanism given in Scheme 1 is proposed.



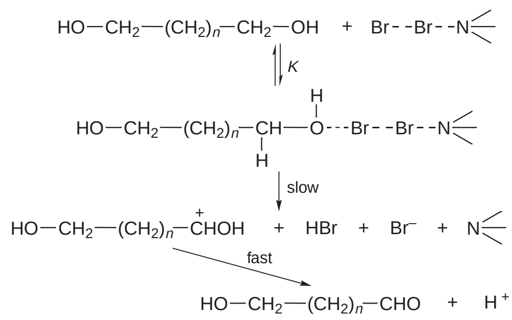
Scheme 1

The formation constants of the HABR–diol complexes are not sensitive to the structure of the diol. However, the rate constants k_2 showed considerable variation. Although the rate constants did not show satisfactory correlation with either the polar or the steric substituent constants,[15] excellent correlations were obtained in terms of the dual substituent parameter (DSP) equation (7) of Pavelich and Taft.[16]

$$\log k = \rho_I \Sigma\sigma_I + \delta\Sigma E_s + \log k_0 \qquad (7)$$

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 probably due to an increase in the steric relief on going from tetrahedral (sp^3) carbon atoms to trigonal (sp^2) ones, with increasing substitution at the carbon.

The linear correlation between log k_2 at 288 and 318 K ($r = 0.9948$, slope $= 0.9613 \pm 0.0492$) for the oxidation of four non-vicinal diols, 3-methoxybutan-1-ol and 2-methoxyethanol shows that all the compounds are oxidized *via* the same mechanism.[12] 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 proposed for the monohydric alcohols[3] (Scheme 2).



Scheme 2

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Techniques used: Spectrophotometry, correlation analysis

Schemes: 2

References: 17

Figure: 1

Table 1: Analysis of products in the oxidation of diols by HABR

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

Table 3: Formation constants and thermodynamic parameters of the diol–HABR complexes

Table 5: Reaction constants of the oxidation of vicinal diols by HABR

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