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# OXIDATION OF SUBSTITUTED ETHANOLS BY SODIUM *N*-BROMOBENZENESULPHONAMIDE: A KINETIC STUDY

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## ABSTRACT

The kinetics of the oxidation of seven substituted ethanols by sodium *N*-bromobenzenesulphonamide or bromamine-B (BAB) in the presence of HCl was studied at 45 °C. The rate shows a first-order dependence on $[\mathrm{BAB}]_0$ and is fractional in $[\text{alcohol}]_0$, $[\mathrm{H}^+]$ and $[\mathrm{Cl}^-]$. Ionic strength variations, addition of benzenesulphonamide reaction product and variation of dielectric constant of the medium have no effect on the rate. The solvent isotope effect $k'_{\mathrm{H_2O}}/k'_{\mathrm{D_2O}} \approx 0{\cdot}97$. The rates do not correlate satisfactorily with Taft's substituent constants. Activation parameters $\Delta H^{\ne}$, $\Delta S^{\ne}$, $\Delta G^{\ne}$ and log $A$ were calculated by studying the reaction at different temperatures (308–323 K). It was found that $\Delta H^{\ne}$ and $\Delta S^{\ne}$ are linearly related and an isokinetic relationship is observed with isokinetic temperature $\beta = 393$ K, indicating enthalpy as a controlling factor.

## INTRODUCTION

Considerable attention has centred around the chemistry of *N*-metallo-*N*-aryl halosulphonamides because of their versatility in behaving as mild oxidants, halogenating agents and *N*-anions, which act as both bases and nucleophiles. The chlorine compound chloramine-T (CAT), which is a by-product during saccharin manufacture, is well known as an analytical reagent for the determination of diverse substrates, and mechanistic aspects of these reactions have been documented.[1,2] However, there is meagre information in the literature on the bromine analogues, bromamine-T (BAT) and bromamine-B (BAB). The pioneering work of Hardy and Johnston[3] on the oxidation of *p*-nitrophenol by BAB and the study of the reaction of dialkyl sulphides with BAT by Ruff and Kucsman[4] are two important examples, and recent investigations include the kinetics of oxidation of α-amino acids,[5] methionine,[6] dimethyl sulphoxide,[7] primary alcohols,[8] substituted benzyl alcohols[9] and diphenylmethanol,[10] ketones[11] and EDTA[12] by the bromamines.

The mechanism of the oxidation of primary alcohols to aldehydes by mild to strong oxidants has been investigated by several workers. Waters[13] suggested that the conversion occurs either by a series of facile reactions in which the OH group is first involved or by a concerted process in which both CH and OH groups are severed together. Mahadevappa and Naidu[14] and Herlihy[15] have reported on the oxidation of the conjugated alcohols allyl, cinnamyl and crotyl

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alcohols by CAT in HCl medium. The rate is found to be first order each in [CAT], [$H^+$] and [$Cl^-$]. Similar results have been obtained with CAB.[16] Mushran *et al.*[17] oxidized n-butanol, isobutanol and n-pentanol with CAT. The proposed mechanism involves HOCl as the reactive species. Uma and Mayanna[18] reported the oxidation of primary alcohols by CAT in alkaline medium, catalysed by $OsO_4$. Oxidation of primary alcohols by CAB in the presence of $HClO_4$ was reported by Mukherji and Banerji.[19] The probable oxidizing species is $PhSO_2NHCl$. A mechanism involving transfer of hydride ion to the oxidant was suggested. Gunasekaran and Venkatasubramanian reported the kinetics of the oxidation of substituted diphenylmethanols[20] and substituted fluoren-9-ols[21] by BAT. Singh *et al.*[22] investigated the mechanism of the ruthenium(III)-catalysed oxidation of methanol and ethanol by BAT in acid medium. Similar results[23] were obtained in the oxidation of n-propanol and n-butanol by BAT.

As a part of our mechanistic studies of the oxidation of substrates by *N*-aryl bromosulphonamides, we report here on the kinetics of the oxidation of seven primary alcohols, ethanol, 2-ethoxyethanol, 2-methoxyethanol, 2-aminoethanol, 2-chloroethanol, 2-bromoethanol and 2-nitroethanol, by BAB in the presence of HCl at 45 °C.

## EXPERIMENTAL

### Preparation of bromamine-B

Bromamine-B (BAB) was prepared[24] by the partial debromination of dibromamine-B (DBB), which was obtained as follows. Pure chlorine was bubbled through an aqueous solution of chloramine-B (30 g in 560 ml of water) and liquid bromine (6 ml) was added dropwise from a burette with constant stirring. The yellow precipitate of DBB that formed was thoroughly washed with water, filtered under suction and dried in a vacuum desiccator. Dibromamine-B (31·5 g) was digested in small batches with costant stirring in 50 ml of 4 mol $dm^{-3}$ NaOH. The mass was cooled in ice, filtered under suction and the product dried over anhydrous calcium chloride.

The purity of BAB was checked iodimetrically through its active bromine content and the compound was further characterized by its $^{13}C$ FT-NMR spectrum (obtained on a Bruker WH 270-MHz nuclear magnetic resonance spectrometer) with $D_2O$ as solvent and TMS as the internal standard (ppm relative to TMS) 143·38 (C-1, carbon attached to S atom), 134·30 (CH, *para* to the hetro atom), 131·26 (C-2,6), 129·31 (C-3,5). An aqueous solution of BAB was standardized iodimetrically and preserved in brown bottles to prevent its photochemical deterioration.

AnalaR-grade alcohols were further distilled. All other reagents were of AnalaR grade. Triply distilled water was employed in preparing the aqueous solutions. The ionic strength was kept constant at a high value by adding a concentrated solution of $NaClO_4$. Heavy water ($D_2O$, 99·2%) was supplied by the Bhabha Atomic Research Centre, Trombay.

### Kinetic measurements

The reaction was carried out in glass-stoppered Pyrex boiling tubes whose outer surface was coated black to eliminate photochemical effects. Solutions containing appropriate amounts of alcohol, HCl and water (to keep the total volume constant for all runs), were placed in the tube and thermostated at 45 °C. A measured amount of BAB solution, also thermostated at the same temperature, was rapidly added to the mixture. The progress of the reaction was monitored by withdrawing aliquots from the reaction mixtures at regular time intervals and determining the unreacted BAB iodimetrically. The course of the reaction was studied up to two half-lives. The calculated pseudo-first-order rate constants, $k'$, were reproducible to within ±3%.

Regression analysis of the experimental data to obtain the regression coefficient $r$ and $s$, the standard deviation of the points from the regression line, was carried out a EC-72 statistical calculator.

## Stoichiometry

Various ratios of BAB to alcohol were equilibrated in the presence of 0·1 mol dm$^{-3}$ HCl for 24 h. The determination of unconsumed BAB exhibited a 1:1 stoichiometry:

$$\mathrm{RNBrNa} + \mathrm{R'CH_2CH_2OH} \rightarrow \mathrm{RNH_2} + \mathrm{R'CH_2CHO} + \mathrm{Na^+} + \mathrm{Br^-} \qquad (1)$$

where $\mathrm{R{=}C_6H_5SO_2}$ and $\mathrm{R'{=}H}$ for ethanol, $\mathrm{OC_2H_5}$ for 2-ethoxyethanol, $\mathrm{OCH_3}$ for 2-methoxyethanol, $\mathrm{NH_2}$ for 2-aminoethanol, Cl for 2-chloroethanol, Br for 2-bromoethanol and $\mathrm{NO_2}$ for 2-nitroethanol.

## Product analysis

Benzenesulphonamide among the reaction products was detected by thin-layer chromatography, using light petroleum–chloroform–n-butanol (2:2:1, v/v) as the solvent system and iodine as the spray reagent ($R_F = 0{\cdot}88$). The corresponding aldehydes were determined as their 2,4-dinitrophenylhydrazone (2,4-DNP) derivatives.

## RESULTS

## Effect of reactants

With the substrate in excess, at constant [HCl] and [alcohol]$_0$, plots of log [BAB] vs time are linear ($r > 0{\cdot}9909$), indicating a first-order dependence of rate on [BAB]$_0$. Values of the first-order rate constants, $k'$, increase with increase in [alcohol]$_0$ (Table 1). Plots of log $k'$ vs log[alcohol]$_0$ are linear ($r > 0{\cdot}9970$; $s \leqslant 0{\cdot}02$) with slopes of 0·54 (ethanol), 0·59 (2-ethoxyethanol), 0·60 (2-methoxyethanol), 0·52 (2-aminoethanol), 0·43 (2-chloroethanol), 0·60 (2-bromoethanol) and 0·85 (2-nitroethanol), thus indicating a fractional order dependence on [alcohol]$_0$.

Table 1. Effect of concentration of alcohol on the rate of reaction[a]

| | $k' \times 10^4$ (s$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| $10^2$[alcohol]$_0$ (mol dm$^{-3}$) | Ethanol | 2-Ethoxy-ethanol | 2-Methoxy-ethanol | 2-Amino-ethanol | 2-Chloro-ethanol | 2-Bromo-ethanol | 2-Nitro-ethanol |
| 5·0 | 2·85 | 1·61 | 1·27 | 0·22 | 0·55 | 2·56 | 7·21 |
| 10·0 | 4·08 | 2·41 | 1·86 | 0·31 | 0·74 | 3·91 | 10·67 |
| 20·0 | 5·82 | 3·56 | 2·70 | 0·43 | 0·97 | 5·60 | 16·14 |
| 30·0 | 7·40 | 4·69 | 3·55 | 0·56 | 1·22 | 7·65 | 19·80 |
| 40·0 | 8·81 | 5·52 | 4·52 | 0·65 | 1·35 | 9·07 | 24·32 |

[a] [BAB]$_0 = 9{\cdot}0 \times 10^{-4}$ mol dm$^{-3}$; [HCl] = 0·1 mol dm$^{-3}$; $\mu = 1{\cdot}0$ mol dm$^{-3}$; temperature = 45 °C.

## Effect of [HCl]

The rate increases with increase in [HCl] and plots of log $k'$ vs log[HCl] are linear ($r > 0{\cdot}9957$; $s \leqslant 0{\cdot}02$) with fractional slopes (0·4–0·7).

## Effect of [H$^+$]

At constant [Cl$^-$] = 0·6 mol dm$^{-3}$, maintained by adding NaCl, the rate increased with increase in [H$^+$] (Table 2), which was varied by adding HCl and a plot of log $k'$ vs log[H$^+$] was linear ($r > 0{\cdot}9947$; $s \leqslant 0{\cdot}02$) with a fractional slope (0·2–0·4).

## Effect of halide ions

At constant [H$^+$] = 0·1 mol dm$^{-3}$, the rate increased with the addition of NaCl (Table 2) and a plot of log $k'$ vs log[Cl$^-$] was linear ($r > 0{\cdot}9933$; $s \leqslant 0{\cdot}01$) with a fractional slope (0·2–0·3). Addition of Br$^-$ ions in the form of NaBr ($5 \times 10^{-4}$–$20 \times 10^{-4}$ mol dm$^{-3}$) had a negligible effect on the rate.

## Effect of benzenesulphonamide

Addition of the reaction product, benzenesulphonamide ($5 \times 10^{-4}$–$20 \times 10^{-4}$ mol dm$^{-3}$), had a negligible effect on the rate, indicating that it is not involved in a pre-equilibrium to the rate-limiting step.

## Effect of ionic strength

Variation of the ionic strength of the medium by adding NaClO$_4$ (0.2–1.0 mol dm$^{-3}$) had no effect on the rate.

Table 2. Effect of [H$^+$] and [Cl$^-$] on the rate of reaction[a]

| | $k' \times 10^4$(s$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| 10$^2$[H$^+$] or 10$^2$[NaCl] (mol dm$^{-3}$) | Ethanol | 2-Ethoxy-ethanol | 2-Methoxy-ethanol | 2-Amino-ethanol | 2-Chloro-ethanol | 2-Bromo-ethanol | 2-Nitro-ethanol |
| | A[b] B[b] | A B | A B | A B | A B | A B | A B |
| 5·0(10·0) | 4·80(4·08) | 3·22(2·41) | 2·08(1·86) | 0·33(0·31) | 0·82(0·74) | 4·52(3·91) | 12·58(10·67) |
| 10·0(20·0) | 6·21(4·81) | 4·24(2·98) | 2·77(2·15) | 0·42(0·35) | 1·02(0·85) | 5·43(4·55) | 14·11(12·00) |
| 20·0(40·0) | 8·28(5·55) | 5·33(3·70) | 3·59(2·48) | 0·56(0·41) | 1·34(0·97) | 6·98(5·12) | 16·60(13·63) |
| 30·0(60·0) | 10·05(5·98) | 6·10(4·12) | 4·26(2·71) | 0·67(0·45) | 1·55(1·08) | 4·74(5·65) | 17·96(14·98) |
| 40·0(80·0) | 11·50(6·50) | 6·96(4·53) | 4·83(2·93) | 0·74(0·48) | 1·70(1·20) | 8·65(5·99) | 19·48(16·11) |
| 60·0(—) | 13·07(—) | 8·02(—) | 5·59(—) | 0·83(—) | 1·89(—) | 9·78(—) | 22·07(—) |

[a] $[\mathrm{BAB}]_0 = 9{\cdot}0 \times 10^{-4}$ mol dm$^{-3}$; [HCl] = 0·1 mol dm$^{-3}$; $\mu = 1{\cdot}0$ mol dm$^{-3}$; temperature = 45 °C.

[b] A, Variation of [H$^+$] on the rate of reaction at constant [Cl$^-$] = 0·6 mol dm$^{-3}$; B, variation of [Cl$^-$] on the rate of reaction at constant [H$^+$] = 0·1 mol dm$^{-3}$.

### Effect of temperature on the rate

The reaction was studied at different temperatures (308–323 K), and from the Arrhenius plots ($r > 0{\cdot}9974$) of log $k'$ vs $1/T$ values of the activation parameters for the overall reaction were calculated.

### Solvent isotope studies

Studies of the rate in $D_2O$ medium for ethanol and 2-bromoethanol revealed that while $k'_{\mathrm{H_2O}}$ is $4{\cdot}08 \times 10^{-4}\,\mathrm{s}^{-1}$ and $3{\cdot}91 \times 10^{-4}\,\mathrm{s}^{-1}$, $k'_{\mathrm{D_2O}}$ is $4{\cdot}19 \times 10^{-4}\,\mathrm{s}^{-1}$ and $4{\cdot}10 \times 10^{-4}\,\mathrm{s}^{-1}$, respectively. The solvent isotope effect $k'_{\mathrm{H_2O}}/k'_{\mathrm{D_2O}} \approx 0{\cdot}97$.

### Effect of varying dielectric constant of medium

The dielectric constant of the medium was varied by adding methanol (0–40%, v/v) to the reaction mixture, but the rates were not significantly altered. Blank experiments with methanol indicated that oxidation of methanol was negligible during the period of the experiment.

### Test for free radicals

Addition of the reaction mixtures to acrylamide did not initiate polymerizations, showing the absence of free-radical species.

## DISCUSSION

The experimental rate law was found to be Rate $= k[\mathrm{BAB}]\,[\mathrm{alcohol}]^x[\mathrm{HCl}]^y$, where $x$ and $y$ are fractions.

Bromamine-B, being analogous[25] to CAT, behaves like a strong electrolyte in aqueous solutions and dissociates as

$$\mathrm{RNBrNa} \rightleftharpoons \mathrm{RNBr^-} + \mathrm{Na^+} \tag{2}$$

The anion picks up a proton in acidic solutions to give the free acid monobromamine-B, RNHBr (*N*-bromobenzenesulphonaminde):

$$\mathrm{RNBr^-} + \mathrm{H^+} \underset{K_a}{\rightleftharpoons} \mathrm{RNHBr} \tag{3}$$

where $K_a = 1{\cdot}5 \times 10^{-5}$ at 25 °C. The free acid has not been isolated. It undergoes disproportionation giving rise to benzenesulphonamide ($\mathrm{RNH_2}$) and dibromamine-B ($\mathrm{RNBr_2}$):

$$2\,\mathrm{RNHBr} \overset{K_d}{\rightleftharpoons} \mathrm{RNH_2} + \mathrm{RNBr_2} \tag{4}$$

where $K_d = 5{\cdot}8 \times 10^{-2}$ at 25 °C. Dibromamine-B and the free acid hydrolyse to give hypobromous acid (HOBr):

$$\mathrm{RNBr_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{RNHBr} + \mathrm{HOBr} \tag{5}$$

$$\mathrm{RNHBr} + \mathrm{H_2O} \overset{K'_h}{\rightleftharpoons} \mathrm{RNH_2} + \mathrm{HOBr} \tag{6}$$

where $K_h' = 4{\cdot}21 \times 10^{-3}$. Finally, HOBr ionizes as

$$\mathrm{HOBr} \xrightleftharpoons{K_a} \mathrm{H^+} + \mathrm{OBr^-} \tag{7}$$

where $K_a = 2{\cdot}0 \times 10^{-9}$ at 25 °C.

The possible oxidizing species in acidified BAB solutions are therefore RNHBr, $RNBr_2$ and HOBr. If $RNBr_2$ were to be the reactive species, then from equation (4) the rate law should predict a second-order dependence of rate on $[\mathrm{BAB}]_0$, which is contrary to experimental observations. Further, equation (6) indicates that the hydrolysis is slight and, if HOBr is primarily involved, a first-order retardation of the rate by the added benzenesulphonamide is expected. However, no such effect was noticed. Hardy and Johnston[3] made detailed calculations of the concentration dependence of conjugate acid, HOBr and $BrO^-$ ion on pH, in aqueous BAB solutions ($6 \times 10^{-3}$ mol dm$^{-3}$) in the pH range 7–13. It is seen from their results that [RNHBr] is high at pH 7 and is of the order of $4{\cdot}1 \times 10^{-5}$ mol dm$^{-3}$, while $[\mathrm{HOBr}] \approx 6{\cdot}0 \times 10^{-6}$ mol dm$^{-3}$ and $[\mathrm{BrO^-}] \approx 10^{-7}$ mol dm$^{-3}$. A comparison with the concentration of species present in acidified CAT solution indicates that RNHBr is the likely oxidizing species in acidic medium for reacting with the substrates. Further, variation of ionic strength of the medium or addition of the reaction product benzenesulphonamide has virtually no effect on the rate, ruling out HOBr as the active species. Hence RNHBr is responsible for the oxidation of alcohols. In view of these facts, proton catalysis of the oxidation of alcohols by BAB at constant $[\mathrm{Cl^-}]$ can be explained by Scheme 1:

$$\mathrm{RNHBr} + \mathrm{H^+} + \mathrm{S} \xrightleftharpoons{K_1} \mathrm{X} \qquad \text{(fast)}$$

$$\mathrm{X} \xrightarrow[\mathrm{H_2O}]{k_2} \text{products} \qquad \text{(rate limiting)}$$

Scheme 1

From Scheme 1, if $[\mathrm{BAB}]_t$ represents the total BAB concentration, then $[\mathrm{BAB}]_t = [\mathrm{RNHBr}] + [\mathrm{X}]$, from which the rate law

$$-\frac{d[\mathrm{BAB}]}{dt} = \frac{k_2K_1[\mathrm{BAB}]_t[\mathrm{H^+}][\mathrm{S}]}{1 + K_1[\mathrm{H^+}][\mathrm{S}]} \tag{8}$$

can be derived. Rate law (8) is in agreement with the fractional orders noted with respect to $[\mathrm{H^+}]$ and $[\text{alcohol}]_0$ and the first-order dependence of rate on $[\mathrm{BAB}]_0$.

Since Rate = $k'[\mathrm{BAB}]$, equation (8) can be transformed into

$$k' = \frac{k_2K_1[\mathrm{H^+}][\mathrm{S}]}{1 + K_1[\mathrm{H^+}][\mathrm{S}]} \tag{9}$$

and

$$\frac{1}{k'} = \frac{1}{k_2K_1[\mathrm{H^+}][\mathrm{S}]} + \frac{1}{k_2} \tag{10}$$

From the slope and intercept of the double reciprocal plot, $1/k'$ vs $1/[\mathrm{H^+}]$ ($r > 0{\cdot}9826$), values of the formation constant $K_1$ and the decomposition constant $k_2$ have been calculated (Table 3).

The decomposition constant $k_2$ for the rate-limiting step was also determined by varying $[\text{alcohol}]_0$ at different temperatures (308–323 K) and the values are given in Table 4. Using these values, activation parameters for the decomposition step of the alcohol–BAB complex (Scheme 1) were determined by an Arrhenius plot of log $k_2$ vs $1/T$ ($r > 0{\cdot}9928$). These are shown in Table 5.

## Solvent isotope effect

It is interesting that the rate increased only slightly in $D_2O$ medium, contrary to expectations in proton-catalysed reactions.[26] It is well known that $D_3O^+$ is a stronger acid than $H_3O^+$ (ca 2–3 times) and hence a rate increase of the same magnitude is expected in $D_2O$. However, it should be noted that the rate decreases in $D_2O$ when O—H/O—D exchange takes place and

Table 3. Values of formation constants $K_1$ and $K_1'$ and decomposition constants $k_2$ and $k_2'$ from double reciprocal plots

| Alcohol | $K_1$(dm$^6$ mol$^{-2}$) | $K_1'$(dm$^6$ mol$^{-2}$) | $10^4k_2$(s$^{-1}$) | $10^4k_2'$(s$^{-1}$) |
|---|---|---|---|---|
| Ethanol | 106·9 | 152·7 | 13·2 | 6·6 |
| 2-Ethoxyethanol | 130·2 | 102·4 | 7·9 | 4·8 |
| 2-Methoxyethanol | 111·6 | 158·5 | 5·6 | 3·0 |
| 2-Aminoethanol | 119·5 | 163·4 | 0·9 | 0·5 |
| 2-Chloroethanol | 129·9 | 154·6 | 2·0 | 1·2 |
| 2-Bromoethanol | 167·8 | 169·5 | 9·5 | 6·1 |
| 2-Nitroethanol | 280·9 | 183·2 | 20·7 | 16·1 |

Table 4. Values of the decomposition constant ($k_2$) of acohol–BAB complex at different temperatures[a]

| | $k' \times 10^4$(s$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| Temperature (K) | Ethanol | 2-Ethoxy-ethanol | 2-Methoxy-ethanol | 2-Amino-ethanol | 2-Chloro-ethanol | 2-Bromo-ethanol | 2-Nitro-ethanol |
| 308 | 4·63 | 2·39 | 1·71 | 0·20 | 0·39 | 3·91 | 13·52 |
| 313 | 7·17 | 4·85 | 3·44 | 0·45 | 0·83 | 7·61 | 20·78 |
| 318 | 10·47 | 7·11 | 5·40 | 0·76 | 1·51 | 11·68 | 30·57 |
| 323 | 16·11 | 13·43 | 10·07 | 1·44 | 2·74 | 17·19 | 44·72 |

[a] $[BAB]_0 = 9{\cdot}0 \times 10^{-4}$ mol dm$^{-3}$; [alcohol] $= 0{\cdot}1$ mol dm$^{-3}$; [HCl] $= 0{\cdot}1$ mol dm$^{-3}$; $\mu = 1{\cdot}0$ mol dm$^{-3}$.

Table 5. Kinetic and thermodynamic parameters for the oxidation of alcohols by BAB in the presence of hydrochloric acid calculated from the values of $k_2$ shown in Table 4

| Alcohol | $E_a$ (kJ mol$^{-1}$) | $\Delta H^{\ddagger}$ (kJ mol$^{-1}$) | $\Delta S^{\ddagger}$ (J K$^{-1}$ mol$^{-1}$) | $\Delta G^{\ddagger}$ (kJ mol$^{-1}$) | Log $A$ |
|---|---|---|---|---|---|
| Ethanol | 73·4 | 65·4 | −96·9 | 95·9 | 9·4 |
| 2-Ethoxyethanol | 92·0 | 89·4 | −24·1 | 97·0 | 13·2 |
| 2-Methoxyethanol | 95·5 | 92·9 | −15·7 | 97·8 | 13·6 |
| 2-Aminoethanol | 107·2 | 104·3 | + 3·9 | 103·1 | 14·5 |
| 2-Chloroethanol | 106·1 | 104·3 | +11·3 | 101·4 | 14·7 |
| 2-Bromoethanol | 81·3 | 78·7 | −54·6 | 95·9 | 11·5 |
| 2-Nitroethanol | 65·8 | 63·2 | −95·2 | 93·2 | 9·3 |

the O—H/O—D bond is cleaved during the reaction. It is therefore likely that, since the protonation step is followed by hydrolysis where the normal kinetic isotope effect, $k'_H/k'_D > 1$ due to the OH/OD exchange could counterbalance the solvent isotope effect, $k'_{H_2O}/k'_{D_2O} < 1$, during pre-equilibrium fast proton transfer and the net result makes $k'_H/K'_D \geqslant 1$.

## Chloride catalysis

The reaction is catalysed by $Cl^-$ ion and chloride catalysis at constant $[H^+]$ can be rationalized by Scheme 2:

$$RNHBr + Cl^- + S \underset{}{\overset{K'_1}{\rightleftharpoons}} X \qquad \text{(fast)}$$

$$X \xrightarrow[H_2O]{k'_2} \text{product} \qquad \text{(rate limiting)}$$

Scheme 2

Scheme 2 leads to the rate law

$$\text{Rate} = \frac{k'_2 K'_1 [BAB]_t [S] [Cl^-]}{1 + K'_1 [S] [Cl^-]} \tag{11}$$

Equation (11) can be transformed into

$$k' = \frac{k'_2 K'_1 [BAB]_t [S] [Cl^-]}{1 + k'_1 [S] [Cl^-]} \tag{12}$$

and

$$\frac{1}{k'} = \frac{1}{k'_2 K'_1 [S] [Cl^-]} + \frac{1}{k'_2} \tag{13}$$

A double reciprocal plot of $1/k'$ vs $1/[cl^-]$ ($r > 0{\cdot}9881$) provides the values of $k'_2$ and $K'_1$ (Table 3).

## Mixed order found in [HCl]

Oxidation of alcohols by BAB is catalysed by both $H^+$ and $Cl^-$ ions and the mixed-order kinetics observed in [HCl] can be rationalized in terms of the equations

$$\text{Rate} = k_{obs}[BAB] = a[BAB][H^+][\text{alcohol}] + b[BAB][Cl^-] \tag{14}$$

and

$$k_{obs} = \{a[S] + b\}[HCl] \tag{15}$$

since $[H^+] = [Cl^-] = [HCl]$ in aqueous solution.

Equation (15) predicts that a plot of $k_{obs}/[HCl]$ vs [S] should be a straight line ($r > 0.9919$), from which $a$ and $b$ can be evaluated. This is found to be the case, as shown in Figure 1.

## Effect of varying dielectric constant of medium

The effect of varying solvent composition on the rate of reaction has been described in

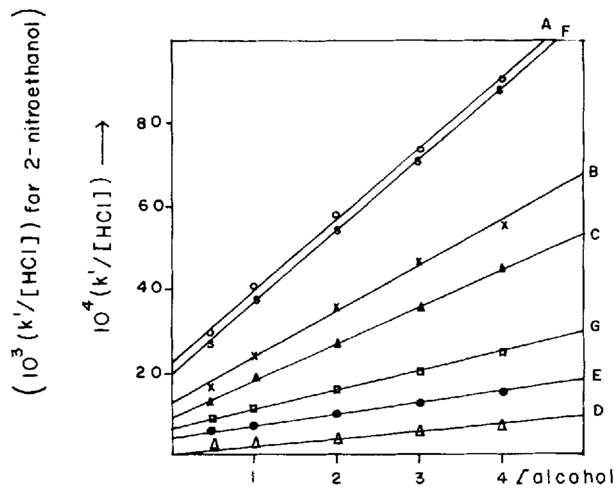


Figure 1. Plots of $k'/[HCl]$ vs $[alcohol]_0$: (A) ethanol; (B) 2-ethoxyethanol; (C) 2-methoxyethanol; (D) 2-aminoethanol; (E) 2-chloroethanol; (F) 2-bromoethanol; (G) 2-nitroethanol

detail.[27–32] For the limiting case of zero angle of approach between two dipoles or an ion–dipole system, Amis[31] has shown that a plot of log $k_{obs}$ vs $1/D$, where $D$ is the dielectric constant of the medium, gives a straight line with a negative slope for a reaction between a negative ion and a dipole or between two dipoles, where a positive slope results for a positive ion–dipole interaction. The total absence of the effect of varying dielectric constant on rate cannot be explained by the Amis theory.[31] Applying the Born equation, Laidler[28c] derived the following for a dipole–dipole reaction:

$$\ln k' = \ln k_0 + \frac{3}{8kT}\left(\frac{2}{D}-1\right)\left[\frac{\mu_A^2}{r_A^3}+\frac{\mu_B^2}{r_B^3}-\frac{\mu_\ddagger^2}{r_\ddagger^3}\right] \quad (16)$$

where $k_0$ is the rate constant in a medium of infinite dielectric constant, $\mu$ represents the dipole moment and $r$ refers to the radii of the reactants and activated complex. It is seen that the rate should be greater in a medium of lower dielectric constant, when $r_\ddagger^3 > r_A^3 + r_B^3$. On the other hand, $r_\ddagger^3 \approx r_A^3 + r_B^3$ implies the absence of a dielectric effect of solvent on the rate, as was observed in the present investigations, signifying that the transition state is not very different from the reactants.

## Structure–reactivity correlations

Structure–reactivity correlations made by attempting to fit the Taft equation[33] through single parameters $\sigma^*$ and $E_s$ and through the four-parameter form of the Pavelich–Taft equations,[34] $\log k/k_0 = \sigma^*\rho^* + \delta E_s$, were not satisfactory. A plot of log $k_2$ vs $\sigma^*$ is curved, as shown in Figure 2. This suggests a concerted mechanism, the degree of concertedness depending on whether the hydride transfer from the C—H bond to the oxidant is synchronous with the removal of a proton from the O—H group by a water molecule. In earlier work on the oxidation of primary alcohols by BAT[8b] and BAB,[35] it was noted that electron-donating groups increase the rate. This indicates that the rupture of the C—H bond occurs ahead of O—H bond cleavage, creating a carbonium ion centre which is stabilized by the electron-donating character

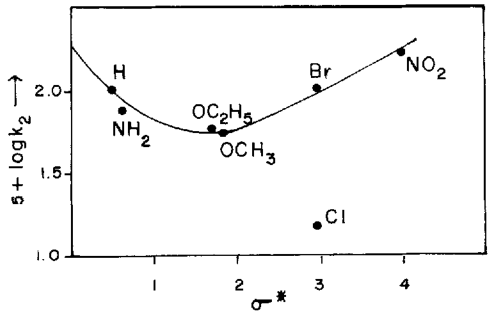
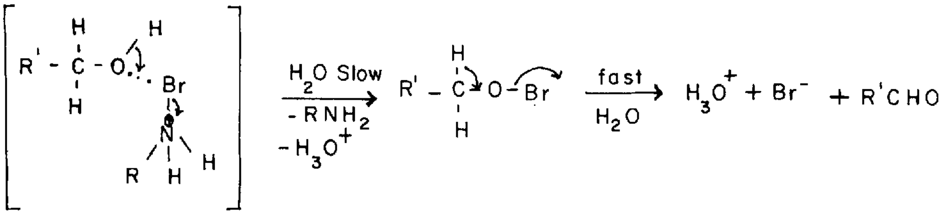
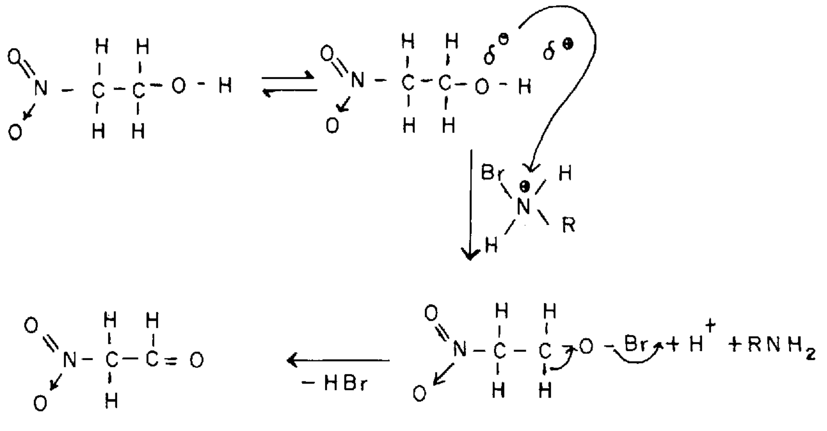


Figure 2. Plot of log $k_2$ vs $\sigma^*$



Scheme 3



Scheme 4

of alkyl groups. In the presence case (Scheme 3), the decrease in rate with electron-withdrawing groups is in agreement with this observation. On the other hand, the rates are higher when the substituent X is Br or $NO_2$. The rupture of O—H bond then occurs ahead of the C—H bond cleavage and the carbon atom becomes electron rich in the transition state, which is stabilized by the electron-withdrawing bromo and nitro groups. The enormous three-fold increase in rate with $X = NO_2$ may alternatively be explained by Scheme 4, where ionization of nitroethanol is a likely process with the oxygen of alcohol acquiring a slightly polar character, thus facilitating the electrophillic attack by the positive halogen.

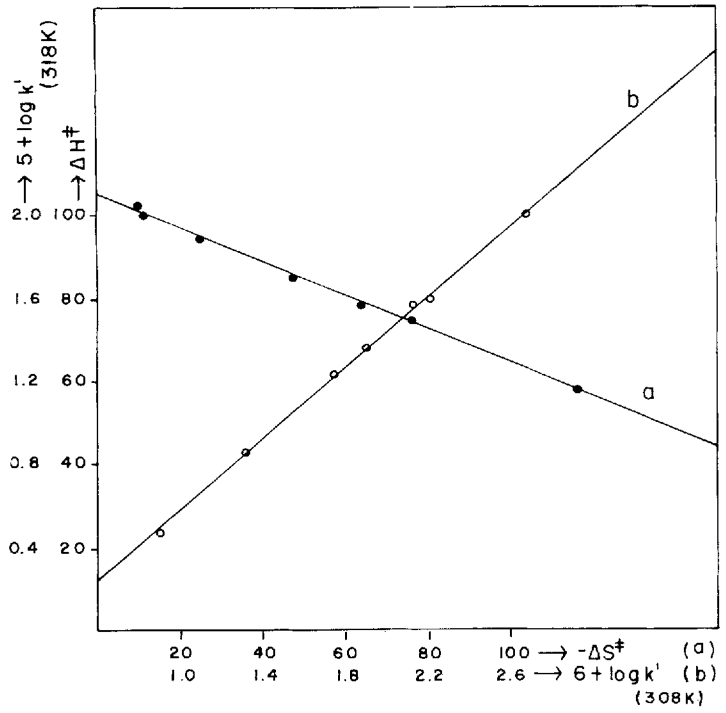


Figure 3. Isokinetic plots of (a) $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ and (b) log $k'_{(318K)}$ vs log $k'_{(308K)}$

### Isokinetic relationship

It is seen from Table 5 that the activation energy is highest for the slowest reaction, indicating that the reaction is enthalpy controlled. Further, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be correlated linearly (Figure 3; $r = 0{\cdot}9913$), resulting in an isokinetic relationship. From the slope, the value of the isokinetic temperature $\beta$ is 393 K, which is much higher than the experimental temperature. The relationship was proved to be genuine through the Exner criterion[36] by plotting low $k'_{318\,K}$ vs log $k'_{308\,K}$ (Figure 3; $r = 0{\cdot}9987$). The value of $\beta$ was calculated from the equation

$$\beta = \frac{T_1(1 - q)}{(T_1/T_2) - q}$$

where $q$ is the slope of the Exner plot; $\beta$ was found to be 398 K.

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