

## Mechanistic investigations of the oxidation of phenethyl alcohols by sodium-N-bromo-benzenesulphonamide in acid medium

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**Abstract.** The kinetics of oxidation of six substituted phenethyl alcohols ( $X-C_6H_4-CH_2-CH_2-OH$  where  $X = -H, -Cl, -Br, -CH_3, -OCH_3$  and  $-NO_2$ ) by sodium-N-bromo-benzenesulphonamide or bromamine-B (BAB) in the presence of HCl at 35°C showed that the rate has first-order dependence on  $[BAB]_0$  and  $[H^+]$  and fractional order on  $[PEA]_0$  and  $[Cl^-]$ . Ionic strength variations, addition of reaction product of benzenesulphonamide and variation of dielectric constant of the medium have no effect on the rate. The solvent isotope effect  $k^1(H_2O)/k^1(D_2O) \simeq 0.82$ . Proton inventory studies have been made in  $H_2O-D_2O$  mixtures. The Hammett plot is biphasic and the reaction constant  $\rho$  was  $-3.2$  for electron-releasing substituents and  $-0.34$  for electron-withdrawing groups. The activation parameters  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  follow an isokinetic relationship.

**Keywords.** Phenethyl alcohols; bromamine-B; oxidation kinetics; oxidation of phenethyl alcohols.

### 1. Introduction

Considerable attention has centred around the chemistry of N-metallo-N-arylhalosulphonamides generally known as organic haloamines, because of their versatility in behaving as mild oxidants, halogenating agents and N-anions, which act as both bases and nucleophiles. The important 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. Mechanistic aspects of many of these reactions have been documented (Campbell and Johnson 1978; Mahadevappa *et al* 1981, 1984). Recently, sodium-N-bromo-benzenesulphonamide or bromamine-B (BAB) has been introduced as an oxidant and this reagent in aqueous solution can specifically oxidise primary and secondary alcohols (Mahadevappa and Ananda 1985; Mahadevappa and Puttaswamy 1989; Mohan *et al* 1990) to aldehydes and ketones respectively, in good yields under very mild conditions.

Mild oxidation of alcohols to carbonyl compounds is a very important operation in organic synthesis. Although considerable work has been done on mechanistic studies involving oxidations of alcohols by transition metal ions such as chromium (VI), vanadium (V), cobalt (III), manganese (VII), cerium (IV) in acid medium (Wiberg 1965) and with copper (II) (Trahanovsky 1973) and ruthenium tetroxide in alkaline medium

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and ferrate (VI) ion (Richards 1969; Andette *et al* 1972) not much information is available in the literature concerning the oxidation of different alcohols by organic haloamines in acid medium. After examining several oxidising reagents, we found in BAB an excellent oxidant to perform controlled oxidation of alcohols to carbonyl compounds and this system is adaptable for large-scale operations. To shed some light on the mechanism of BAB oxidation of alcohols, we have studied the reactions of six substituted phenethyl alcohols (PEA) with this oxidant. Optimum conditions for the formation of phenacetaldehyde, which is an important constituent of perfumes and is an intermediate in many organic synthesis, have been ascertained. The Hammett free energy relationship has been deduced together with the other thermodynamic parameters.

## 2. Experimental

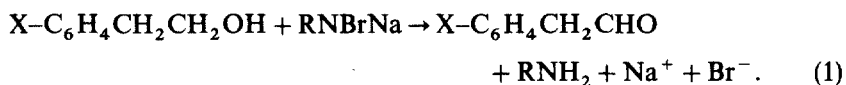
Bromamine-B (BAB) was prepared by the method of Ahmed and Mahadevappa (1980). Its purity was checked by iodometry and by UV, IR and NMR spectra. An aqueous solution of the compound was prepared, iodometrically standardized and stored in brown bottles to prevent its photochemical deterioration. Phenethyl alcohols (Aldrich) were of accepted grades of purity and were used without further purification. Solutions of the compounds were prepared in water. All other reagents were of analytical grades of purity. Doubly distilled water was employed in the preparation of aqueous solutions. The ionic strength of the system was maintained at a constant high value using a concentrated solution of  $\text{NaClO}_4$ . Solvent isotope studies were made with  $\text{D}_2\text{O}$  (99.4%) supplied by the Bhabha Atomic Research Centre (Bombay). Regression analysis of experimental data was carried out using an EC-72 statistical calculator.

### 2.1 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 PEA, HCl and water (to keep the total volume constant for all runs), were placed in the tube and thermostatted at  $35^\circ\text{C}$ . A measured amount of BAB solution, also thermostatted 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 iodometrically. The course of reaction was studied up to two half-lives. The calculated pseudo-first order rate constants,  $k^1$ , were reproducible to within  $\pm 3\%$ .

### 2.2 Stoichiometry

Various ratios of BAB to PEA were equilibrated in the presence of  $0.1 \text{ mol dm}^{-3}$  HCl for 24 hours. The determination of unconsumed BAB in the reaction mixture showed that one mole of PEA consumed one mole of BAB,



Here, X = -H, -Cl, -Br, - $\text{CH}_3$ , - $\text{OCH}_3$  and - $\text{NO}_2$  and R =  $\text{C}_6\text{H}_5\text{SO}_2$ .

The reaction products were subjected to column chromatography on silica gel. (60–200 mesh) using gradient elution (dichloro methane to chloroform). After initial

**Table 1.** Effect of varying reactant concentrations on the rate.  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ ,  $\mu = 0.5 \text{ mol dm}^{-3}$ , temperature =  $35^\circ\text{C}$ 

$10^4[\text{BAB}]_0$ ( $\text{mol dm}^{-3}$ )	$10^3[\text{PEA}]_0$ ( $\text{mol dm}^{-3}$ )	$10^4 k^1$ ( $\text{s}^{-1}$ )	$10^4[\text{BAB}]_0$ ( $\text{mol dm}^{-3}$ )	$10^3[\text{PEA}]_0$ ( $\text{mol dm}^{-3}$ )	$10^4 k^1$ ( $\text{s}^{-1}$ )
2.0	10.0	6.22	5.0	5.0	3.62
5.0	10.0	5.98	5.0	8.0	5.00
8.0	10.0	5.75	5.0	10.0	5.98
10.0	10.0	5.56	5.0	20.0	9.90
15.0	10.0	5.65	5.0	30.0	13.95
20.0	10.0	5.98	5.0	40.0	17.50
-	-	-	5.0	50.0	19.50

**Table 2.** Effect of varying  $[\text{HCl}]$ ,  $[\text{H}^+]$  and  $[\text{Cl}^-]$  on the rate.  $[\text{BAB}]_0 = 0.0005 \text{ mol dm}^{-3}$ ,  $[\text{PEA}]_0 = 0.01 \text{ mol dm}^{-3}$ ,  $\mu = 0.5 \text{ mol dm}^{-3}$ , temperature =  $35^\circ\text{C}$ 

$[\text{HCl}]$ ( $\text{mol dm}^{-3}$ )	$10^4 k^1$ ( $\text{s}^{-1}$ )	$[\text{H}^+]^a$ ( $\text{mol dm}^{-3}$ )	$10^4 k^1$ ( $\text{s}^{-1}$ )	$[\text{Cl}^-]^b$ ( $\text{mol dm}^{-3}$ )	$10^4 k^1$ ( $\text{s}^{-1}$ )
0.08	3.92	0.10	9.52	0.20	7.70
0.10	5.98	0.15	14.00	0.25	8.90
0.15	10.92	0.20	18.12	0.30	10.57
0.20	19.28	0.25	22.45	0.35	11.23
0.30	38.25	0.30	28.25	0.40	12.35
0.40	58.65	0.35	33.12	0.50	15.26
—	—	0.40	38.26	—	—

<sup>a</sup> $[\text{Cl}^-] = 0.4 \text{ mol dm}^{-3}$  (constant); <sup>b</sup> $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$  (constant)

separation the products were further purified by recrystallization. Materials were identified by comparison with commercially available samples.

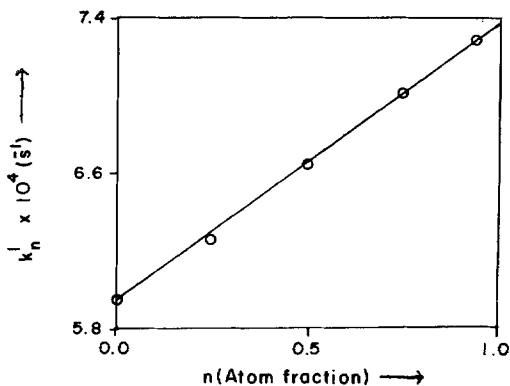
Phenacetaldehyde was recrystallized from dichloromethane/petroleum ether, (m.p. =  $32\text{--}33^\circ\text{C}$ ), known m.p. =  $33\text{--}34^\circ\text{C}$  (Merck index 11, 7236). The phenacetaldehyde was further identified by its 2,4-dinitro phenylhydrazone (2,4-DNP) derivative. It was recrystallized from ethanol (recovery 67.8%) and was found to be identical with the DNP derivative of an authentic sample.

Benzenesulphonamide ( $\text{RNH}_2$ ) was recrystallized from dichloromethane/petroleum ether (m.p. =  $149\text{--}151^\circ\text{C}$ ), known m.p. =  $150\text{--}152^\circ\text{C}$  (Beil 11, 39).  $R_f$  value of 0.36 was determined from TLC using ( $\text{CH}_2\text{Cl}_2 + \text{CHCl}_3$ , 7:3, v/v) as the solvent system and iodine as the spray reagent.

### 3. Results

With the substrate in excess, at constant  $[\text{HCl}]$  and  $[\text{PEA}]_0$ , plots of  $\log [\text{BAB}]$  vs time are linear ( $r > 0.998$ ), indicating a first-order dependence of rate on  $[\text{BAB}]_0$ . Values of pseudo-first order rate constants ( $k^1$ ) are given in table 1 (average  $10^4 k^1 = 5.86 \pm 0.20(\text{s}^{-1})$ ).

The rate increases initially with increase in  $[\text{PEA}]_0$ . A plot of  $\log k^1$  vs  $\log [\text{PEA}]_0$  was linear ( $r = 0.997$ , table 1) with a fractional slope (0.75). The rate increases with increase in  $[\text{HCl}]$  and plot of  $\log k^1$  vs  $\log [\text{HCl}]$  was linear ( $r = 0.999$ , table 2) with



**Figure 1.** Proton inventory plot of  $k_n^1$  vs the deuterium atom fraction 'n' in  $H_2O-D_2O$  mixtures.  $[BAB]_0 = 0.0005 \text{ mol dm}^{-3}$ ,  $[PEA]_0 = 0.01 \text{ mol dm}^{-3}$ ,  $[HCl] = 0.1 \text{ mol dm}^{-3}$ ,  $\mu = 0.5 \text{ mol dm}^{-3}$ , temperature =  $35^\circ\text{C}$ .

**Table 3.** Proton inventory studies for PEA in  $H_2O-D_2O$  mixtures.

$[BAB]_0 = 0.0005 \text{ mol dm}^{-3}$ ,  $[PEA]_0 = 0.01 \text{ mol dm}^{-3}$ ,  $[HCl] = 0.1 \text{ mol dm}^{-3}$ ,  $\mu = 0.5 \text{ mol dm}^{-3}$ , temperature =  $35^\circ\text{C}$

Atom fraction of deuterium (n)	$10^4 k_n^1 (s^{-1})$
0.000	5.98
0.250	6.26
0.500	6.62
0.753	7.00
0.947	7.30

**Table 4.** Temperature dependence of the oxidation of 4-substituted PEA by BAB.

$[BAB]_0 = 0.0005 \text{ mol dm}^{-3}$ ,  $[PEA]_0 = 0.01 \text{ mol dm}^{-3}$ ,  $[HCl] = 0.1 \text{ mol dm}^{-3}$ ,  $\mu = 0.5 \text{ mol dm}^{-3}$ , MeOH = 5% (v/v), X = substituent at position 4

X	$10^4 k^1 (s^{-1})$ at temperature (K)			
	303	308	313	318
$\text{NO}_2$	1.99	2.69	3.76	4.96
Cl	2.72	3.80	5.92	7.45
Br	3.45	4.10	7.48	10.62
H	4.26	5.98	9.87	13.99
$\text{CH}_3$	13.36	19.95	23.66	34.62
$\text{OCH}_3$	32.17	44.66	69.26	99.28

a slope of 1.66. At constant  $[Cl^-] = 0.4 \text{ mole dm}^{-3}$ , maintained by adding NaCl, the rate increased with increase in  $[H^+]$ , which was varied by adding HCl and a plot of  $\log k^1$  vs  $\log [H^+]$  was linear ( $r = 0.998$  table 2) with unit slope. At constant

**Table 5.** Kinetic and thermodynamic parameters for the oxidation of 4-substituted phenethyl alcohols by BAB.

[BAB]<sub>0</sub> = 0.0005 mol dm<sup>-3</sup>, [X-PEA]<sub>0</sub> = 0.01 mol dm<sup>-3</sup>, [HCl] = 0.1 mol dm<sup>-3</sup>, μ = 0.5 mol dm<sup>-3</sup>, MeOH = 5% (v/v), X = substituent at position 4

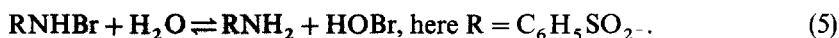
X	<i>E<sub>a</sub></i> (kJ mol <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$-\Delta S^\ddagger$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )
NO <sub>2</sub>	42.1	39.5 ± 0.1	184.7 ± 0.3	96.8 ± 0.3
Cl	51.0	48.4 ± 0.1	152.9 ± 0.2	95.9 ± 0.5
Br	53.0	50.4 ± 0.1	144.6 ± 0.4	95.3 ± 0.6
H	60.9	58.3 ± 0.1	116.8 ± 0.4	95.6 ± 0.6
CH <sub>3</sub>	65.8	63.2 ± 0.1	99.0 ± 0.4	91.9 ± 0.5
OCH <sub>3</sub>	72.0	69.4 ± 0.1	77.3 ± 0.5	89.4 ± 0.4

[H<sup>+</sup>] = 0.1 mol dm<sup>-3</sup>, the rate increased with the addition of NaCl and a plot of log *k*<sup>1</sup> vs log [Cl<sup>-</sup>] was linear (*r* = 0.998, table 2) with a fractional slope (0.70). Addition of Br<sup>-</sup> ions in the form of NaBr (5 × 10<sup>-4</sup> – 20 × 10<sup>-4</sup> mol dm<sup>-3</sup>) had a negligible effect on the rate. Addition of the reaction product, BSA (5 × 10<sup>-4</sup> – 20 × 10<sup>-4</sup> mol dm<sup>-3</sup>) had a negligible effect on the rate, indicating that it is not involved in a pre-equilibrium to the rate-limiting step.

Variation of the ionic strength of the medium by adding NaClO<sub>4</sub> (0.2–1.0 mol dm<sup>-3</sup>) had no effect on the rate. 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. Studies of the rate in D<sub>2</sub>O medium for PEA revealed that while *k*<sup>1</sup>(H<sub>2</sub>O) is 5.98 × 10<sup>-4</sup> s<sup>-1</sup>, *k*<sup>1</sup>(D<sub>2</sub>O) is 7.30 × 10<sup>-4</sup> s<sup>-1</sup>. The solvent isotope effect *k*<sup>1</sup>(H<sub>2</sub>O)/*k*<sup>1</sup>(D<sub>2</sub>O) was 0.82. Proton inventory studies have been made by carrying out the reaction in H<sub>2</sub>O–D<sub>2</sub>O mixtures with varying atom fractions 'n' of deuterium (figure 1; table 3). The reaction was studied at different temperatures (303–318 K), and from the Arrhenius plots of log *k*<sup>1</sup> vs 1/*T*, values of the activation parameters for the composite reaction were calculated (tables 4 and 5). Addition of the reaction mixtures to acrylamide did not initiate polymerization, showing the absence of free radical species.

#### 4. Discussion

Several types of equilibria are present in aqueous acidic solutions of BAB (Hardy and Johnston 1973; Mahadevappa *et al* 1985).



If RNBr<sub>2</sub> were to be the reactive species, then the rate law predicts a second-order dependence of rate on [BAB]<sub>0</sub>, which is contrary to the experimental observations. If

HOBr is primarily involved, a first-order retardation of rate by the added benzenesulphonamide ( $\text{RNH}_2$ ) is expected. Since no such effect is noticed, HOBr can be ruled out as the oxidising species. Hence  $\text{RNHBr}$  is responsible for the oxidation of phenethyl alcohols. In view of these facts, scheme 1 can be proposed for the oxidation of PEA by BAB:

Scheme 1 assumes the formation of a tight ion pair ( $\text{X}^1$ ), which is an intermediate, and at the same time indicates simultaneous catalysis by  $\text{H}^+$  and  $\text{Cl}^-$  ions (Gilliom 1970). The latter reacts with PEA through an equilibrium step to form a PEA-BAB complex (Y) which decomposes in a rate-limiting step to the products. The fractional order on  $[\text{PEA}]_0$  indicates a pre-equilibrium step (ii) in scheme 1. Assuming  $[\text{BAB}]_t = [\text{RNHBr}] + [\text{X}^1] + [\text{Y}]$ , rate law (6) can be derived for the oxidation of phenethyl alcohols by BAB,

$$-\frac{d[\text{BAB}]}{dt} = \frac{k_3 K_1 K_2 [\text{BAB}]_t [\text{H}^+] [\text{Cl}^-] [\text{PEA}]_0}{1 + K_1 [\text{H}^+] [\text{Cl}^-] \{1 + K_2 [\text{PEA}]_0\}} \quad (6)$$

Since  $[\text{H}^+] = [\text{Cl}^-] = [\text{HCl}]$  in aqueous solutions, (6) is converted into

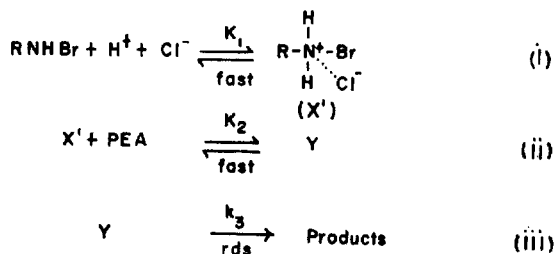
$$-\frac{d[\text{BAB}]}{dt} = \frac{k_3 K_1 K_2 [\text{BAB}]_t [\text{HCl}]^2 [\text{PEA}]_0}{1 + K_1 [\text{HCl}]^2 \{1 + K_2 [\text{PEA}]_0\}} \quad (7)$$

Since  $\text{rate} = k_{\text{obs}}[\text{BAB}]$ , (7) can be transformed into

$$\frac{1}{k^1} = \frac{1}{k_3 K_2 [\text{PEA}]_0} \left\{ \frac{1}{K_1 [\text{HCl}]^2} + 1 \right\} + \frac{1}{k_3} \quad (8)$$

From the double reciprocal plots (figures 2 and 3) of  $k^1$  vs  $[\text{PEA}]_0$  and  $k^1$  vs  $[\text{HCl}]^2$ , values of  $k_3$ ,  $K_1$  and  $K_2$  are evaluated. Using  $k_3$  values ( $1.66 \times 10^{-3}$ ,  $2.94 \times 10^{-3}$ ,  $5.00 \times 10^{-3}$  and  $6.25 \times 10^{-3} \text{ s}^{-1}$  at 303, 308, 313 and 318 K respectively) obtained by varying  $[\text{PEA}]_0$  at each temperature (figure 2), activation parameters were determined for the rate-limiting step:  $E_a = 74.4 \text{ kJ mole}^{-1}$ ,  $\Delta H^\ddagger = 71.8 \pm 0.1 \text{ kJ mole}^{-1}$ ,  $\Delta S^\ddagger = -73.2 \pm 0.3 \text{ JK}^{-1} \text{ mole}^{-1}$ . The values of equilibrium constants  $K_1$  and  $K_2$  are 4.5 and  $568 \text{ dm}^3 \text{ mol}^{-1}$  at 308 K respectively.

A detailed mode of oxidation of phenethyl alcohols by BAB and the structure of the intermediates can be seen in scheme 2. It is interesting to note that the rate increases only slightly in  $\text{D}_2\text{O}$  medium. Since  $\text{D}_3\text{O}^+$  ion is a stronger acid than  $\text{H}_3\text{O}^+$  ion by a factor of 2–3, a solvent isotope effect of this magnitude is to be expected. But the slight increase in  $\text{D}_2\text{O}$  medium shows that since the protonation step is followed by hydrolysis involving the O–H bond scission, the normal kinetic isotope effect  $k_H/k_D > 1$  could probably counter balance the solvent-isotope effect. Proton inventory studies in



Scheme 1.

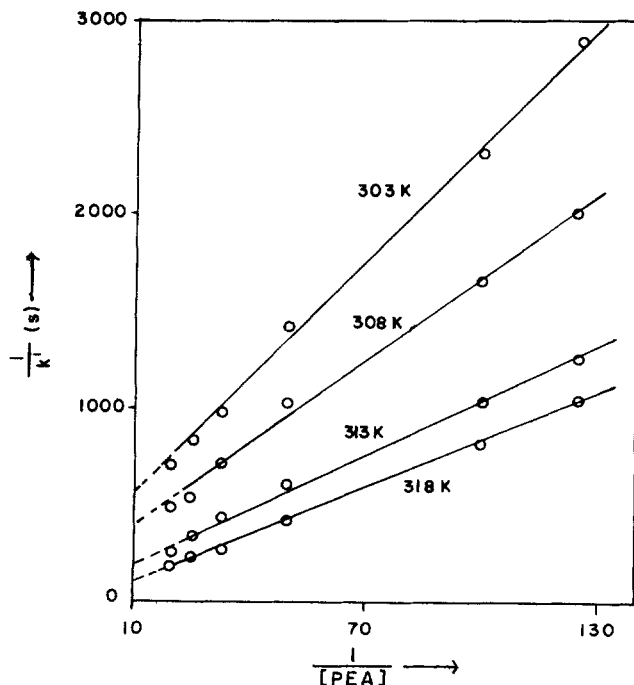


Figure 2. Double reciprocal plots of  $k^1$  vs  $[\text{PEA}]_0$  at 303, 308, 313 and 318 K.  $[\text{BAB}]_0 = 0.0005 \text{ mol dm}^{-3}$ ,  $[\text{PEA}]_0 = 0.01 \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ ,  $\mu = 0.5 \text{ mol dm}^{-3}$ , temperature =  $35^\circ\text{C}$ .

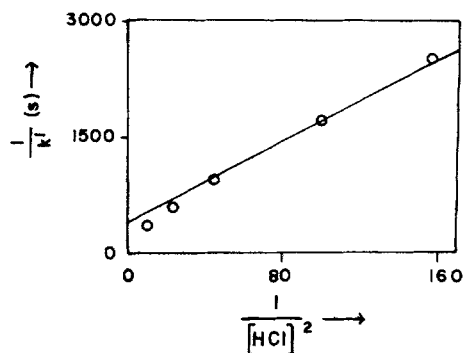
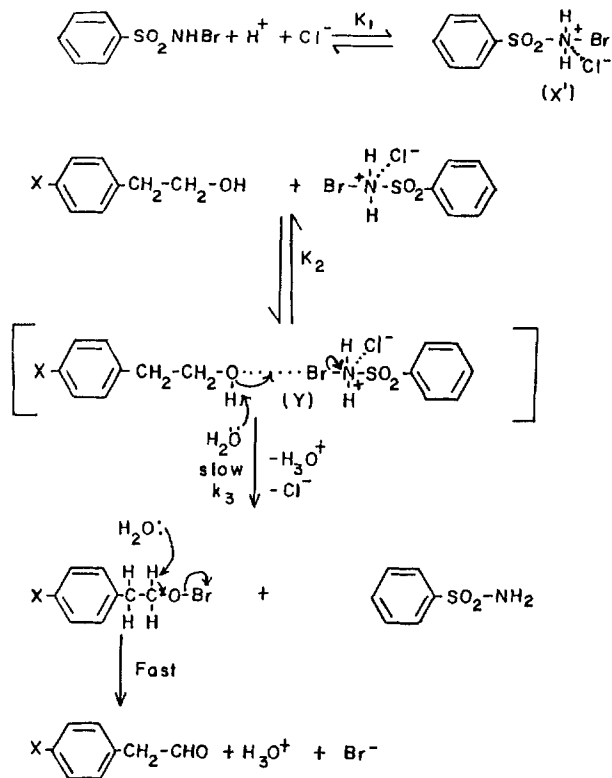


Figure 3. Double reciprocal plot of  $k^1$  vs  $[\text{HCl}]^2$  at  $35^\circ\text{C}$ .  $[\text{BAB}]_0 = 0.0005 \text{ mol dm}^{-3}$ ,  $[\text{PEA}]_0 = 0.01 \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ ,  $\mu = 0.5 \text{ mol dm}^{-3}$ , temperature =  $35^\circ\text{C}$ .

$\text{H}_2\text{O}$ - $\text{D}_2\text{O}$  mixtures could throw light on the nature of the transition state. The dependence of the rate constant ( $k_n^1$ ) on 'n', the atom fraction of deuterium in a solvent mixture of  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$ , is given (Albery and Davies 1972; Gopalakrishnan and Hogg 1985) in the form of a proton inventory plot.

The curvature of the proton inventory plot could reflect the number of exchangeable protons in the reaction (Issacs 1987). A plot of  $k_n^1$  vs the deuterium atom fraction 'n' (figure 1, table 3) in the present case is more or less a straight line with the least



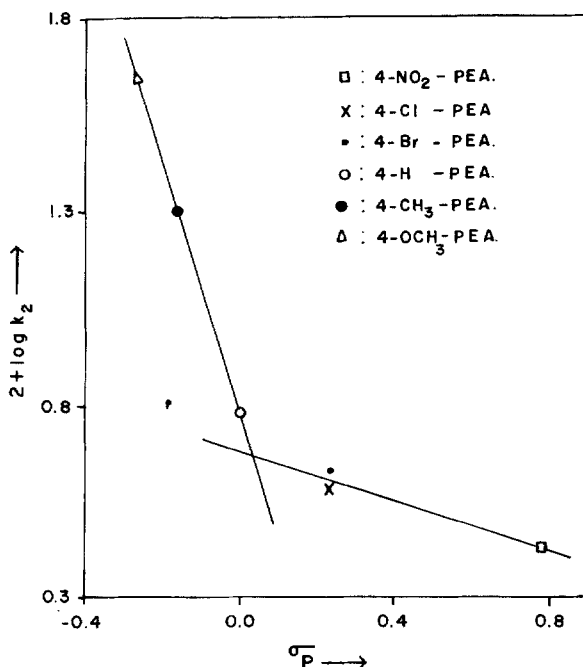
Scheme 2.

curvature. Comparison with the standard curves (Issacs 1987) clearly indicates the involvement of a single proton or H–D exchange during the reaction sequence. Hence the participation of  $\text{H}^+$  ion in the formation of transition state is inferred.

## 5. Structure–reactivity correlations

Structure–reactivity correlations were made by attempting to fit the Hammett equation. The Hammett plot shows two distinct (figure 4, table 6) lines, for each of which there is good correlation between the substituent constants and the logarithm of the rate constants, particularly when  $\sigma_p$ , the Okamoto–Brown constant (Brown and Okamoto 1958) is used for the electron-releasing substituents. Of these, one has a much larger  $\rho$  of  $-3.2$  and the other a relatively low  $\rho$  of  $-0.34$  at  $35^\circ\text{C}$ . The break in the Hammett plot could suggest 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 organic haloamines (Mahadevappa and Ananda 1985; Mahadevappa and Puttaswamy 1989), 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 stabilised by the electron-donating groups. In the present case, the decrease in rate with electron-withdrawing groups is in agreement with this observation.





**Figure 4.** Plot of  $\log k_2$  vs  $\sigma_P$  for six substituted phenethyl alcohols.  $[\text{BAB}]_0 = 0.0005 \text{ mol dm}^{-3}$ ,  $[\text{X-PEA}]_0 = 0.01 \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ ,  $\mu = 0.5 \text{ mol dm}^{-3}$ ,  $\text{MeOH} = 5\% \text{ (v/v)}$ , temperature =  $35^\circ\text{C}$ .

**Table 6.** Second-order rate constants for the oxidation of 4-substituted phenethyl alcohols by BAB.

$[\text{BAB}]_0 = 0.0005 \text{ mol dm}^{-3}$ ,  $[\text{X-PEA}]_0 = 0.01 \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ ,  $\mu = 0.5 \text{ mol dm}^{-3}$ ,  $\text{MeOH} = 5\% \text{ (v/v)}$ , temperature =  $35^\circ\text{C}$ , X = substituent at position 4

X	$10^2 k_2 = k^1 / [\text{X-PEA}]_0$ ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )	$\sigma_P$
$\text{NO}_2$	2.69	0.78
Cl	3.80	0.23
Br	4.10	0.23
H	5.98	0.00
$\text{CH}_3$	19.95	-0.17
$\text{OCH}_3$	44.66	-0.27

## 6. Isokinetic relationship

The enthalpy of activation is low for the oxidation of phenethyl alcohols by bromamine-B. The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the oxidation of phenethyl alcohols are linearly related (table 5,  $r = 0.9989$ ) and the isokinetic temperature  $\beta = 333 \text{ K}$ . The genuine nature of the isokinetic relationship was verified by the Exner criterion (Exner

1964) by plotting  $\log k^1$  (318 K) vs  $\log k^1$  (303 K). The value of  $\beta$  was calculated from the equation,

$$\beta = \frac{T_1(1-q)}{[(T_1/T_2) - q]}, \quad (9)$$

where  $q$  is the slope of the Exner plot and  $T_1 > T_2$ . The value of  $\beta$  is 335 K. It is seen that the value of  $\beta$  is higher than the experimental temperature (308 K) indicating enthalpy control on the reactions.

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