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OXIDATION OF SUBSTITUTED PHENETHYL ALCOHOLS BY SODIUM *N*-CHLOROBENZENESULPHONAMIDE: A KINETIC STUDY

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The kinetics of the oxidation of six substituted phenethyl alcohols by sodium *N*-chlorobenzenesulphonamide or chloramine-B (CAB) in the presence of HCl was studied at 35 °C. The rate shows a first-order dependence on $[CAB]_0$ and $[H^+]$ and is fractional order in $[PEA]_0$ and $[Cl^-]$. Ionic strength variations, addition of reaction product of benzenesulphonamide and variation of the dielectric constant of the medium have no effect on the rate. The solvent isotope effect $k'H_2O/k'D_2O \approx 0{\cdot}78$. Proton inventory studies were made in H_2O–D_2O mixtures. The rates correlate satisfactorily with the Hammett linear free energy relationship. The reaction constant ρ was $-3{\cdot}5$ for electron-releasing and $-0{\cdot}30$ for electron-withdrawing groups at 35 °C. Activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$ and log A were calculated for the reaction. An isokinetic relationship is observed with $\beta = 338$ K, indicating enthalpy as a controlling factor.

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 byproduct formed 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.[1-3] The benzene analogue chloramine-B ($C_6H_5SO_2NClNa \cdot 1{\cdot}5H_2O$) (CAB) is becoming important as a mild oxidant[4,5] and the compound can be easily prepared from benzenesulphonamide and chlorine.

Mild oxidation of alcohols to carbonyl compounds is a very important synthetic operation in organic synthesis.[6,7] Although a considerable amount of work has been done on mechanistic studies involving oxidations of alcohols by transition metal ions[8] such as chromium(VI), vanadium(V), cobalt(III), manganese(VII) and cerium(IV) in acidic media and with copper(II)[9] and ruthenium tetroxide in alkaline media and ferrate(VI)[10,11] ion, not much information is available concerning the oxidation of different alcohols by organic haloamines in acidic media. After examining several oxidizing reagents, we found CAB to be an excellent oxidant for performing controlled oxidation of alcohols to carbonyl compounds, and this system is adaptable for large-scale operations. To shed some light on the mechanism of the CAB oxidation of alcohols, we 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 works an intermediate in many organic syntheses, were ascertained. The Hammett linear free energy relationship (LFER) was deduced together with the other thermodynamic parameters.

EXPERIMENTAL

Chloramine-B (CAB) was prepared as reported earlier.[4,12] An aqueous solution of the compound was prepared, standardized iodimetrically 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 grade. Doubly distilled water was employed in the preparation of aqueous

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solutions. The ionic strength of the system was maintained at a constant high value using a concentrated solution of $NaClO_4$. Solvent isotope studies were made with D_2O (99·4%) supplied by the Bhabha Atomic Research Centre (Bombay, India). Regression analysis of experimental data was carried out with an EC-72 Statistical Calculator.

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 thermostated at 35 °C. A measured amount of CAB 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 CAB iodimetrically. The course of reaction was studied up to two half-lives. The calculated pseudo-first order rate constants, k^1, were reproducible to within ±3%.

Stoichiometry. Various ratios of CAB to PEA were equilibrated in the presence of 0·1 mol dm^{-3} HCl for 24 h. The determination of unconsumed CAB in the reaction mixture showed that 1 mol of PEA consumed 1 mol of CAB:

$$XC_6H_4CH_2CH_2OH + RNClNa \rightarrow XC_6H_4CH_2CHO + RNH_2 + Na^+ + Cl^1 \quad (1)$$

Here X = H, Cl, Br, CH_3, OCH_3 and NO_2 and $R = C_6H_5SO_2$.

Product analysis. The reaction products were subjected to column chromatography on silica gel (60–200 mesh) using gradient elution (from dichloromethane to chloroform). After initial separation, the products were further purified by recrystallization. Materials were identified by comparison with commercially available samples.

Phenacetaldehyde. Phenacetaldehyde was recrystallized from dichloromethane–light petroleum [m.p. = 32–33 °C]; known m.p. = 33–34 °C (Merck Index, No. 11 7236)]. The phenacetaldehyde was further identified as its 2,4-dinitrophenylhydrazone (2,4-DNP) derivative. The latter was recrystallized from ethanol (recovery 66·6%) and was found to be identical with the DNP derivative of an authentic sample.

Benzenesulphonamide. Benzenesulphonamide ($PhSO_2NH_2$) (BSA) was detected by TLC, using light petroleum–chloroform–butan-1-ol (2 : 2 : 1, v/v/v) as the solvent and iodine for detection ($R_f = 0·88$)

RESULTS

Effect of reactants

With the substrate in excess, at constant [HCl] and [PEA]0, plots of log[CAB] vs time are linear ($r > 0·998$), indicating a first-order dependence of rate on $[CAB]_0$Values of the pseudo-first order rate constants (k^1) are given in Table 1.

The rate increases initially with increase in $[PEA]_0$. A plot of log k^1 vs log$[PEA]_0$ was linear ($r = 0$ 997) (Table 1) and Michaelis–Menten kinetics were obeyed.

Effect of [HCl]

The rate increases with increase in [HCl] and a plot of log k^1 vs log[HCl] was linear ($r = 0·999$) (Table 2) with a slope of 1.60.

Effect of $[H^+]$

At constant $[Cl^-] = 0·4$ mol 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 a slope of unity.

Effect of halide ions

At constant $[H^+] = 0·1$ mol dm^{-3}, the rate increased with the addition of NaCl and a plot of log k^1 vs log$[Cl^-]$ was linear ($r = 0·998$) (Table 2) with a fractional slope (0·63). Addition of Br^- ions in the form of NaBr (5×10^{-4}–20×10^{-4} mol dm^{-3}) had a negligible effect on the rate.

Table 1. Effect of varying reactant concentrations on the rate[a]

$[CAB]_0 \times 10^4$ (mol dm^{-3})	$[PEA]_0 \times 10^3$ (mol dm^{-3})	$k^1 \times 10^4$(s^{-1})
2·0	10·0	3·68
5·0	10·0	3·68
8·0	10·0	3·61
10·0	10·0	3·71
15·0	10·0	3·70
20·0	10·0	3·68
5·0	5·0	2·20
5·0	8·0	3·15
5·0	10·0	3·68
5·0	20·0	6·02
5·0	30·0	8·12
5·0	40·0	9·38
5·0	50·0	11·50

[a] [HCl] = 0·1 mol dm^{-3}; $\mu = 0·5$ mol dm^{-3}; $T = 308$ K.

Table 2. Effect of varying HCl, H^+ and Cl^- concentrations on the rate[a]

[HCl] × 10^2 (mol dm^{-3})	$k^1 \times 10^4$ (s^{-1})	$[H^+]^b \times 10^2$ (mol dm^{-3})	$k^1 \times 10^4$ (s^{-1})	$[Cl]^c \times 10^2$ (mol dm^{-3})	$k^1 \times 10^4$ (s^{-1})
8·0	2·55	10·0	8·18	20·0	6·32
10·0	3·68	15·0	12·01	25·0	7·70
15·0	6·52	20·0	15·50	30·0	8·70
20·0	10·70	25·0	18·50	35·0	9·30
30·0	19·19	30·0	24·31	40·0	10·50
40·0	30·70	35·0	27·22	50·0	12·00
—	—	40·0	30·70	—	—

[a] $[CAB]_0 = 5 \times 10^{-4}$ mol dm^{-3}; $[PEA]_0 = 10 \times 10^{-3}$ mol dm^{-3}; $\mu = 0{\cdot}5$ mol dm^{-3}; $T = 308$ K.
[b] Variation at constant $[Cl^-] = 0{\cdot}4$ mol dm^{-3}.
[c] Variation at constant $[H^+] = 0{\cdot}1$ mol dm^{-3}

Effect of benzenesulphonamide (BSA)

Addition of the reaction product, BSA (5×10^{-4}–20×10^{-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.

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.

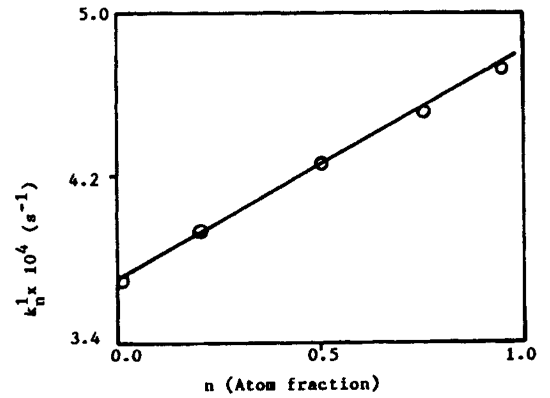


Figure 1. Proton inventory plot of k_n^1 vs deuterium atom fraction n in H_2O–D_2O mixtures

Solvent isotope studies

Studies of the rate in D_2O medium for PEA revealed that whereas $k^{-}H_2O = 3{\cdot}68 \times 10^{-4}\ s^{-1}$, $k^1D_2O = 4{\cdot}72 \times 10^{-4}\ s^{-1}$, giving a solvent isotope effect k^1H_2O/k^1D_2O of 0·78. Proton inventory studies were performed by carrying out the reaction in H_2O–D_2O mixtures with various atom fractions n of deuterium (Figure 1, Table 3).

Effect of temperature on the rate

The reaction was studied at different temperatures (308–318 K), and from the Arrhenius plots of log k^1 vs $1/T$, values of the activation parameters for the composite reaction were calculated. (Tables 4 and 5).

Test for free radicals

Addition of the reaction mixtures to acrylamide did not initiate polymerization, snowing the absence of free radical species.

Table 3. Proton inventory studies for PEA in H_2O–D_2O mixtures at 308 K[a]

Atom fraction of deuterium (n)	$k_n^1 \times 10^4$ (s^{-1})
0·000	3·68
0·250	3·95
0·500	4·27
0·753	4·52
0·947	4·72

[a] $[CAB]_0 = 5 \times 10^{-4}$ mol dm^{-3}; $[PEA]_0 = 10 \times 10^{-3}$ mol dm^{-3}; [HCl] = 0·1 mol dm^{-3}; $\mu = 0{\cdot}5$ mol dm^{-3}; $T = 308$ K.

Table 4. Temperature dependence of the oxidation of 4-substituted PEA by CAB[a]

Substrate X = PEA	$k^1 4 10^4$ (s^{-1}) 303 K	308 K	313 K	318 K
X = 4-NO_2	1·23	1·74	2·23	2·63
X = 4-Cl	1·55	2·30	3·09	4·00
X = 4-Br	2·09	2·60	4·07	5·37
X = 4-H	2·69	3·68	5·62	8·32
X = 4-CH_3	8·99	13·18	21·87	33·88
X = 4-OCH_3	15·84	29·50	44·66	74·13

[a] $[CAB]_0 = 5 \times 10^{-4}$ mol dm^{-3}; $[X\text{-}PEA]_0 = 10 \times 10^{-3}$ mol dm^{-3}; [HCl] = 0·1 mol dm^{-3}; $\mu = 0·5$ mol dm^{-3}; [MeOH] = 5% (v/v).

DISCUSSION

Chloramine-B acts as an oxidizing agent in both acidic and alkaline media. In general, CAB undergoes a two-electron change in its reactions. The reduction potential of CAB/RNH_2 is pH dependent and decreases with increase in the pH of the medium (values are 1·14 V at pH 0·65 and 0·5 V at pH 12 for CAT). Depending on the pH of the medium, CAB furnishes different types of reactive species in solution, such as RNHCl, $RNCl_2$, HOCl and possibly H_2OCl^+ in acidic solutions:[4,13,14]

$$RNClNa \rightleftharpoons RNCl^- + Na^+ \quad (2)$$

$$RNCl^- + H_2O \rightleftharpoons RNHCl + OH^- \quad (3)$$

$$RNHCl + RNHCl \overset{K_d}{\rightleftharpoons} RNCl_2 + RNH_2 \quad (4)$$

$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl \quad (5)$$

If $RNCl_2$ were to be the reactive species, then the rate law predicts a second-order dependence of rate on $[CAB]_0$, which is contrary to the experimental observations. If HOCl is primarily involved, a first-order retardation of rate by the added benzenesulphonamide (BSA) is expected. Since no such effect is noticed,

$$RNHCl + H^+Cl^- \overset{K_1}{\rightleftharpoons} RN^+H_2Cl\cdots Cl^- \qquad \text{fast (i)}$$
$$(X')$$

$$X + PEA \overset{K_2}{\rightleftharpoons} Y \qquad \text{fast (ii)}$$

$$Y \xrightarrow{k_3} \text{products} \qquad \text{rds (iii)}$$

Scheme 1

HOCl can be ruled out as the oxidizing species. Hence RNHCl is responsible for the oxidation of phenethyl alcohols. In view of these facts, Scheme 1 can be proposed for the oxidation of PEA by CAB.

Scheme 1 assumes the formation of a tight ion pair[15] (X′), which is an intermediate and at the same time indicates simultaneous catalysis by H^+ and Cl^- ions. The latter reacts with PEA through an equilibrium step to form a PEA–CAB complex (Y), which decomposes in a rate-limiting step to the products. The Michaelis–Menten kinetics obeyed by the substrate indicates a pre-equilibrium step (ii) in Scheme 1. Assuming $[CAB]_t = [RNHCl] + [X'] + [Y]$, rate law (6) can be derived for the oxidation of phenethyl alcohols by CAB:

$$-\frac{d[CAB]}{dt} = \frac{k_3K_1K_2[CAB]_t[H^+][Cl^-][PEA]}{1 + K_1[H^+][Cl^-] + K_2[PEA]} \quad (6)$$

Equation (6) can be transformed into

$$\frac{1}{k^1} = \frac{1}{k_3K_2[PEA]}\left(\frac{1}{K_1[H^+][Cl^-]} + 1\right) + \frac{1}{k_3} \quad (7)$$

From the double reciprocal plots of k^1 vs [PEA] and k^1 vs $[HCl]^2$, since $[H^+] = [Cl^-] = [HCl]$, (Figures 2 and 3), values of k_3, K_1 and K_2 are evaluated. Using k_3 values ($1·34 \times 10^{-3}$, $1·67 \times 10^{-3}$, $2·86 \times 10^{-3}$ and $5·00 \times 10^{-3}$ s^{-1} at 303, 308, 313 and 318 K, respectively) obtained by varying $[PEA]_0$ at each temperature (Figure 2), activation parameters were determined for

Table 5. Kinetic and thermodynamic parameters for the oxidation of 4-substituted phenethyl alcohols by CAB[a]

Substrate X-PEA	E_a (kJ^{-1} mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	ΔG^* (kJ mol^{-1})	Log *A*
X = 4-NO_2	34·6	32·0	−213·2	98·2	5·2
X = 4-Cl	39·4	36·8	−195·2	97·4	6·1
X = 4-Br	48·7	46·1	−163·1	96·7	7·8
X = 4-H	59·8	57·2	−124·5	95·9	9·8
X = 4-CH_3	68·0	65·4	−88·0	92·4	11·8
X = 4-OCH_3	74·4	73·7	−60·6	90·6	13·2

[a] $[CAB]_0 = 5 \times 10^{-4}$ mol dm^{-3}; $[X\text{-}PEA]_0 = 10 \times 10^{-3}$ mol dm^{-3}; [HCl] = 0·1 mol dm^{-3}; $\mu = 0·5$ mol dm^{-3}; [MeOH] = 5% (v/v).

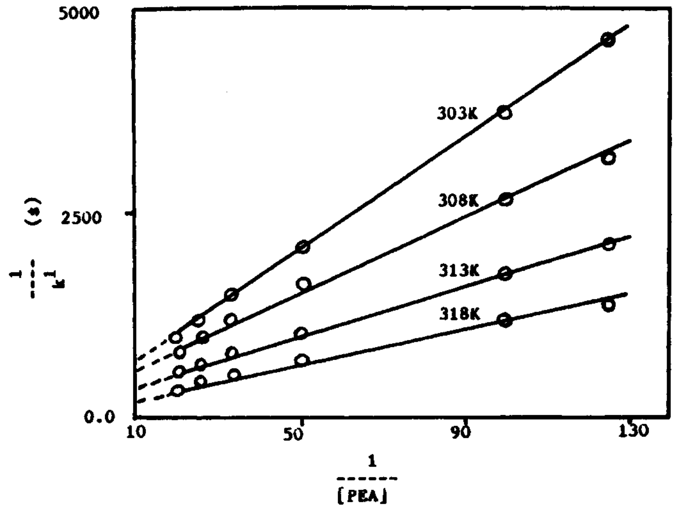


Figure 2. Double reciprocal plots of k^1 vs [PEA]

the rate-limiting step and were as follows: $E_a = 66{\cdot}9\ \mathrm{kJ\,mol^{-1}}$, $\Delta H^* = 64{\cdot}4\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^* = -87{\cdot}8\ \mathrm{J\,K^{-1}mol^{-1}}$, $\Delta G^* = 91{\cdot}6\ \mathrm{kJ\,mol^{-1}}$, $\log A = 11{\cdot}7$, $K_1 = 3{\cdot}5\ \mathrm{dm^6\,mol^{-2}}$ and $K_2 = 890\ \mathrm{dm^3\,mol^{-1}}$.

The detailed mechanism of the oxidation of phenethyl alcohols by CAB and the structure of the intermediates are shown in Scheme 2.

It is interesting to note that the rate has increased only slightly in D_2O medium. Since D_3O^+ ion is a stronger acid than H_3O^+ ion by a factor of 2–3, a solvent isotope effect of this magnitude is to be expected. However, the slight increase in D_2O medium probably shows that since the protonation step is followed by hydrolysis involving the O—H bond scisson, the normal kinetic isotope effect $K_H/K_D > 1$ could counterbalance the solvent isotope effect. Proton inventory studies in H_2P–D_2O 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 D_2O and H_2O, is given[16,17] by a form of the Gross–Butler equation:

$$\frac{k^0_{\text{obs}}}{k^n_{\text{obs}}} = \frac{\pi^{\text{TS}}(1 - n + n\phi_i)}{\pi^{\text{RS}}(1 - n + n\phi_j)} \tag{8}$$

where ϕ_i and ϕ_j are the isotopic fractionation factors for isotopically exchangeable hydrogen sites in the transition states (TS) and reactant site (RS), respectively. Equation (8) allows the calculation of the fractionation factor of TS, if reactant fractionation factors are known. However the curvature of the proton inventory plot could reflect the number of exchangeable protons in the reaction.[18] A plot of k_n^1 versus the deuterium atom fraction n (Figure 1, Table 3) in the present case is more or less a straight line with the least curvature. Comparison with the standard curves[18] clearly indicates the involvement of a single proton or H–D exchange during the reaction sequence. Hence the participation of H^+ ion in the formation of transition state is inferred.

The moderate values of the enthalpy of activation, a large negative entropy of activation and the fairly high ΔG^* values support the mechanism. The near constancy of the ΔG^* values indicates a solvated state and operation of a similar mechanism for the oxidation of all alcohols.

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

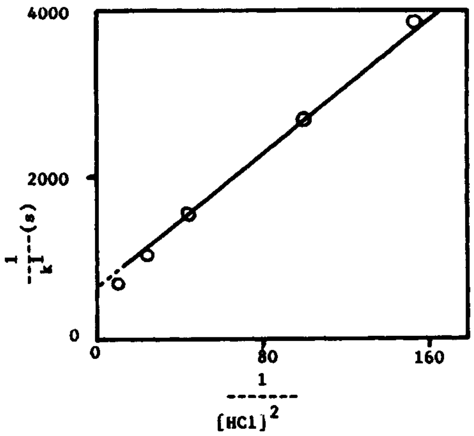
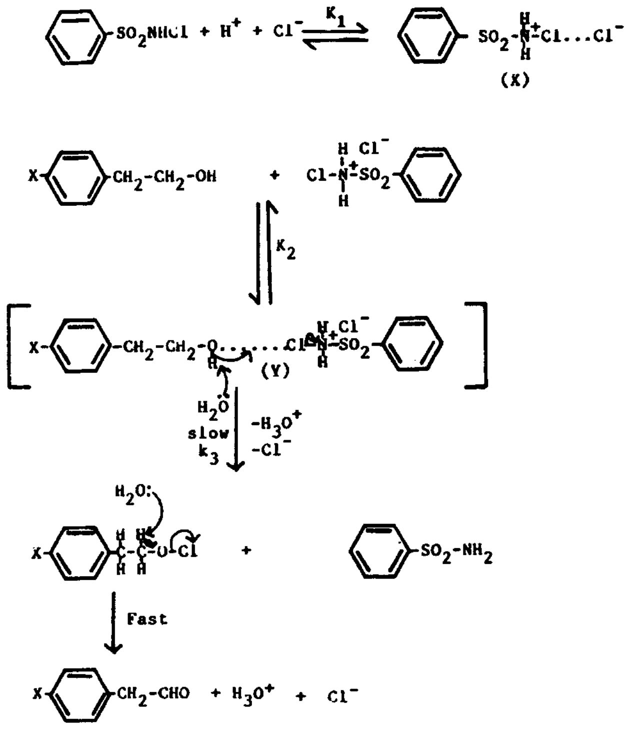


Figure 3. Double reciprocal plot of k^1 vs $[\mathrm{HCl}]^2$ at 308 K



Scheme 2

monographs.[19-24] For the limiting case of zero angle of approach between two dipoles or an ion–dipole system, Amis[23] 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, whereas a positive slope results for a positive ion–dipole interaction. The total absence of the effect of varying dielectric constant on rate in the present work cannot be explained by the Amis theory.[23] Applying the Born[25] equation, Laidler and co-workers[20] derived the following equation for a dipole–dipole reaction:

$$\ln k^1 = \ln k_0 + \frac{3}{8kT}\left(\frac{2}{D} - 1\right)\left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_\ddagger^2}{r_\ddagger^3}\right) \quad (9)$$

where, k_0 is the rate constant in a medium of infinite dielectric constant, μ 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 $r_*^3 > r_A^3 + r_B^3$. On the other hand, $r_*^3 \approx r_A^3 + r_B^3$ 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 were made by attempting to fit the Hammett equation. The Hammett plot shows two distinct lines (Figure 4, Table 6), for each of which there is good correlation between the substituent constants and the logarithm of the rate constants, particularly when σ_p the Okamoto–Brown constant,[25] is used for the electron-releasing substituents. Of these, one has a much larger ρ of −3·5 and the

Table 6. Second order rate constants for the oxidation of 4-substituted phenethyl alcohols by CAB[a]

Substrate X-PEA	$k_2 \times 10^2 = k^1/[\text{X-PEA}]$ ($dm^3\ mol^{-1}\ s^{-1}$)	σ_p
X = 4-NO_2	1·74	0·78
X = 4-Cl	2·30	0·23
X = 4-Br	2·60	0·23
X = 4-H	3·68	0.00
X = 4-CH_3	13·18	−0.17
X = 4-OCH_3	29·50	−0·27

[a] $[CAB]_0 = 5 \times 10^{-4}$ mol dm^{-3}; $[\text{X-PEA}]_0 = 10 \times 10^{-3}$ mol dm^{-3}; [HCl] = 0·1 mol dm^{-3}; $\mu = 0·5$ mol dm^{-3}; $T = 308$ K; [MeOH] = 5% (v/v).

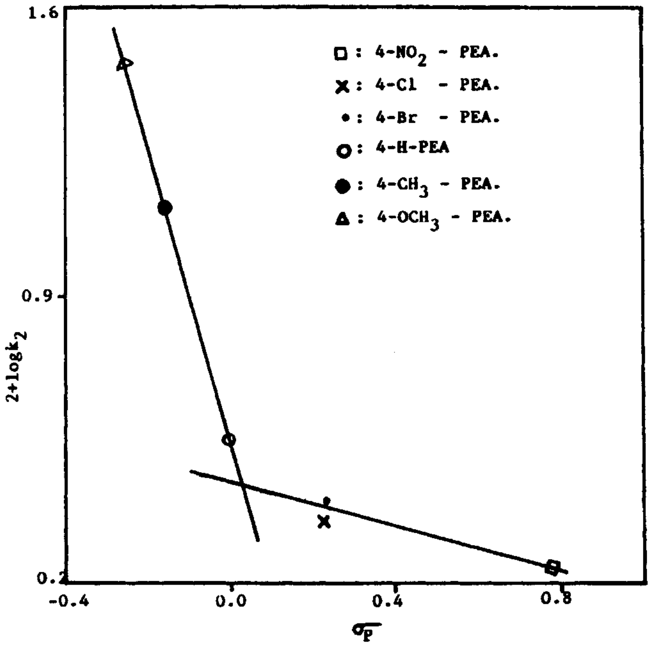


Figure 4. Plot of log k_2 vs σ_P for six substituted phenethyl alcohols at 308 K

other a relatively low ρ of −0·30 at 35 °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 OH group by a water molecule. In earlier work on the oxidation of primary alcohols by organic haloamines,[26] 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 carborium ion centre which is stabilized by the electron donating groups. In the present case, the decrease in rate with electron-withdrawing groups is in agreement with this observation. The biphasic Hammett plot could probably indicate a change in mechanism as a result of a change in the nature of the substituents. Alternatively, the measured rate constant $k^1 = k_{\mathrm{obs}}$ could be a composite quantity like $k_{\mathrm{obs}} = Kk$. The Michaelis–Menten character of the substrate dependence can point towards a substrate-independent mechanism such as

$$\mathrm{RNHCl} + \mathrm{H_2O} \xrightarrow{\mathrm{rds}} \mathrm{RNH_2} + \mathrm{HOCl}$$

$$\mathrm{HOCl} + \mathrm{PEA} \xrightarrow{\mathrm{fast}} \text{products}$$

The above mechanism with a stronger electrophile such as HOCl may be operative along with that in which simultaneous catalysis by H^+ and Cl^- ions is taking place (Scheme 1).

Isokinetic relationship

The enthalpy of activation is low for the oxidation of phenethyl alcohols by chloramine-B. The values of a ΔH^* and ΔS^* for the oxidation of phenethyl alcohols are linearly related (Table 5) and the isokinetic temperature $\beta = 338$ K. The genuine nature of the isokinetic relationship was verified by the Exner[27] criterion by plotting log k^1 (318 K) vs log k^1 (303 K). The value of β was calculated from the equation,

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

where q is the slope of Exner plot and $T_1 > T_2$. The value of β is 340 K. It is seen that the value of β is higher than the experimental temperature (308 K), indicating enthalpy control on the reactions (Figure 5).

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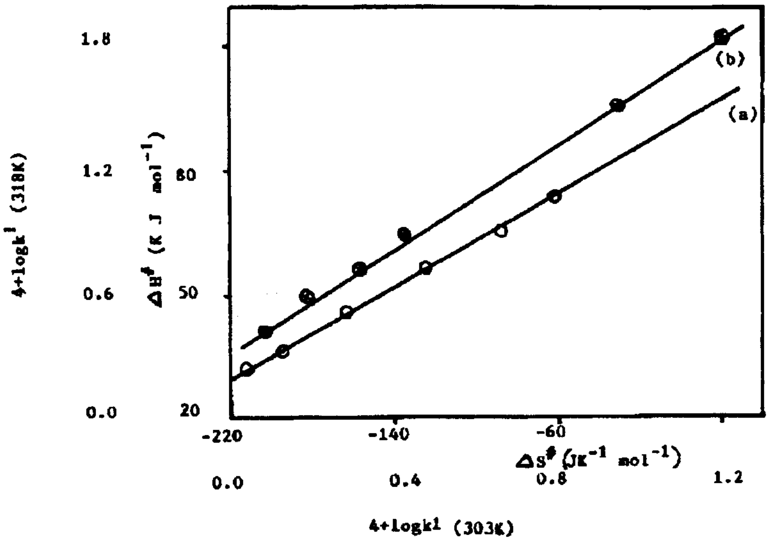

Figure 5. (a) Isokinetic plot of ΔH^* vs ΔS^* for the oxidation of six substituted phenethyl alcohols by CAB. (b) Exner plot of log k^1 (318 K) vs log k^1 (308 K)

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