Oxidation of Substituted Phenethyl Alcohols by Sodium-N-chloro-p-toluene sulfonamide: A Kinetic Study

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Summary. The kinetics of the oxidation of six p-substituted phenethyl alcohols (PEA, $R = -H, -Cl,$ $-Br, -CH_3, -OCH_3,$ and $-NO_2$) by sodium-N-chloro-p-toluene sulfonamide (chloramine-T, CAT) in the presence of HCl was studied at 35 °C. The rate shows a first order dependence on $[CAT]_0$ and $[H^+]_0$ and a fractional order in $[PEA]_0$ and $[Cl^-]_0$. Ionic strength variations, addition of reaction product toluene sulfonamide, 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} amounts to about 0.90. Proton inventory studies have been made in $H_2O–D_2O$ mixtures. The rates correlate satisfactorily with Hammett's relationship. The reaction constant ρ was -3.3 for electron releasing substituents and -0.25 for electron withdrawing groups at 35 °C. The activation parameters $\Delta H^{\#}, \Delta S^{\#}, \Delta G^{\#},$ and $\log A$ were derived. $\Delta H^{\#}$ and $\Delta S^{\#}$ are linearly related, and an isokinetic relationship is observed with $\beta = 166.7\,K$, indicating entropy as a controlling factor.

Keywords. Substituted phenethyl alcohols; Oxidation; Chloramine-T; Kinetics; Linear free energy relationships.

Die Oxidation substituierter Phenethylalkohole mit Natrium-N-chlor-p-toluolsulfonamid: Kinetische Untersuchungen

Zusammenfassung. Die Kinetik der Oxidation von sechs p-substituierten Phenethylalkoholen (PEA), $R = -H, -Cl, -Br, -OCH_3$ und NO_2) mit Natrium-N-chlor-p-toluolsulfonamid (Chloramin-T, CAT) in Gegenwart von HCl bei 35 °C wurde untersucht. Die Reaktionsgeschwindigkeit ist in bezug auf $[CAT]_0$ und $[H^+]_0$ ester und hinsichtlich $[PEA]_0$ und $[Cl]_0$ gebrochener Ordnung. Variation der Ionenstärke, Zusatz von Reaktionsprodukt oder Toluolsulfonamid und Variation der Dielektrizitätskonstante des Mediums haben keinen Einfluß auf die Reaktionsgeschwindigkeit Der Lösungsmittel-Isotopeneffekt k'_{H_2O}/k'_{D_2O} beläuft sich auf etwa 0.90. Die Protonenbilanz wurde in $H_2O–D_2O$ Mischungen untersucht. Die Geschwindigkeiten korrelieren zufriedenstellend nach der Hammettschen Beziehung. Die Reaktionskonstante wurde mit $\rho = -3.3$ für elektronenabgebende und $\rho = -0.25$ für elektronenanziehende Substituenten bei 35 °C bestimmt. Die Aktivierungsparameter $\Delta H^{\#}, \Delta S^{\#}, \Delta G^{\#}$ und $\log A$ wurden abgeleitet; $\Delta H^{\#}$ und $\Delta S^{\#}$ korrelieren linear, und eine isokinetische Beziehung mit $\beta = 166.7\,K$ weist auf die Entropie als kontrollierenden Faktor hin.

Introduction

Considerable attention has centered around the chemistry of N-metallo-N-aryl-halosulfonamides, generally known as organic haloamines, because of their versatility as mild oxidants, halogenating agents, and providers of N-anions which act as both bases and nucleophiles. The important chlorine compound chloramine-T (*CAT*) which is a byproduct of 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]. Chloramine-T has been found [4, 5] to specifically oxidize primary and secondary alcohols to aldehydes and ketones in good yield under very mild conditions in aqueous solution. Mild oxidation of alcohols to carbonyl compounds is a very important synthetic operation in organic synthesis [6, 7]. Although considerable amount of work has been done on the mechanistic studies involving oxidations of alcohols by transition metal ions [8,9], ruthenium tetroxide in alkaline medium, and ferrate(VI) ion [10,11], only little information is available concerning the oxidation of alcohols by organic haloamines in acidic medium. After examining several oxidizing reagents, we found *CAT* to be an excellent oxidant for the controlled oxidation of alcohols to carbonyl compounds. Moreover, this system is adaptable for large scale operations. To shed some light on the mechanism of *CAT* oxidation of alcohols, we now present our studies on the reactions of six substituted phenethyl alcohols with this oxidant.

Results and Discussion

Effect of reactants

With the substrate in excess and at constant [HCl] and $[PEA]_0$, plots of $\log[CAT]$ vs. time are linear ($r > 0.998$), indicating a first-order dependance of the rate on $[CAT]_0$. Values of pseudo-first order rate constants (k') are given in Table 1.

Table 1. Pseudo-first order rate constants for the variation of $[CAT]$ at 35 °C

$[CAT]_0 \times 10^4 (M)$	20	15	10	08	05	02
$k' \times 10^4 (s^{-1})$	2.24	2.32	2.50	2.75	2.90	2.66

$[PEA]_0 = 0.01\,M$; [HCl] $= 0.1\,M$

The rate increases initially with an increase in $[PEA]$. A plot of $\log k'$ vs. $\log[PEA]$ is linear ($r = 0.997$, Fig. 1, Table 2) with a slope of 0.78.
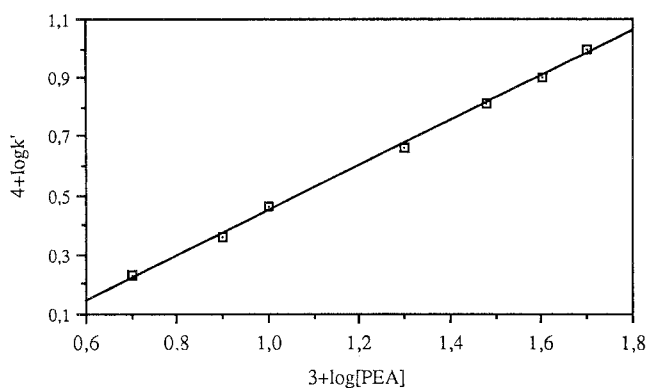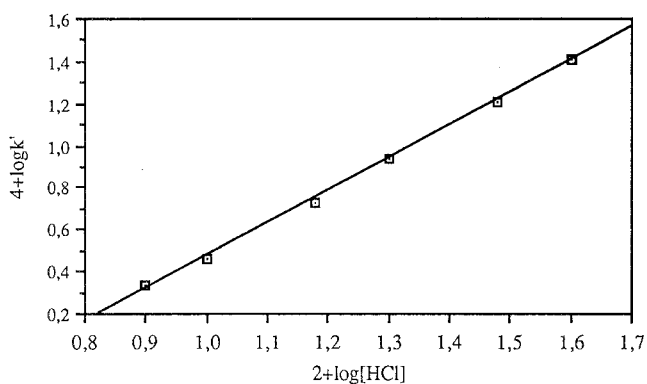
Fig. 1. Plot of $\log k'$ vs. $\log[PEA]$ at 308 K

Table 2. Pseudo-first order rate constants for the variation of $[PEA]$ at 35 °C

$[PEA]_0 \times 10^3\,(M)$	5.0	8.0	10.0	20.0	30.0	40.0	50.0
$k' \times 10^4\,(s^{-1})$	1.70	2.30	2.90	4.60	6.50	7.95	9.90

$[CAT]_0 = 0.0005\,M$; $[HCl] = 0.1\,M$

Effect of [HCl]

The rate increases with an increase in [HCl], and the plot of $\log k'$ vs. $\log[HCl]$ is linear ($r = 0.999$, Fig. 2, Table 3) with a slope of 1.54.

Fig. 2. Plot of $\log k'$ vs. $\log[HCl]$ at 308 K

Table 3. Pseudo-first order rate constants for the variation of [HCl] at 35 °C

$[HCl]_0 \times 10^2\,(M)$	8.0	10.0	15.0	20.0	30.0	40.0
$k' \times 10^4\,(s^{-1})$	2.12	2.90	5.32	8.63	16.20	25.51

$[CAT]_0 = 0.0005\,M$; $[PEA]_0 = 0.01\,M$

Effect of [H⁺]

At constant $[Cl^-] = 0.4\,mol\cdot dm^{-3}$, maintained by adding NaCl, the rate increases with an increase in $[H^+]$ which was varied by adding HCl. A plot of $\log k'$ vs. $\log[H^+]$ is linear ($r = 0.998$, Fig. 3, Table 4) with a slope of 1. This is also confirmed by varying $[HClO_4]$ (Table 5).
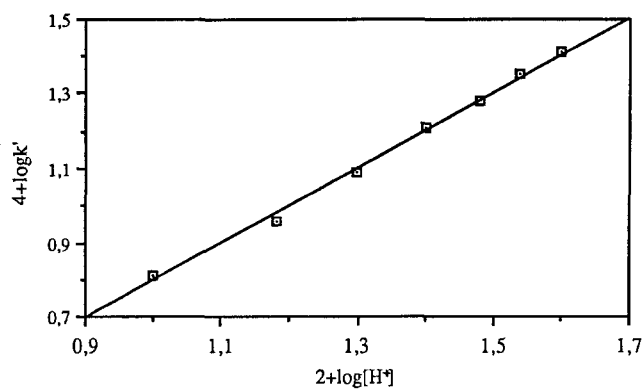

Fig. 3. Plot of $\log k'$ vs. $\log[H^+]$ at 308 K; $[NaCl] = 0.4\,M$

Table 4. Pseudo-first order rate constants for the variation of $[H^+]$ at constant $[NaCl] = 0.4\,M$ at 35 °C

$[HCl]_0 \times 10^2\,(M)$	10.0	15.0	20.0	25.0	30.0	35.0	40.0
$k' \times 10^4\,(s^{-1})$	6.50	9.10	12.40	16.20	19.19	22.20	25.50

$[CAT]_0 = 0.0005\,M$; $[PEA]_0 = 0.01\,M$

Effect of [HClO₄]

The rate increases with an increase in $[HClO_4]$ in presence of constant $[NaCl] = 0.4\,M$, and the plot of $\log k'$ vs. $\log[HClO_4]$ is linear ($r = 0.999$, Fig. 4, Table 5) with a slope of 1.
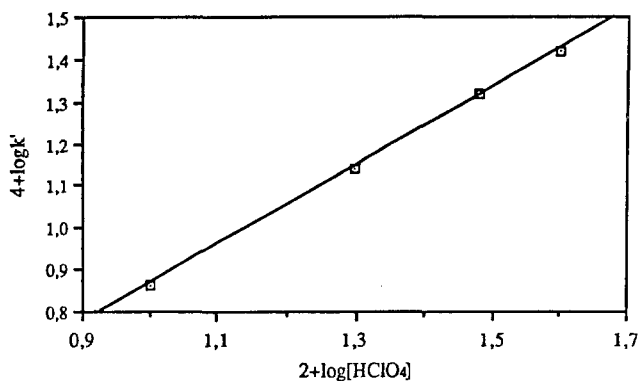

**Fig. 4.** Plot of $\log k'$ vs. $\log[HClO_4]$ at 308 K; $[NaCl] = 0.4\,M$

Table 5. Pseudo-first order rate constants for the variation of [$HClO_4$] at constant [$NaCl$] = 0.4 M at 35 °C

[$HClO$]$_4$ × 10^2 (M)	10.0	20.0	30.0	40.0
k' × 10^4 (s^{-1})	7.26	13.74	20.66	26.10

[CAT]$_0$ = 0.0005 M; [PEA]$_0$ = 0.01 M

Effect of halide ions

At constant [H^+] = 0.1 mol·dm^{-3}, the rate increases with the addition of NaCl. A plot of logk' vs. log[Cl^-] is linear (r = 0.998, Fig. 5, Table 6) with a slope of 0.6. Addition of Br$^-$ ions in the form of NaBr (5 × 10^{-4} − 20 × 10^{-4} mol·dm^{-3}) has negligible effect on the rate.
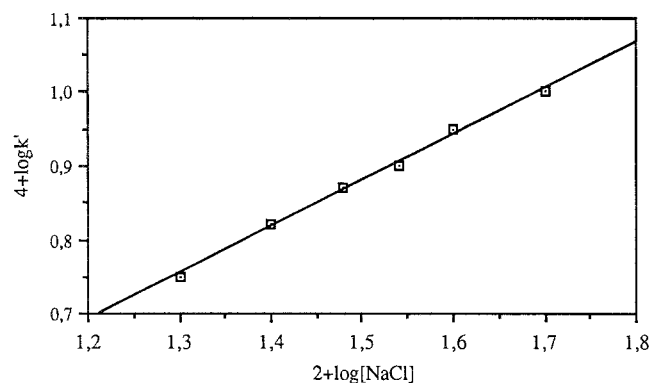
Fig. 5. Plot of log k' vs. log[NaCl] at 308 K; [HCl] = 0.1 M

Table 6. Pseudo-first order rate constants for the variation of [Cl^-] at constant [HCl] = 0.1 M at 35 °C

[$NaCl$]$_0$ × 10^2 (M)	20.0	25.0	30.0	35.0	40.0	50.0
k' × 10^4 (s^{-1})	5.60	6.58	7.32	8.00	8.90	10.0

[CAT]$_0$ = 0.0005 M; [PEA]$_0$ = 0.01 M

Effect of p-toluene sulfonamide (PTS)

Addition of PTS (5 × 10^{-4} − 20 × 10^{-4} mol·dm^{-3}) has a negligible effect on the rate, indicating that 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}) has no effect on the reaction rate (Table 7).

Table 7. Effect of ionic strength on rate of reaction at 35 °C

$[NaClO_4]_0 (M)$	0.0	0.2	0.4	0.6	0.8	1.0
$k' \times 10^4 (s^{-1})$	2.90	2.75	2.80	2.90	2.95	2.92

$[CAT]_0 = 0.0005\,M$; $[PEA]_0 = 0.01\,M$; $[HCl] = 0.1\,M$

Effect of varying dielectric constant of the medium

The dielectric constant of the medium was varied by adding methanol (0–40% v/v) to the reaction mixture. The rates are not significantly altered. Blank experiments with methanol indicated that oxidation of methanol was negligible during the period of the experiment (Table 8).

Table 8. Effect of variation of dielectric constant on rate of reaction at 35 °C

%MeOH (v/v)	0.0	10.0	20.0	30.0	40.0
$k' \times 10^4 (s^{-1})$	2.90	2.86	2.74	2.69	2.62

$[CAT]_0 = 0.0005\,M$; $[PEA]_0 = 0.01\,M$; $[HCl] = 0.1\,M$

Solvent isotope studies

Studies of reaction rate of *PEA* in D_2O reveals that whereas k'_{H_2O} is $2.90 \times 10^{-4}\,s^{-1}$, k'_{D_2O} is $3.22 \times 10^{-4}\,s^{-1}$. The solvent isotope effect k'_{H_2O}/k'_{D_2O} is thus found to be 0.90. Proton inventory studies were made by carrying out the reaction in H_2O–D_2O mixtures with varying atom fractions of deuterium. (Fig. 6, Table 9).
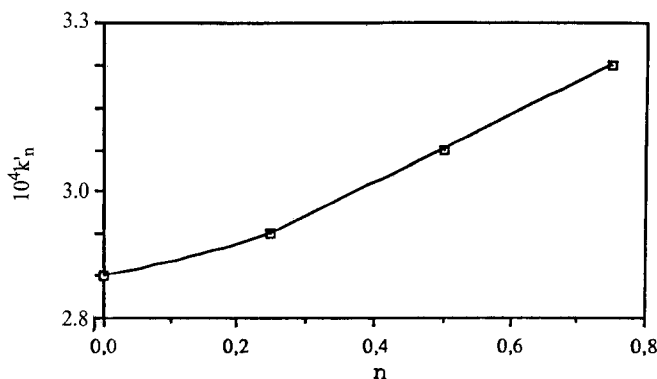
Fig. 6. Proton inventory plot of k'_n vs. the deuterium atom fraction n in H_2O–D_2O mixtures

Table 9. Proton inventory studies for *PEA* in H_2O–D_2O mixtures by *CAT* along with k_{D_2O} and k_{H_2O} values at 35 °C

| $k'_{H_2O} \times 10^4 (s^{-1})$	$k'_{D_2O} \times 10^4 (s^{-1})$	k'_{H_2O}/k'_{H_2O}	k'_{D_2O}/k'_{H_2O}
2.90	3.22	0.90	1.11

Atom fraction of Deuterium (*n*)	0.00	0.25	0.50	0.76
$k'_n \times 10^4 (s^{-1})$	2.90	2.96	3.07	3.22

$[CAT]_0 = 0.0005\,M$; $[PEA]_0 = 0.01\,M$; $[HCl] = 0.1\,M$

Effect of temperature on the rate

The reaction was studied at different temperatures (308–318 K); from the *Arrhenius* plots of logk' *vs.* $1/T$, values of the activation parameters for the composite reaction are calculated. (Fig. 7, Tables 10 and 11).
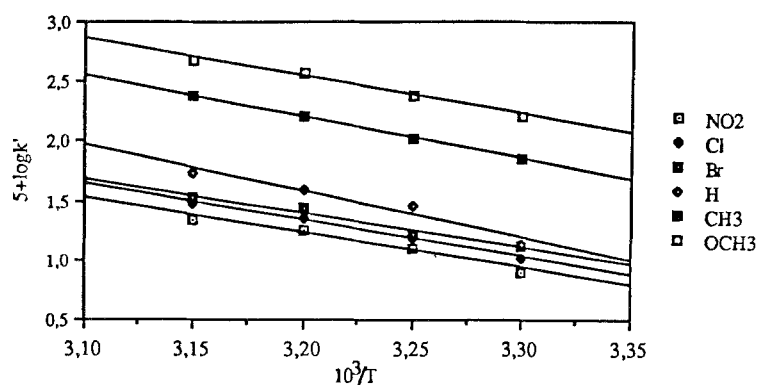
Fig. 7. Plots of logk' *vs.* $10^3/T$

Table 10. Effect of temperature on the oxidation of substituted phenethyl alcohols by *CAT*

Substrates	$k' \times 10^5 (s^{-1})$			
	303 K	308 K	313 K	318 K
4-NO_2-*PEA*	7.9	12.5	18.0	22.0
4-Cl-*PEA*	10.2	15.5	23.0	30.0
4-Br-*PEA*	12.9	16.7	27.6	33.3
PEA	13.4	29.0	39.2	54.3
4-CH_3-*PEA*	71.9	104.0	162.4	237.9
4-OCH_3-*PEA*	166.8	239.8	383.8	482.5

$[CAT]_0 = 0.0005\,M$; $[S]_0 = 0.01\,M$; $[HCl] = 0.1\,M$; MeOH = 5% (v/v)

Table 11. Kinetic and thermodynamic parameters for the oxidation of substituted phenethyl alcohols by CAT

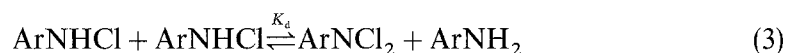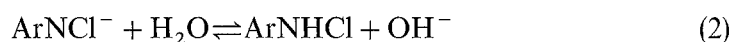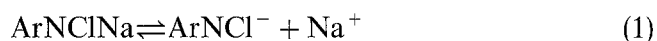| Substrates	E_a (kJ/mol)	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/K·mol)	$\Delta G^{\#}$ (kJ/mol)	log$A$
4-NO$_2$-PEA	51.6	49.1	-160.7	98.9	7.9
4-Cl-PEA	52.2	49.6	-156.8	98.3	8.1
4-Br-PEA	52.4	50.0	-154.6	97.6	8.2
PEA	54.6	52.1	-144.4	96.9	8.8
4-CH$_3$-PEA	58.8	56.3	-118.9	93.2	10.1
4-OCH$_3$-PEA	60.1	57.6	-108.1	91.0	10.7

$[CAT]_0 = 0.0005\ M$; $[S]_0 = 0.01\ M$; $[HCl] = 0.1\ M$; MeOH $= 5\%$ (v/v)
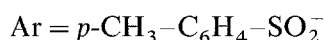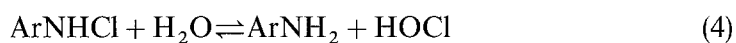
Test for free radicals

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

Evaluation of experimental results

N-Chloro-N-Sodio-p-toluene sulfonamide (CAT) acts as an oxidising agent in both acidic and alkaline media. In general, CAT undergoes a two-electron change in its reactions. The reduction potential of CAT/ArNH$_2$ is pH dependent and decreases with an increase in the pH of the medium, having values of 1.14 V at pH 0.65 and 0.5 V at pH 12. Depending on the pH of the medium, CAT furnishes different types of reactive species in solutions (Eqs. 1–4), such as ArNHCl, ArNCl$_2$, HOCl, and possibly H$_2$OCl$^+$ in acid solutions [4, 13, 14].
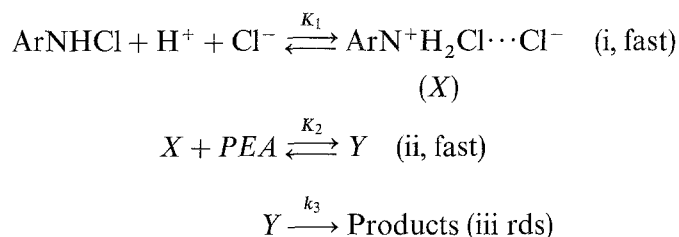
$$ArNClNa \rightleftharpoons ArNCl^- + Na^+ \tag{1}$$

$$ArNCl^- + H_2O \rightleftharpoons ArNHCl + OH^- \tag{2}$$

$$ArNHCl + ArNHCl \overset{K_d}{\rightleftharpoons} ArNCl_2 + ArNH_2 \tag{3}$$

$$K_d = 6.1 \times 10^{-2} \text{ at } 25\,^\circ C$$

$$ArNHCl + H_2O \rightleftharpoons ArNH_2 + HOCl \tag{4}$$

$$Ar = p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2^-$$

If ArNCl$_2$ were to be the reactive species, then the rate law would predict a second-order dependence of the rate on $[CAT]$ which is contrary to the experimental observations. If HOCl is primarily involved, a first-order retardation of the rate by added p-toluene sulphonamide (PTS) has to be expected. Since no such effect is noticed, HOCl can be ruled out as the oxidizing species. Hence, ArNHCl is responsible for the oxidation of the phenethyl alcohols (PEA). In view of these facts,

Scheme 1 can be proposed for the oxidation of *PEA* by *CAT*:

$$\text{ArNHCl} + \text{H}^+ + \text{Cl}^- \underset{}{\overset{K_1}{\rightleftharpoons}} \text{ArN}^+\text{H}_2\text{Cl}\cdots\text{Cl}^- \quad \text{(i, fast)}$$

$$(X)$$

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

$$Y \overset{k_3}{\longrightarrow} \text{Products (iii rds)}$$

Scheme 1

Scheme 1 assumes the formation of a tight ion pair (X, [15]) as an intermediate. The latter equilibrates with *PEA* to form a *PEA–CAT* complex (Y) which decomposes in a rate-limiting step to the products. The fractional order on $[PEA]_0$ indicates a pre-equilibrium step (ii) in Scheme 1. Assuming $[CAT]_t = [\text{ArNHCl}] + [X] + [Y]$, the rate law given by Eq. 5 can be derived for the oxidation of phenethyl alcohols by *CAT*:

$$-\frac{d[CAT]}{dt} = \frac{k_3 K_1 K_2 [CAT]_t [\text{H}^+][\text{Cl}^-][PEA]}{1 + K_1 [\text{H}^+][\text{Cl}^-](1 + K_2 [PEA])} \quad (5)$$

Equation 5 can be transformed into Eq. 6:

$$\frac{1}{k'} = \frac{1}{k_3 K_2 [PEA]} \left(\frac{1}{K_1 [\text{H}^+][\text{Cl}^-]} + 1 \right) + \frac{1}{k_3} \quad (6)$$

From the double reciprocal plots of k' vs. $[PEA]$ and k' vs. $[\text{H}^+]\cdot[\text{Cl}^-]$, values of k_3, K_1, and K_2 are evaluated. Using k_3 values ($6.66 \times 10^{-4}\,\text{s}^{-1}$, $12.5 \times 10^{-4}\,s^{-1}$, $20 \times 10^{-4}\,\text{s}^{-1}$, and $33.3 \times 10^{-4}\,\text{s}^{-1}$ at 303, 308, 313, and 318 K) obtained by varying $[PEA]_0$ at different temperatures, activation parameters were determined for the rate limiting step. The values are: $E_a = 81.3\,\text{kJ/mole}$, $\Delta H^{\#} = 78.8\,\text{kJ/mole}$, $\Delta S^{\#} = -45.4\,\text{J/K·mole}$, $\Delta G^{\#} = 93.0\,\text{kJ/mole}$, $\log A = 10.3$, $K_1 = 3.21\cdot\text{dm}^6\,\text{mol}^{-2}$, $K_2 = 800\,\text{dm}^3\,\text{mol}^{-1}$.

A possible mechanism of the oxidation of phenethyl alcohols by *CAT* and the structure of the intermediates are illustrated in Scheme 2.

It is interesting to note that the rate is only slightly increased in D_2O. Since D_3O^+ ion is a stronger acid than H_3O^+ by a factor of 2–3, a solvent isotope effect of this magnitude is to be expected. The only slight increase in D_2O probably shows that, since the protonation step is followed by hydrolysis involving 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_2O–D_2O mixtures could shed light on the nature of the transition state. The dependence of the rate constant on n, (k'_n) the atom fraction of deuterium in a solvent mixture of D_2O and H_2O, is given by a form of the *Gross-Butler* equation [16, 17]

$$\frac{k^0_{obs}}{k^n_{obs}} = \frac{\Pi^{TS}(1 - n + n\Phi_i)}{\Pi^{RS}(1 - n + n\Phi_i)} \quad (7)$$

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.

Scheme 2
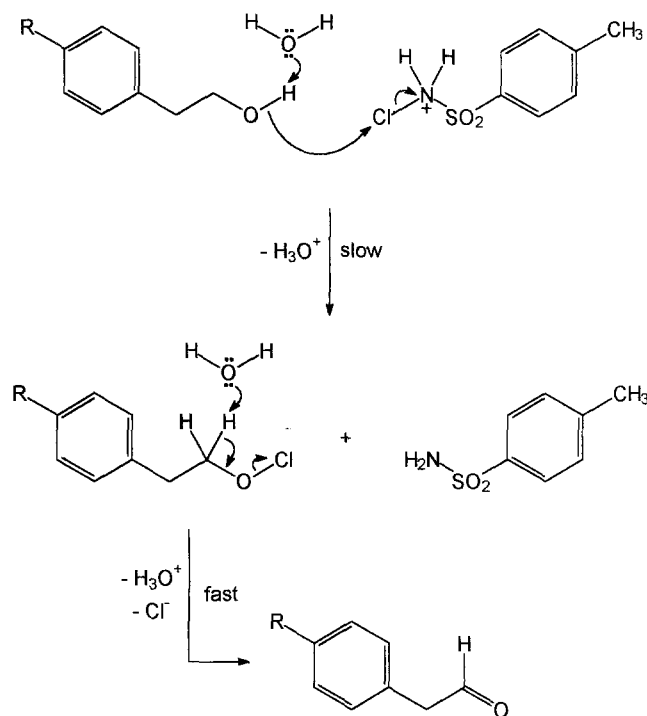
Equation 7 allows the calculation of the fractionation factor of TS, if reactant fractionation factors are known. However, the curvature of the proton inventory plot could reflect the number of exchangeable protons in the reaction [18]. A plot of k'_n vs. the deuterium atom fraction n (Fig. 6, Table 9) in the present case is more or less a straight line. A comparison with standard curves [18] clearly indicates the involvement of a single proton or H–D exchange during the reaction sequence. Hence, the participation of a H^+ ion in the formation of the transition state is inferred.

The moderate values of enthalpy of activation, a large negative entropy of activation, and the fairly high $\Delta G^{\#}$ values support this mechanism. The nearly constant $\Delta G^{\#}$ values indicate a solvated state and operation of a similar mechanism for the oxidation of all alcohols studied.

The effect of varying the solvent composition on the rate of the reaction has been described in detail in Refs. [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 $\log k'$ 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 the rate cannot be explained by the Amis theory [23]. Applying the Born [25] equation, Laidler [20] has derived the following equation for a dipole–dipole reaction:

$$\ln k' = \ln k_0 + \frac{3}{8kT}\left(\frac{2}{D} - 1\right)\left(\frac{\mu^2 A}{r^3 A} + \frac{\mu^2 B}{r^3 B} + \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3}\right) \tag{8}$$

Here, 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 reactants and activated complex. It can be 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 (Table 8).

Structure-Reactivity Correlations

Structure-reactivity correlations were made by attempting to fit the results to the *Hammett* equation. The *Hammett* plot shows two distinct lines (Fig. 8, Table 12).
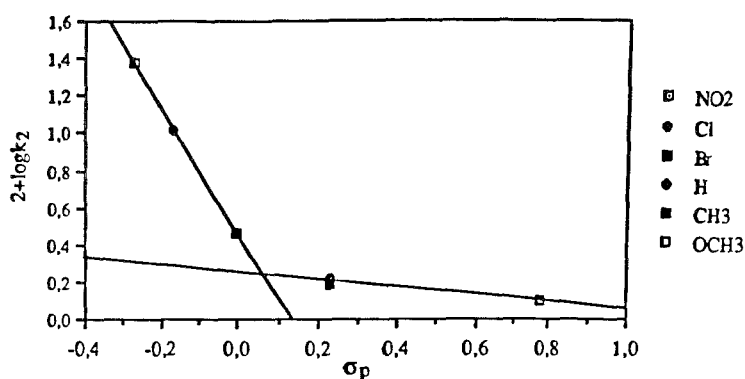

**Fig. 8.** Plot of $\log k_2$ *vs.* σ_p for 4-R-Phenethylalcohols at 308 K

Table 12. Second order rate constants for the oxidation of substituted phenethyl alcohols by CAT at 35 °C

Substrates	$k_2 = k'/[S]$ $(dm^3 \cdot mol^{-1} \cdot s^{-1})$	σ_P
4-NO_2-PEA	1.25	0.78
4-Cl-PEA	1.55	0.23
4-Br-PEA	1.67	0.23
PEA	2.90	0.00
4-CH_3-PEA	10.40	−0.17
4-OCH_3-PEA	23.98	−0.27

$[CAT]_0 = 0.0005$ M; $[S]_0 = 0.01$ M; $[HCl] = 0.1$ M; $MeOH = 5\%$ (v/v)

For each of them there is a good correlation between the substituent constant 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 -3.3 and the other a relatively low ρ of -0.25 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 O–H group by a water molecule or not. In an earlier work on the oxidation of primary alcohols by organic haloamines, it was noted that electron donating groups increase the rate. This indicates that the rupture of the C–H bond occurs ahead of the O–H bond cleavage, creating a carbonium 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 could be a composite quantity like $k' = K \cdot k$. The *Michaelis-Menten* character of the substrate dependence can point towards a substrate independent mechanism such as

$$ArNHCl + H_2O \rightarrow ArNH_2 + HOCl \quad (rds)$$
$$HOCl + PEA \rightarrow Products \quad (fast)$$
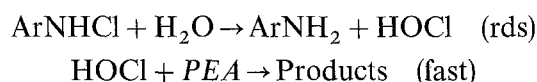
The above mechanism with a stronger electrophile like HOCl may be operative along with one where simultaneous catalysis by H^+ and Cl^- ions takes place (Scheme 1).

Iso-kinetic relationsip

The enthalpy of activation is low for the oxidation of phenethyl alcohols by chloramine-T. The values of $\Delta H^{\#}$ and $\Delta S^{\#}$ for the oxidation of phenythyl alcohols are linearly related ($r = 0.989$), and the iso-kinetic temperature $\beta = 166.7$ K (Fig. 9). The genuine nature of the isokinetic relationship was verified by the *Exner* criterion [26] by plotting $\log k'$ (318 K) *vs.* $\log k'$ (303 K). The value of β was calculated from

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

where q is the slope of *Exner* plot and $T_1 > T_2$. The value of β is 166.7 K (Fig. 10). It can be seen that the value of β is lower than the experimental temperature (308 K), indicating entropy controlled reactions.
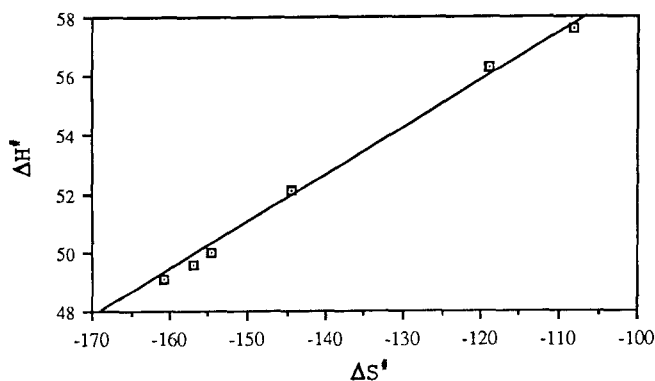
Fig. 9. Isokinetic plot of $\Delta H'$ *vs.* $\Delta S'$ for the oxidation of substituted phenethyl alcohols by CAT
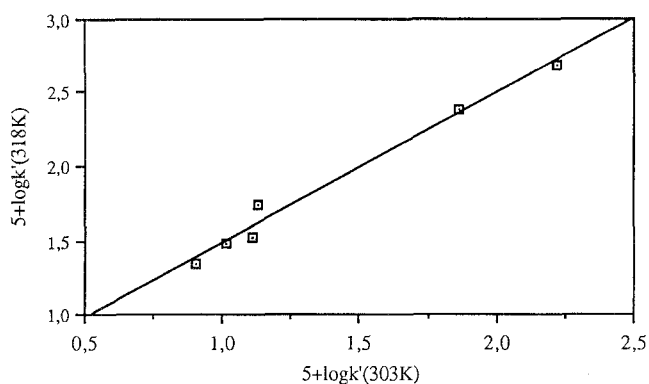
Fig. 10. *Exner* plot of log k' (318 K) vs. log k' (303 K) for the oxidation of substituted phenethyl alcohols by CAT

Table 13. Observed kinetic orders for the oxidation of PEA by CAT in the presence of HCl at 35 °C

$[CAT]$	$[PEA]$	$[HCl]$	$[H^+]$	$[Cl^-]$	$[HClO_4]$	$[Br^-]$	$[PTS]$	μ	D
1.0	0.78	1.54	1.0	0.6	1.0	–	–	–	–

Experimental

Chloramine-T (CAT, Romali) was purified according to Ref. [12]. An aqueous solution of the compound was prepared, iodometrically standardized, and stored in brown bottles to prevent its photochemical deterioration. Phenethyl alcohols (Aldrich) were used without further purification. Solutions of the compounds were prepared in water. All other reagents were of analytical grades. Doubly distilled water was employed in the preparation of aqueous solutions.

Kinetic Measurements

The reactions were 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 °C. A measured amount of CAT 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 time intervals and determining the unreacted CAT iodometrically. The course of reaction was studied up to two half-lives. The calculated pseudo-first order rate constants, k', were reproducible to within 1%.

Stoichiometry

Various ratios of CAT to PEA were equilibrated in the presence of 0.1 mol·dm^{-3} HCl for 24 hours. The determination of unconsumed CAT in the reaction mixture showed that one mode of PEA consumed one mole of CAT (Scheme 3).

Product Analysis

The reaction products were subjected to column chromatography on silica gel (60–200 mesh) using gradient elution (dichloromethane to chloroform). After initial separation, the products were further
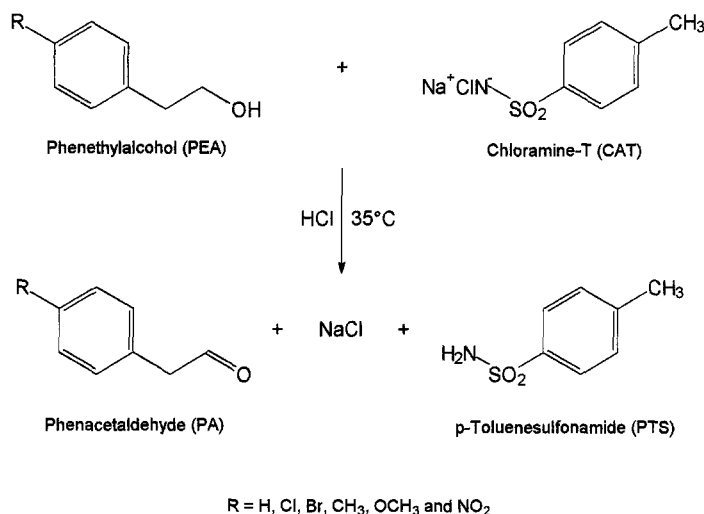
Scheme 3

purified by recrystallization. Materials were identified by comparison with commercially available samples.

Phenacetaldehyde

Recrystallization from dichloromethane/petroleum ether, m.p. = 32–33 °C (Ref. [27]: m.p. = 33–34 °C). The phenacetaldehyde was further identified by its 2,4-dinitro phenylhydrazone (2,4-*DNP*) derivative. It was recrystallized from ethanol (recovery 74.2%) and was found to be identical with a *DNP* derivative of an authentic sample.

p-Toluene sulfonamide (PTS)

Recrystallized from dichloromethane/petroleum ether, m.p. = 134–136 °C (Ref. [28]: m.p. = 137–140 °C). R_f value: 0.34 (TLC: $CH_2Cl_2 + CHCl_3$, 7:3 v/v iodine as spray reagent).

Acknowledgements

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