# Kinetics and mechanism of oxidation of α-phenylbenzenemethanols by sodium-*N*-bromo-*p*-toluenesulphonamide catalysed by ruthenium(III)

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The kinetics of oxidation of six *p*-substituted α-phenylbenzenemethanols (Y-PBM, where Y = H, Cl, Br, NO$_2$, CH$_3$ and OCH$_3$) by sodium-*N*-bromo-*p*-toluenesulphonamide or bromamine-T (BAT) in the presence of HCl and catalysed by RuCl$_3$ in 30% (v/v) methanol medium has been studied at 35°C. The experimental rate law is found to be, rate = $k^1[BAT]_0[PBM]_0^x [RuCl_3]^y[H^+]^z$ where x = y = z < 1. Addition of reaction product, *p*-toluenesulphonamide (TsNH$_2$) retards the reaction. An increase in the dielectric constant of the medium decreases the rate. Rate studies in D$_2$O medium show that the solvent isotope effect $k^1(H_2O)/k^1(D_2O) = 0.56$. Proton inventory studies have been made in H$_2$O-D$_2$O mixtures. The rates correlate satisfactorily with Hammett σ relationship and the plot is biphasic. The reaction constant ρ is −2.1 for electron releasing substituents and −0.26 for electron withdrawing groups at 35°C. The activation parameters ΔH$^\neq$, ΔS$^\neq$ are linearly related and an isokinetic relationship is observed with β = 340K indicating enthalpy as a controlling factor.

The organic halomine class of compounds are capable of producing halonium cations in aqueous solution. The important chlorine compound of this group is chloramine-T (CAT), which is a byproduct during saccharin manufacture, and is a well known analytical reagent. Mechanistic aspects of many of its reactions have been documented[1]. The bromine analogue (BAT) can be easily prepared by the bromination of CAT and is found to be a better oxidising agent than the chloro compound. Mild oxidation of alcohols to carbonyl compounds is a very important synthetic operation in organic synthesis. Considerable amount of work has been done on the mechanistic studies involving oxidations of alcohols by transition metal ions[2] such as chromium(VI), vanadium(V), cobalt(III), manganese(VII), cerium(IV) in acid medium and with copper(II)[3] and ruthenium tetroxide in alkaline medium and ferrate(VI)[4,5] ion. The organic haloamines are capable of oxidising aliphatic and aromatic primary alcohols[6] to the corresponding aldehydes. However, information is meagre in the literature concerning the oxidation of secondary aromatic alcohols[7] by these reagents. After examining several oxidising reagents, we found BAT to be an excellent oxidant to perform controlled oxidation of alcohols to carbonyl compounds in acid medium in presence of the catalyst RuCl$_3$. To shed some light on the mechanism of BAT oxidation of secondary alcohols, we have studied the reactions of six substituted α-phenylbenzenemethanols (PBM) generally known as benzhydrols or diphenylcarbinols, with this oxidant. Optimum conditions are devised for the formation of benzophenone, which is an important constituent of perfumes and is further used in the manufacture of antihistamines, hypnotics and insecticides. Hammett free energy relationship has been tested and an isokinetic relation has been deduced together with the computed thermodynamic parameters.

## Materials

Bromamine-T(BAT) was prepared by the method of Nair *et al.*[8] An aqueous solution of the compound was prepared, iodometrically standardized and stored in brown bottles to prevent its photochemical deterioration. α-Phenylbenzenemethanols (Aldrich) were of accepted grades of purity and were used without further purification and their solutions were prepared in 30% v/v methanol. Solution of RuCl$_3$ (Arora-Mathey) in 0.5 mol dm$^{-3}$ HCl was used as catalyst in acid medium. Allowance was made for the amount of HCl present in the catalyst solution while preparing solutions for kinetic runs. All other chemicals used were of analytical grades of purity. Triply distilled water was used for preparing aqueous solutions. The solvent isotope studies were made with D$_2$O (99.2%) supplied by BARC, Bombay.

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The ionic strength of reaction mixture was kept at a high value with a concentrated solution of NaClO$_4$. Regression analysis of experimental data was carried out on an EC-72 Statistical Calculator supplied by the Electronic Corporation, India.

## 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 PBM, HCl, RuCl$_3$ 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 BAT 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 different time intervals and determining the unreacted BAT 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 ± 5%.

## Stoichiometry

Investigations under the conditions [BAT] $\geqslant$ [PBM] revealed that one mole of BAT was consumed by one mole of PBM (Eqn. 1)

$$Y - C_6H_4 - CHOH - C_6H_5 + TsNBrNa \xrightarrow{35°C}$$
$$Y - C_6H_4 - CO - C_6H_5 + TsNH_2 + Na^+ + Br^-$$
$$\dots (1)$$
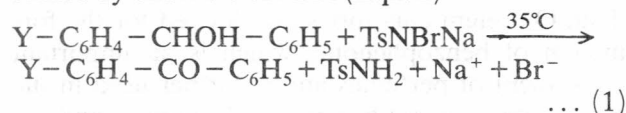
Here Y$ = -$H, $-$Cl, $-$Br, $-$CH$_3$, $-$OCH$_3$ and NO$_2$ and Ts $=$ CH$_3$ $-$ C$_6$H$_4$ $-$ SO$_2$ $-$

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

## Benzophenone

Recrystallized from ethanol, m.p. 49-50°, known m.p. = 49-51° (Merck index 11, 1108). The compound was identified by TLC using dichloromethane as the solvent and iodine as the spray reagent (R$_f$ 0.82). The benzophenone was further identified by its 2, 4-DNP derivative, which was recrystallized from ethanol (recovery 76.2%) and was found to be identical with a DNP derivative of an authentic sample, m.p. 237-38° (lit. m.p. 238°).

## p-Toluenesulphonamide (TsNH$_2$)

Recrystallised from dichloromethane and pet. ether m.p. 137-39° (lit. m.p. 137-40°) (Beil 11, 104). The p-toluenesulphonamide was identified by TLC using dichloromethane as the solvent and iodine as the spray reagent (R$_f$ 0.26).

## Results

**Effect of reactants.** With the substrate in excess, at constant [HCl], [PBM]$_0$, and [RuCl$_3$], plots of log[BAT] vs time are linear (r > 0.996), indicating a first-order dependence of rate on [BAT]$_0$. Values of pseudo-first order rate constants ($k^1$) are given in Table I. Further, the values of $k^1$ are unaltered with variation in [BAT]$_0$ confirming the first order dependence on [oxidant]$_0$.

The rate increases initially with increase in [PBM]$_0$. A plot of log $k^1$ vs log [PBM]$_0$ is linear (r = 0.998, Table I) with a fractional slope of 0.83. The rate levels off at higher [PBM]$_0$.

**Effect of [HCl].** The rate increases with increase in [HCl] and plot of log $k^1$ vs log [HCl] is linear (r = 0.999, Table II) with fractional slope of 0.80.

**Effect of [H$^+$].** At constant [Cl$^-$] = 0.4 mole dm$^{-3}$ maintained by adding NaCl, the rate increased with increase in [H$^+$], which was varied by adding HCl. A plot of log $k^1$ vs log [H$^+$] is linear (r = 0.998, Table II) with fractional slope of

Table I—Effect of varying [reactant] on the reaction rate

{[HCl] = 0.1 mol dm$^{-3}$, [RuCl$_3$] = 4.82 × 10$^{-5}$ mol dm$^{-3}$, μ = 0.4 mol dm$^{-3}$, MeOH = 30% (v/v), T = 308K}

| [BAT]$_0$ × 10$^4$ (mol dm$^{-3}$) | [PBM]$_0$ × 10$^3$ (mol dm$^{-3}$) | $k^1$ × 10$^4$ (sec$^{-1}$) | [BAT]$_0$ × 10$^4$ (mol dm$^{-3}$) | [PBM]$_0$ × 10$^3$ (mol dm$^{-3}$) | $k^1$ × 10$^4$ (sec$^{-1}$) |
|---|---|---|---|---|---|
| 05.0 | 10.0 | 9.28 | 10.0 | 05.0 | 4.49 |
| 10.0 | 10.0 | 9.20 | 10.0 | 07.5 | 6.60 |
| 15.0 | 10.0 | 9.09 | 10.0 | 10.0 | 9.20 |
| 20.0 | 10.0 | 9.32 | 10.0 | 15.0 | 12.02 |
| 25.0 | 10.0 | 9.08 | 10.0 | 20.0 | 15.84 |
| 30.0 | 10.0 | 9.36 | 10.0 | 30.0 | 24.54 |
| 35.0 | 10.0 | 9.10 | 10.0 | 40.0 | 31.62 |
| 40.0 | 10.0 | 9.22 | 10.0 | 50.0 | 34.67 |
| 50.0 | 10.0 | 9.38 | 10.0 | 60.0 | 38.02 |

Table II—Effect of varying [HCl], [H$^+$] and [RuCl$_3$] on the reaction rate

{[BAT]$_0$ = 10.0 × 10$^{-4}$mol dm$^{-3}$, [PBM]$_0$ = 10.0 × 10$^{-3}$ mol dm$^{-3}$, μ = 0.4 mol dm$^{-3}$, MeOH = 30% v/v, T = 308 K}

| [HCl] × 10$^2$ (mol dm$^{-3}$) | $k^1$ × 10$^4$ (sec$^{-1}$) | [H$^+$]* × 10$^2$ (mol dm$^{-3}$) | $k^1$ × 10$^4$ (sec$^{-1}$) | [RuCl$_3$] × 10$^{-5}$ (mol dm$^{-3}$) | $k^1$ × 10$^4$ (sec$^{-1}$) |
|---|---|---|---|---|---|
| 05.0 | 5.24 | 10.0 | 09.20 | 1.96 | 5.49 |
| 08.0 | 7.41 | 15.0 | 12.58 | 2.52 | 6.30 |
| 10.0 | 9.20 | 20.0 | 15.85 | 3.64 | 7.41 |
| 15.0 | 12.02 | 25.0 | 19.95 | 4.82 | 9.20 |
| 20.0 | 15.80 | 30.0 | 22.90 | 7.24 | 10.71 |
| 30.0 | 20.89 | 40.0 | 29.51 | 9.26 | 12.58 |
| 40.0 | 25.11 | — | — | 11.22 | 14.48 |

* Variation at constant [Cl$^-$] = 0.4 mol dm$^{-3}$.

Table III—Effect of varying [TsNH$_2$] and dielectric constant on the reaction rate

{[BAT]$_0$ = 10.0 × 10$^{-4}$ mol dm$^{-3}$, [PBM]$_0$ = 10.0 × 10$^{-3}$ mol dm$^{-3}$, [HCl] = 0.1 mol dm$^{-3}$, [RuCl$_3$] = 4.82 × 10$^{-5}$ mol dm$^{-3}$, μ = 0.4 mol dm$^{-3}$, T = 308 K}

| [TsNH$_2$] × 10$^4$ (mol dm$^{-3}$) | $k^1$ × 10$^4$ (sec$^{-1}$) | % MeOH v/v | Dielectric constant (D) | $k^1$ × 10$^4$ (sec$^{-1}$) |
|---|---|---|---|---|
| 2.0 | 8.62 | 30.0 | 56.73 | 9.20 |
| 4.0 | 5.62 | 40.0 | 51.08 | 7.08 |
| 6.0 | 4.26 | 50.0 | 45.30 | 4.46 |
| 10.0 | 3.54 | 55.0 | 42.66 | 3.71 |
| 15.0 | 2.82 | 60.0 | 40.40 | 3.02 |

0.81. The results were the same even when [Cl$^-$] was not maintained at a constant high value.

**Effect of halide ions.** Added Cl$^-$ or Br$^-$ ions in the form of NaCl or NaBr (5 × 10$^{-4}$-20 × 10$^{-4}$ mole dm$^{-3}$) at fixed [H$^+$] = 0.1 mole dm$^{-3}$ had no effect on reaction rate.

**Effect of RuCl$_3$.** The rate increased with increase in [RuCl$_3$] (Table II) and plot of log $k^1$ vs log [RuCl$_3$] is linear with fractional slope of 0.57 (r = 0.997).

**Effect of *p*-toluenesulphonamide (TsNH$_2$).** The rate decreased with the addition of TsNH$_2$. A plot of log $k^1$ vs log [TsNH$_2$] is linear with a negative fractional slope of 0.58 (r = 0.999, Table III) indicating that TsNH$_2$ is 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 negligible effect on the rate.

**Effect of varying dielectric constant of medium.** The dielectric constant of the medium was varied by adding methanol (30-60%, v/v) to the reaction mixture. The rate decreased with the increase in methanol content. A plot of log $k^1$ vs 1/D is linear (r = 0.987 Table III) with a negative slope supporting a rate limiting step with partial ionization. Blank experiment with methanol, showed that there is a slight decomposition of solvent under experimental conditions. This was allowed for in the calculation of the net reaction rate constant for the oxidation of phenylbenzenemethanols.

**Solvent isotope studies.** Studies of the rate of oxidation of PBM by BAT in D$_2$O revealed that whereas $k^1$ (H$_2$O) is 9.20 × 10$^{-4}$s$^{-1}$, $k^1$(D$_2$O) is 16.52 × 10$^{-4}$s$^{-1}$. The solvent isotope effect $k^1$(H$_2$O)/$k^1$(D$_2$O) is thus found to be 0.56. Proton inventory studies have been made by carrying out the reaction in H$_2$O-D$_2$O mixtures with varying atom fractions 'n' of deuterium, (Figure 1).

**Effect of temperature on the rate.** The reaction was studied at different temperatures (303-318K), and from the Arrhenius plots of log $k^1$ vs 1/T, values of the activation parameters for the composite reaction were calculated (Table IV).

**Test for free radicals.** Addition of the reaction mixtures to acrylamide did not initiate polymerization, showing the absence of free radical species.

## Discussion

*N*-Bromo-*N*-sodio-p-toluenesulphonamide or bromamine-T acts as an oxidizing agent in both acidic and alkaline media. In general BAT undergoes a two-electron change in its reactions. The oxidation potential of BAT/TsNH$_2$ is *p*H dependent and decreases with increase in the *p*H of the medium (values are 1.14v at *p*H 0.65 and 0.5 v at *p*H 12). Depending on the *p*H of the medium, BAT furnishes different types of reactive species

Table IV—Thermodynamic parameters for the oxidation of substituted α-phenylbenzenemethanols by BAT

$\{[BAT]_0 = 10 \times 10^{-4} \text{ mol dm}^{-3}, [Y\text{-PBM}]_0 = 10 \times 10^{-3} \text{ mol dm}^{-3}, [HCl] = 0.1 \text{ mol dm}^{-3},$
$[RuCl_3] = 4.82 \times 10^{-5} \text{ mol dm}^{-3}, \mu = 0.4 \text{ mol dm}^{-3}, MeOH = 30\% \text{ v/v}\}$

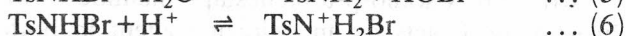| Substrate Y-PBM Y = | Ea ($kJ \text{ mol}^{-1}$) | $\Delta H \neq$ ($kJ \text{ mol}^{-1}$) | $\Delta S \neq$ ($JK^{-1} \text{ mol}^{-1}$) | $\Delta G \neq$ ($kJ \text{ mol}^{-1}$) | log A |
|---|---|---|---|---|---|
| 4-NO$_2$ | 26.9 | 24.3 | −232.2 | 96.4 | 6.4 |
| 4-Cl | 37.3 | 34.7 | −196.3 | 95.6 | 8.3 |
| 4-Br | 42.5 | 39.9 | −178.1 | 95.3 | 9.2 |
| 4−H | 58.0 | 55.4 | −124.2 | 93.8 | 12.0 |
| 4-CH$_3$ | 74.7 | 72.2 | −64.0 | 92.1 | 15.2 |
| 4-OCH$_3$ | 86.4 | 83.8 | −24.1 | 90.2 | 17.2 |
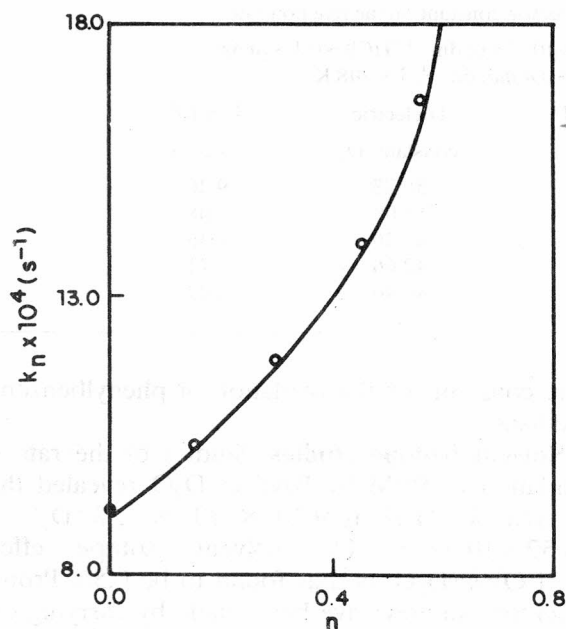


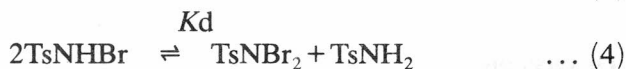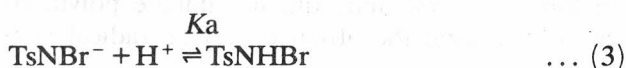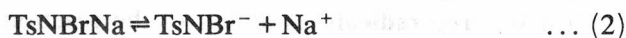Figure 1—Proton inventory plot of $K_n$ vs the deuterium atom fraction(n) in $H_2O - D_2O$ mixtures

in solutions (Eqns 2-7) such as TsNHBr, TsNBr$_2$, HOBr and possibly $H_2O^+Br$ in acid solutions[9-12].

$$TsNBrNa \rightleftharpoons TsNBr^- + Na^+ \qquad \ldots (2)$$

$$\overset{Ka}{TsNBr^- + H^+ \rightleftharpoons TsNHBr} \qquad \ldots (3)$$

$$\overset{Kd}{2TsNHBr \rightleftharpoons TsNBr_2 + TsNH_2} \qquad \ldots (4)$$

$$TsNHBr + H_2O \rightleftharpoons TsNH_2 + HOBr \qquad \ldots (5)$$

$$TsNHBr + H^+ \rightleftharpoons TsN^+H_2Br \qquad \ldots (6)$$

$$TsN^+H_2Br + H_2O \rightleftharpoons TsNH_2 + H_2O^+Br \qquad \ldots (7)$$
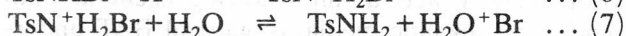
If the dibromamine, TsNBr$_2$ were to be the reactive species, then the rate law would predict a second-order dependence of rate on $[BAT]_0$ (Eqn 4), which is contrary to the experimental observations. The rate increases with increase in $[H^+]$

but is retarded by the added reaction product *p*-toluenesulphonamide. Hence Eqns 6 and 7 play a dominant role in the oxidation of PBM by BAT.

Electronic spectral studies of Cady and Connick[13], Connick and Fine[14] reveal that species such as $[RuCl_5(H_2O)]^{2-}$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^{2+}$ do not exist in the aqueous solution of RuCl$_3$. A study on oxidation states of ruthenium has shown that Ru(III) exists in the following equilibrium[15-17] in acid medium.

$$[Ru(III)Cl_6]^{3-} + H_2O \rightleftharpoons$$
$$[Ru(III)Cl_5(H_2O)]^{2-} + Cl^-$$
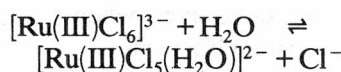
Singh *et al.*[18,19] employed the above equilibrium in Ru(III) catalysed BAT oxidation of some primary alcohols in acid medium and in the Ru(III) chloride catalysed oxidation of ethyleneglycols by *N*-bromoacetamide (NBA) in HClO$_4$ medium. However in the present case, addition of Cl$^-$ ion in the form of NaCl at fixed $[H^+]$ had no effect on the rate indicating that $[Ru(III)Cl_6]^{3-}$ itself is the most likely catalysing species.

Ultraviolet spectral measurements showed that PBM solution has two sharp absorption bands at 255.2 and 222.4 nm while bands around 204 and 224.3 nm were noticed for Ru(III) and BAT solutions respectively in the presence of 0.1 mol dm$^{-3}$ HCl. With mixtures of (i) PBM and Ru(III) and (ii) BAT and Ru(III) solutions in the presence of 0.1 mol dm$^{-3}$ HCl, there were no changes in $\lambda_{max}$, but when BAT and PBM solutions were mixed in presence of 0.1 mol dm$^{-3}$ HCl a single sharp absorption band was noticed at 216.0 nm indicating that complex formation takes place only between BAT and PBM. In view of these facts, Scheme I is proposed for the oxidation of α-phenylbenzenemethanol by BAT.

Scheme I assumes the formation of $H_2O^+Br$ due to the protonation of TsNHBr by $H^+$ ion and subsequent hydrolysis, which complexes with the
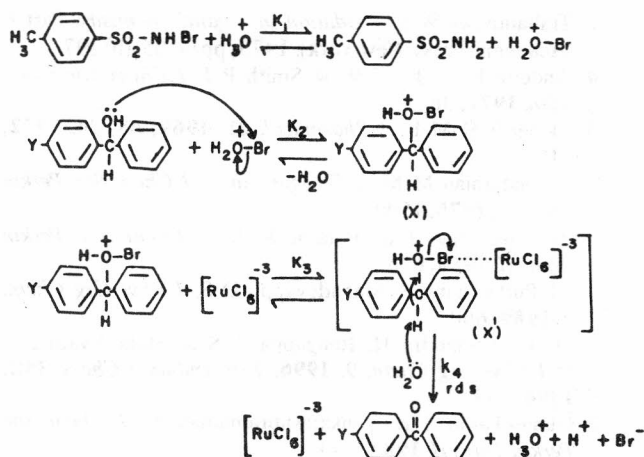
**Scheme I**

substrate (X). The latter reacts with $RuCl_3$ through an equilibrium step to form complex ($X^1$) which decomposes in a rate-limiting step to yield products. The fractional order on $[RuCl_3]$ indicates a pre-equilibrium step (iii) in Scheme I. Assuming $[BAT]_t = [TsNHBr] + [H_2O^+Br] + [X] + [X^1]$, rate law Eqn 8 can be derived for the oxidation of PBM by BAT.

$$-\frac{d[BAT]}{dt}$$

$$= \frac{k_4 K_1 K_2 K_3 [BAT]_t [H_3O^+][PBM]_0[Ru]}{[TsNH_2] + K_1[H_3O^+] + K_1 K_2[H_3O^+][PBM]_0\{1 + K_3[Ru]\}} \quad \ldots (8)$$

It is interesting to note that the rate has increased 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[20]. But the observed inverse solvent isotope effect $k^1(D_2O)/k^1(H_2O)$ of 1.80 probably shows that since the protonation is followed by hydrolysis in the rate-limiting step which involves $O-H$ 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 throw light on the nature of the transition state. The dependence of the rate constant ($k^n$) on 'n', the atom fraction of deuterium in a solvent mixture of $D_2O$ and $H_2O$ is given[21,22] by a form of Gross-Butler equation (Eqn 9),

$$\frac{k_{obs}^0}{k_{obs}^n} = \frac{\prod^{TS}(1-n+n\Phi_i)}{\prod^{RS}(1-n+n\Phi_j)} \quad \ldots (9)$$

where $\Phi_i$ and $\Phi_j$ are the isotopic fractionation factors for isotopically exchangeable hydrogen sites in the transition states (TS) and reactant site (RS) respectively. Eqn 9 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[23]. A plot of $k_{obs}^n$ vs the deuterium atom fraction 'n' (Figure 1) in the present case is a curve and comparison with the standard curves[23] 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 enthalpy of activation, a large negative entropy of activation and the fairly high $\Delta G \neq$ values support the mechanism (Table IV). The near constancy of $\Delta G \neq$ values indicates a solvated state and operation of a similar mechanism for the oxidation of all α-phenylbenzenemethanols.

**Structure-reactivity correlations**

The Hammett plot shows two distinct 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 McDaniel-Brown constant is used. Of these, one has a much larger $\rho$ value of $-2.1$ for electron releasing groups and the other relatively low value of $-0.26$ for electron withdrawing groups 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. In earlier work on the oxidation of primary alcohols by organic haloamines[6c], 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. Also a reaction involving a carbonium ion ($C^+$) in the transition state will be aided by electron donating substituents and the value of $\rho$ will be negative. A reaction, on the other hand, involving a decrease in the carbonium ion ($C^+$) charge will be facilitated by electron withdrawing substituents. Therefore, the carbonium ion ($C^+$) is more stable when the electron donars are attached to benzene ring system,

which disperses the positive charge on the carbonium ion $(\rho = -2.1)$ than the electron withdrawing groups at the benzene ring system $(\rho = -0.26)$. Because of the above facts no linearity was found in the Hammett plot.

## Isokinetic relationship

The enthalpy of activation is low for the oxidation of α-phenylbenzenemethanols by BAT. The values of $\Delta H\#$ and $\Delta S\#$ for the oxidation of α-phenylbenzenemethanols are linearly related (Table IV, r = 0.9993) and the isokinetic temperature β = 340K. The genuine nature of the isokinetic relationship was verified by the Exner criterion by plotting log $k^1$ (318K) vs log $k'$ (303 K). The value of β was calculated from the equation,

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

where q is the slope of Exner plot and $T_1 > T_2$. The value of β is 349K. It is seen that the value of β is higher than the experimental temperature (308K) indicating enthalpy control on the reactions.

## Acknowledgement

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