

## Oxidation of secondary alcohols by sodium N-bromobenzene-sulphonamide: A kinetic study

K MOHAN, D S MAHADEVAPPA\* and PUTTASWAMY

Department of Studies in Chemistry, University of Mysore, Manasagangothri, Mysore 570006, India

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**Abstract.** The kinetics of oxidation of 2-propanol, 2-butanol, 2-pentanol, 2-hexanol and 2-heptanol to the respective ketones by sodium N-bromobenzenesulphonamide (bromamine-B) in presence of HCl was studied at 40°C. The rate shows a first-order dependence on both  $[\text{oxidant}]_0$  and  $[\text{alcohol}]_0$  and is fractional in  $[\text{H}^+]$  and  $[\text{Cl}^-]$ . The proposed mechanism assumes the formation of a hypobromite in the rate-limiting step followed by a fast reaction to form products. The magnitude of the solvent isotope effect,  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$  is 0.90. The rates do not correlate satisfactorily with Taft's substituent constants. An isokinetic relation is observed with  $\beta = 331 \text{ K}$  indicating enthalpy as a controlling factor.

**Keywords.** Bromamine-B; secondary alcohols; kinetics; acid medium.

### 1. Introduction

Considerable attention has centred around salts of N-haloarenesulphonamides because of their versatile behaviour as mild oxidants, halogenating agents and N-anions, which act both as bases and nucleophiles. The chlorine compound, chloramine T (CAT), a by-product in saccharin manufacture, is well-known as an analytical reagent, and the mechanistic aspects of its reactions have been documented (Campbell and Johnson 1978; Banerji *et al* 1987; Gowda and Mahadevappa 1983). However, there is meagre information in the literature on the bromine analogues, bromamine T (BAT) and bromamine B (BAB), except for the pioneering work of Hardy and Johnston (1973) on the oxidation of *p*-nitrophenol by BAB and the study of the reaction of dialkyl sulphides with BAT by Ruff and Kucsman (1982). As a part of our mechanistic studies of oxidation of substrates by the N-bromoarenesulphonamides, we report the kinetics of oxidation of five aliphatic alcohols, 2-propanol, 2-butanol, 2-pentanol, 2-hexanol and 2-heptanol by BAB in the presence of HCl.

The mechanism of oxidation of secondary alcohols to ketones by conventional mild to strong oxidants has been investigated (Waters 1964; Westheimer and Novick 1943). Oxidation of secondary alcohols by NBS proceeds (Thiagarajan and Venkatasubramanian 1970), through a cyclic transition state. A similar study with N-chlorosuccinimide in presence of HCl (Srinivasan and Venkatasubramanian 1974) has indicated simultaneous catalysis by  $\text{H}^+$  and  $\text{Cl}^-$  ions. Natarajan and Thiagarajan (1975) oxidized secondary alcohols with CAT in the presence of mineral acids and observed a second-order dependence each on  $[\text{CAT}]$  and  $[\text{H}^+]$  and a first-order

dependence of rate on  $[\text{alcohol}]_0$ . The mediating influence of dichloramine T is assumed to account for the experimental rate law. Negi and Banerji (1982) oxidized a number of secondary alcohols by N-bromoacetamide (NBA) and concluded that the reaction is subject to both polar and steric effects.

## 2. Experimental

### 2.1 Preparation of bromamine-B

BAB was prepared by the partial debromination of dibromamine B (DBB), which in turn was prepared by the bromination of chloramine B (CAB). DBB (31.5g) was added in small quantities at a time and with constant stirring to 50 ml of 4M NaOH. The mass was cooled in ice, filtered under suction and the product dried over anhydrous calcium chloride. The yield was about 25.6g (90%). The compound was recrystallized from hot water (50°C). The purity of BAB was checked iodometrically through its active bromine content and the compound was further characterized by its  $^{13}\text{C}$ -FT-NMR spectrum (obtained on a Bruker WH 270 MHz Nuclear Magnetic Resonance Spectrometer) with  $\text{D}_2\text{O}$  as solvent and TMS as the internal standard: (ppm, relative to TMS) at 143.38 (C-1, carbon attached to S atom), 134.30 (C-4, para to the heteroatom), 131.26 (C-2, 6) and 129.31 (C-3, 5). An aqueous solution of BAB was standardized iodometrically and preserved in brown bottles to prevent its photochemical deterioration.

The alcohols, 2-propanol (IDPL, India), 2-butanol (M & B, England), 2-pentanol (Riedel, Germany), 2-hexanol and 2-heptanol (Wilson Lab, India) were further purified by distillation and aqueous solutions were prepared. All other reagents were of accepted grades of purity. Triple-distilled water was used for preparing aqueous solutions. Solvent isotope studies were made with  $\text{D}_2\text{O}$  (99.6%) supplied by BARC. Ionic strengths of reaction mixtures were kept at high values with concentrated solutions of  $\text{NaClO}_4$ .

Regression analysis of experimental data (to get regression coefficient,  $r$ , and standard deviation of estimate,  $s$ ) was carried out on a TDC-316 (16 bits) computer supplied by Trombay Electronics, India, and an EC-72 statistical calculator.

### 2.2 Kinetic measurements

The reaction was carried out in glass-stoppered Pyrex boiling tubes whose outer surface was coated black to eliminate photochemical effects. Requisite amounts of oxidant, hydrochloric acid, alcohol and  $\text{NaClO}_4$  solutions, and water (to keep the total volume constant for all runs) were taken in the boiling tube and thermostatted at 40°C for attaining thermal equilibrium. A measured amount of oxidant solution also thermostatted at the same temperature was rapidly added to the mixture in the boiling tube. The progress of reaction was monitored by iodometric determination of unreacted BAB in a measured aliquot of the reaction mixture at different intervals of time. The reaction was followed for about three half-lives. The pseudo-first-order rate constants calculated from integrated plots were reproducible to  $\pm 3\%$ .

### 2.3 Stoichiometry

Reaction mixtures containing varying ratios of BAB to alcohol were equilibrated in the presence of  $0.01 \text{ mol dm}^{-3}$  HCl for 24 h. Estimation of the unreacted BAB showed a 1:1 stoichiometry:



Here R = CH<sub>3</sub>- for 2-propanol, C<sub>2</sub>H<sub>5</sub>- for 2-butanol, C<sub>3</sub>H<sub>7</sub>- for 2-pentanol, C<sub>4</sub>H<sub>9</sub>- for 2-hexanol and C<sub>5</sub>H<sub>11</sub>- for 2-heptanol.

The reaction product, benzenesulphonamide was detected by TLC using petroleum ether, chloroform and 1-butanol (2:2:1 v/v), as the solvent, and iodine as the detecting agent ( $R_F = 0.88$ ). The corresponding ketones were quantitatively estimated through their 2, 4-dinitrophenylhydrazone derivatives.

### 3. Results

The kinetics of oxidation of secondary alcohols by BAB were investigated at several initial concentrations of reactants. With the substrate in excess, plots of  $\log [\text{BAB}]_0/[\text{BAB}]$  vs time are linear ( $r = 0.9902$ ) indicating a first-order dependence of rate on  $[\text{BAB}]_0$ . The rate increases with  $[\text{alcohol}]_0$  (table 1) and plots of  $\log k'$  vs  $\log [\text{alcohol}]_0$  are linear ( $r > 0.9964$ ;  $s \leq 0.04$ ) with unit slopes. At constant  $[\text{BAB}]_0$  and  $[\text{alcohol}]_0$ , the rate increases with increase in  $[\text{HCl}]$  (table 2) and plot of  $\log k'$  vs  $\log [\text{HCl}]$  was linear ( $r > 0.9970$ ;  $s \leq 0.02$ ) with fractional slopes. The effect of  $[\text{H}^+]$  on rate was studied by keeping  $[\text{Cl}^-]$  at the highest value ( $0.05 \text{ mol dm}^{-3}$ ) by adding NaCl. The rate increased (table 2) and plots of  $\log k'$  vs  $\log [\text{H}^+]$  were linear ( $r > 0.9908$ ;  $s \leq 0.02$ ) with fractional slopes. Further, the true order with respect to  $[\text{H}^+]$  was ascertained by studying the kinetics with  $\text{HClO}_4$  ( $0.01$  to  $0.05 \text{ mol dm}^{-3}$ ) in presence of  $0.01 \text{ mol dm}^{-3}$  HCl. A log-log plot of  $k'$  vs  $[\text{H}^+]$  gave identical orders. At constant  $[\text{H}^+] = 0.01 \text{ mol dm}^{-3}$ , the rate increases with the addition of NaCl (table 2) and a plot of  $\log k'$  vs  $\log [\text{Cl}^-]$  was linear ( $r > 0.9925$ ;  $s \leq 0.09$ ) with a fractional slope. But addition of NaBr ( $5\text{--}20 \times 10^{-4} \text{ mol dm}^{-3}$ ) did not affect the rate of the reaction.

**Table 1.** Effects of variation of  $[\text{alcohol}]_0$  on the reaction rate at  $40^\circ\text{C}$ .  
 $[\text{BAB}]_0 = 7 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{HCl}] = 0.01 \text{ mol dm}^{-3}$ ;  $\mu = 0.5 \text{ mol dm}^{-3}$

$10^3 [\text{alcohol}]_0$ ( $\text{mol dm}^{-3}$ )	$10^4 k' (\text{s}^{-1})$				
	2-propanol	2-butanol	2-pentanol	2-hexanol	2-heptanol
5.0	0.80	1.58	1.65	1.25	1.39
8.0	1.18	2.50	2.72	1.86	2.33
10.0	1.40	3.19	3.40	2.37	2.76
15.0	—	—	—	—	4.42
20.0	2.78	6.52	6.87	4.65	6.17
30.0	4.22	9.37	10.50	7.19	—
40.0	5.65	12.63	12.90	9.92	—
50.0	8.36	15.71	16.10	11.20	—

**Table 2.** Effect of variation of  $[\text{HCl}]$ ,  $[\text{H}^+]$  and  $[\text{Cl}^-]$  on the reaction rate at  $40^\circ\text{C}$ .  
 $[\text{BAB}]_0 = 7 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{alcohol}]_0 = 1 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $\mu = 0.5 \text{ mol dm}^{-3}$ .

$10^3 [\text{HCl}]$ or $10^3 [\text{H}^+]$ ( $\text{mol dm}^{-3}$ )	$10^4 k' (\text{s}^{-1})$				
	2-propanol	2-butanol	2-pentanol	2-hexanol	2-heptanol
5.0 (1.0)	0.78; 2.25* (1.40) <sup>†</sup>	2.18; 3.35* (3.19)	2.27; 3.59* (3.40)	1.53; 2.77* (2.37)	1.86; 2.89* (2.76)
10.0 (2.0)	1.40; 2.87* (1.96)	3.19; 4.15* (3.80)	3.40; 4.84* (4.00)	2.37; 3.67* (2.65)	2.76; 3.72* (3.06)
20.0 (3.0)	2.35; 3.51* (2.33)	5.10; 5.95* (4.51)	5.29; 6.00* (4.33)	3.65; 4.73* (2.91)	4.17; 4.86* (3.21)
30.0 (4.0)	3.11; 4.17* (2.69)	6.26; 6.19* (4.63)	6.55; 6.53* (4.65)	4.72; 5.36* (3.05)	4.89; 5.46* (3.40)
40.0 (5.0)	3.90; 4.48* (2.87)	6.80; 7.02* (4.96)	7.50; 7.39* (5.01)	5.61; 6.31* (3.22)	5.72; 6.55* (3.54)
50.0 (6.0)	4.73; 4.73* (3.17)	8.18; 8.18* (5.24)	8.47; 8.47* (5.43)	6.52; 6.52* (3.43)	6.87; 6.87* (3.66)

\*Starred values refer to variation of  $[\text{H}^+]$  on the rate at constant  $[\text{Cl}^-] = 0.05 \text{ mol dm}^{-3}$ ;

<sup>†</sup>Values in parentheses refer to variation of  $[\text{Cl}^-]$  on rate at constant  $[\text{H}^+] = 0.01 \text{ mol dm}^{-3}$ .

Addition of the reaction product, benzenesulphonamide ( $5\text{--}20 \times 10^{-4} \text{ mol dm}^{-3}$ ), had no effect on the rate. Similarly, variation of ionic strength with  $\text{NaClO}_4$  ( $0.1\text{--}0.5 \text{ mol dm}^{-3}$ ) did not affect the rate.

The solvent composition was varied by adding methanol ( $0\text{--}30\%$  v/v). The rate increased with increase in the methanol content of the reaction mixture and a plot of  $\log k'$  vs  $1/D$ , where  $D$  is the dielectric constant of the medium, gave straight lines ( $r > 0.9840$ ;  $s \leq 0.06$ ) with positive slopes. Blank experiments with methanol, however, showed that there is slight decomposition of the solvent ( $\sim 2\%$ ) under experimental conditions. This was allowed for in the calculation of the net reaction rate constant for the oxidation of secondary alcohol.

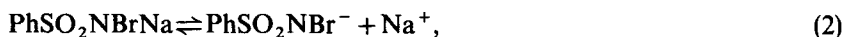
The reaction was studied at different temperatures ( $308\text{--}323 \text{ K}$ ) and from the Arrhenius plots of  $\log k'$  vs  $1/T$  ( $r > 0.9983$ ), the kinetic and thermodynamic parameters computed.

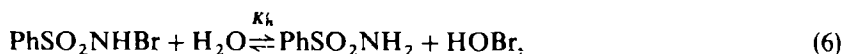
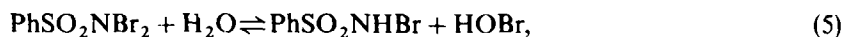
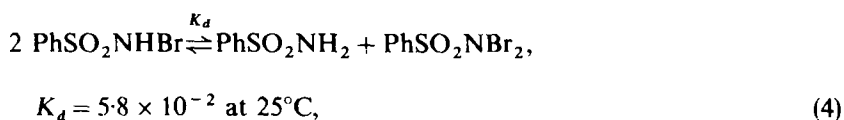
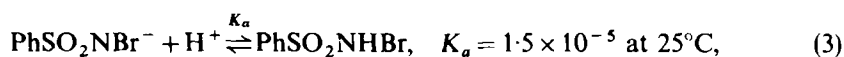
Solvent isotope studies were made in  $\text{D}_2\text{O}$  media with 2-propanol as a probe. Values of  $k'_{\text{D}_2\text{O}}$  and  $k'_{\text{H}_2\text{O}}$  were  $1.55 \times 10^{-4} \text{ s}^{-1}$  and  $1.40 \times 10^{-4} \text{ s}^{-1}$  at experimental conditions,  $[\text{BAB}]_0 = 7.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{alcohol}]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.01 \text{ mol dm}^{-3}$ ;  $\mu = 0.5 \text{ mol dm}^{-3}$ ;  $\text{temp} = 40^\circ\text{C}$ , giving a solvent isotope effect,  $k'_{\text{H}_2\text{O}}/k'_{\text{D}_2\text{O}} = 0.90$ .

Absence of free radicals in the reaction mixture was shown by the negative test with acrylamide, as no polymerization was initiated even after an hour.

#### 4. Discussion

Bromamine-B is analogous to CAT (Bishop and Jennings 1958) and behaves as a strong electrolyte in aqueous solutions. Hardy and Johnston (1973) have shown the existence of the following equilibria in acid BAB solutions:

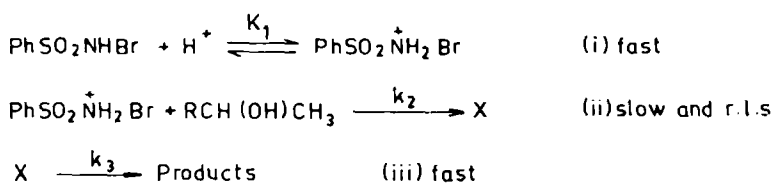




Thus the possible oxidizing species in acidified BAB solutions are  $\text{PhSO}_2\text{NHBr}$ ,  $\text{PhSO}_2\text{NBr}_2$  and  $\text{HOBr}$ . However, Soper (1924) reported that  $[\text{HOCl}]$  is very small in acidified CAT solution and is independent of the [oxidant]. On this basis, the role of  $\text{HOBr}$  in oxidation reactions involving BAB under highly acidic conditions can be ignored. If  $\text{PhSO}_2\text{NBr}_2$  were to be the reactive species, the rate law would then predict a second-order dependence of rate on  $[\text{BAB}]_0$  from (4) which is contrary to experimental observations. Therefore, the most likely oxidant species is  $\text{PhSO}_2\text{NHBr}$  which is responsible for the oxidation of secondary alcohols. Further protonation of  $\text{PhSO}_2\text{NHBr}$  at  $\text{pH} < 2$  according to (8) has been reported recently (Narayan and Rao 1983),



Here when  $\text{R}' = p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2-$ ,  $K = 1.02 \times 10^2$  at  $25^\circ\text{C}$ , while with  $\text{R}' = \text{C}_6\text{H}_5\text{SO}_2-$ ,  $K = 61 \pm 5$  at  $25^\circ\text{C}$ . Hence it is likely that  $\text{PhSO}_2\text{NHBr}$  could be further protonated in acid media. The first-order dependence both on  $[\text{BAB}]_0$  and  $[\text{alcohol}]_0$ , and the fractional order observed in  $[\text{H}^+]$  can be rationalized as in scheme 1.



Scheme 1.

If  $[\text{BAB}]_t$  represents total BAB concentration in solution, then  $[\text{BAB}]_t = [\text{PhSO}_2\text{NHBr}] + [\text{PhSO}_2\overset{+}{\text{N}}\text{H}_2\text{Br}]$ , from which rate law (9) can be derived:

$$\text{Rate} = \frac{k_2 K_1 [\text{BAB}]_t [\text{alcohol}] [\text{H}^+]}{1 + K_1 [\text{H}^+]}, \quad (9)$$

Since  $\text{rate} = k' [\text{BAB}]_t$ ,

$$k' = \frac{k_2 K_1 [\text{alcohol}] [\text{H}^+]}{1 + K_1 [\text{H}^+]}. \quad (10)$$

**Table 3.** Values of protonation and formation constants of alcohol-BAB complex determined from double reciprocal plots.

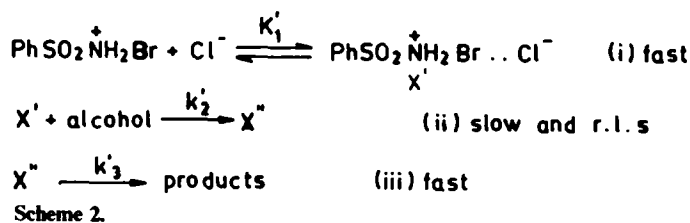
Alcohol	$K_1$ ( $\text{dm}^3 \text{mol}^{-1}$ )	$10^2 k_2$ ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )
2-propanol	156	5.0
2-butanol	119	8.6
2-pentanol	142	8.5
2-hexanol	125	7.0
2-heptanol	127	7.2
Mean	$134 \pm 15$	

Equation (10) can be transformed into (11),

$$\frac{1}{k'} = \frac{1}{k_2[\text{alcohol}]} \times \frac{1}{K_1[\text{H}^+]} + 1. \quad (11)$$

From the slope and intercept of the double reciprocal plot,  $1/k'$  vs  $1/[\text{H}^+]$  ( $r > 0.9892$ ), the protonation constant  $K_1$  and formation constant  $k_2$  of the alcohol-BAB complex were calculated (table 3). It is seen that the protonation constant of BAB obtained, compares favourably with those reported for CAT (Narayan and Rao 1983) and CAB (Subhashini *et al* 1985).

Catalysis of chloride ion during the oxidation of alcohols by BAB at constant  $[\text{H}^+]$  can be rationalized by scheme 2, where a direct reaction between the oxidant species  $\text{PhSO}_2\overset{\oplus}{\text{N}}\text{H}_2\text{Br}$  and  $\text{Cl}^-$  ion is postulated.



The rate law below can be derived from scheme 2 in the form,

$$\text{rate} = \frac{k'_2 K'_1 [\text{BAB}]_i [\text{alcohol}] [\text{Cl}^-]}{1 + K'_1 [\text{Cl}^-]}. \quad (12)$$

Equation (12) shows a first-order dependence of rate on  $[\text{oxidant}]_0$  and  $[\text{alcohol}]_0$  and a fractional order in  $[\text{Cl}^-]$  and is in agreement with the experimental results.

#### 4.1 Mixed-order kinetics in $[\text{HCl}]$

The kinetic orders observed in the gross concentration of  $\text{HCl}$ , and  $\text{H}^+$  and  $\text{Cl}^-$  are given in table 2.

The mixed-order kinetics observed in gross  $[\text{HCl}]$  can be rationalized by (13):

$$\text{Rate} = k_{\text{obs}} [\text{BAB}] = \{k''[\text{H}^+] + k'''[\text{Cl}^-]\} [\text{BAB}] [\text{alcohol}] \quad (13)$$

From (13),  $k' = k_{\text{obs}} = [\text{alcohol}][\text{HCl}] \{k'' + k'''\}$ , since  $[\text{H}^+] = [\text{Cl}^-] = [\text{HCl}]$  in aqueous solution.

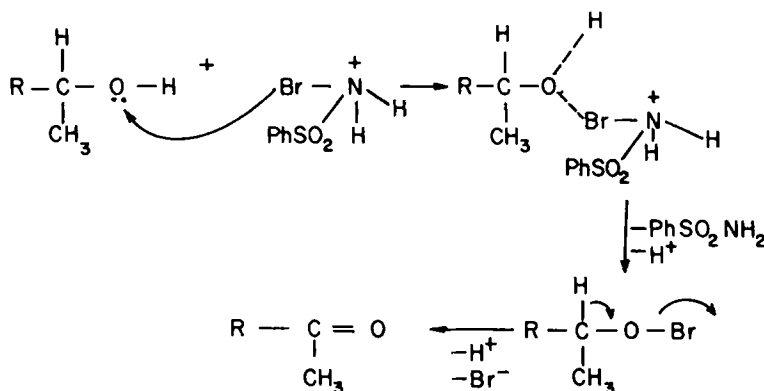
$$\text{Further, } k'/[\text{alcohol}] = (k'' + k''')[\text{HCl}], \quad (14)$$

from which a plot of  $k'/[\text{alcohol}]$  vs  $[\text{HCl}]$  was found to be linear ( $r > 0.9903$ ), proving the validity of (14).

The effect of solvent composition on the rate of reaction has been discussed in well-known monographs by several workers (Laidler and Eyring 1940; Laidler and Landskroener 1957; Benson 1960; Laidler 1965; Amis 1966; Entelis and Tiger 1976). Amis has shown that a plot of  $\log k_{\text{obs}}$  vs  $1/D$  gives a straight line with a positive slope for a positive ion-dipole interaction. Such an observation in the present investigations supports the rate-limiting step in scheme 1 and indicates a transition state which is less polar than the reactants.

For a pre-equilibrium proton transfer, it is expected that rates are higher in  $\text{D}_2\text{O}$  medium than in  $\text{H}_2\text{O}$  (Collins and Bowman 1970). This has been observed in the present case, since the inverse solvent isotope effect,  $k'_{\text{D}_2\text{O}}/k'_{\text{H}_2\text{O}} = 1.1$ .

A detailed mode of oxidation of secondary alcohols by BAB is shown in scheme 3. Negi and Banerji (1982) have demonstrated the absence of a primary kinetic isotope effect in the oxidation of alcohols by NBA. The formation of hypobromite was found to take place in a slow step, while its decomposition to ketone is rapid. In the present studies, absence of a retardation effect by the reaction product, benzenesulphonamide, clearly supports the formation of hypobromite in the slow step and its decomposition to ketone in a fast reaction.



Scheme 3.

Attempts were made to correlate (Gilliom 1970) rates of oxidation of alcohols with the Taft substituent constants  $\sigma^*$  and  $E_s$ , where  $\sigma^*$  represents the polar substituent constant, and  $E_s$  is the steric substituent constant. The following regression equations were obtained when single parameter correlations were made:

$$\log k' = -2.34\sigma^* - 3.82, \quad (r = 0.8280; s = 0.18; n = 5), \quad (15)$$

$$\log k' = -0.42E_s - 3.70, \quad (r = 0.5203; s = 0.32; n = 5), \quad (16)$$

$$\log k' - E_s = -5.30\sigma^* - 3.86, \quad (r = 0.9530; s = 0.08; n = 5). \quad (17)$$

The poor correlation of  $k'$  values with  $\sigma^*$  in (15) indicates that steric effects are important. A negative value of  $\sigma^*$  ( $-2.34$ ) in (15) shows that electron-donating centres increase the rate of reaction. Attempts were also made to use the Pavelich-Taft equation (Pavelich and Taft 1957) in the four parameter form:

$$\log(k'/k'_0) = \sigma^* \rho^* + \delta E_s. \quad (18)$$

Here  $\rho^*$  and  $\delta$  are reaction constants measuring the susceptibility of the reaction series to polar and steric effects, respectively. Using the method of least squares, it was found that  $\rho^* = -3.69$  and  $\delta = 0.46$ . The plot of  $\log(k'/k'_0) - E_s$  against  $\sigma^*$ , is approximately linear ( $r = 0.9421$ ) which indicates that the rates of oxidation of secondary alcohols are governed by both polar and steric effects. A similar observation has been noted by Negi and Banerji (1982) in the oxidation of secondary alcohols by NBA.

The activation parameters, both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  increase in the order:



From the enthalpy-entropy plot, the isokinetic temperature was found to be 336K.

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