OXIDATION OF SECONDARY ALCOHOLS BY SODIUM N-CHLOROBENZENESULPHONAMIDE IN AQUEOUS SOLUTION. A KINETIC STUDY

Chirchingi K. MYTHILY[a], Dandinasivara S. MAHADEVAPPA[a]
and Kanchugarakoppal S. RANGAPPA[b,*]

[a] *Department of Studies in Chemistry, University of Mysore, Manasagangothri, Mysore-570006, India*
[b] *Department of Chemistry, Miami University, Oxford, OH 45056, U.S.A.*

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The kinetics of oxidation of five secondary alcohols by sodium N-chlorobenzenesulphonamide (chloramine-B) has been studied in acid medium at 40°C. The reaction is first order with respect to the oxidant and alcohol and fractional order in $[H^+]$. The influence of added halide ions and of reaction product and the effects of varying ionic strength and dielectric constant of the medium have also been studied. The solvent isotope effects $k'(H_2O)/k'(D_2O)$ were determined. The rates were studied at four different temperatures and the activation parameters were evaluated. Attempts have been made to arrive at a linear free energy relation through the Taft treatment. An isokinetic relation is observed with $\beta = 248$ K, indicating the entropy of activation as the rate controlling factor. Protonated chloramine-T (monochloramine-T) has been postulated as the reactive oxidizing species, the main product of oxidation being the corresponding ketone. A mechanism involving the interaction of protonated haloamine species and the alcohol in a rate limiting step has been proposed.

Although the kinetics and mechanism of reactions of secondary alcohols employing the conventional oxidants have been investigated by several workers, a review of literature shows little information on the kinetics of oxidation of secondary alcohols by N-haloamines. Negi and Banerji[1] studied the oxidation of secondary alcohols by NBA in acid medium. A mechanism involving rate-determining nucleophilic attack of hypobromite ion on the alcohol molecule was proposed. Sharma[2] reported the kinetics of oxidation of 2-propanol by chlorine dioxide which is first order each in [oxidant] and $[\text{alcohol}]_0$. A mechanism involving hydride abstraction was proposed. Kudesia and co-workers[3] studied the relative activation parameters for the oxidation of RCH(OH)Me, where R = Me, Et, Pr, Bu, $Me(CH_2)_5$ by aqueous chlorine and noticed that the increase in reactivity with substitution of H by methyl group is entirely due to an entropy effect.

Extensive investigations on the mechanistic aspects of the oxidation of diverse substrates by organic haloamines[4] has been reported[5] from these laboratories.

There is however meager information in literature on the oxidation of secondary alcohols by positive halogen species. Hence, the present investigation reports the kinetics of oxidation of several secondary alcohols by sodium N-chlorobenzenesulphonamide (chloramine-B) in HCl medium at 40°C.

EXPERIMENTAL

Materials

Chloramine-B ($C_6H_5SO_2NClNa$ 1·5 H_2O, CAB) was prepared by the reported procedure[6]. 2-Propanol (IDLP, India), 2-butanol (Mand B, England), 2-pentanol (Riedel, Germany), 2-hexanol and 2-heptanol (Wilson Lab, India) were further purified by distillation. Aqueous solutions of alcohols were employed. All other reagents were of accepted grades of purity. Solvent isotope studies were made with D_2O (99·6%) supplied by Bhabha Atomic Research Centre, Bombay, India. Ionic strength of reaction mixture was kept at a high value with a concentrated solution of $NaClO_4$.

Kinetic Measurements

The reaction was carried out under pseudo-first order conditions by keeping an excess (× 10 or greater) of the alcohol over CAB. 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 $NaClO_4$ solutions and water (to keep the total volume constant for all runs) were taken in the boiling tube and thermostated at 40°C for attaining thermal equilibrium. A measured amount of oxidant solution also thermostated at the same temperature was rapidly added to the mixture in the boiling tube. The progress of the reaction was monitored by iodometric determination of unreacted CAB 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 *k'* calculated were reproducible to $\pm 3\%$.

Stoichiometry

Alcohol (0·01 mol dm^{-3}, CAB (0·05 mol dm^{-3}) and HCl (0·1 mol dm^{-3}) were made up to 100 ml in water and were equilibrated for 24 h. When the reaction was complete the residual CAB was determined iodometrically. Several determinations with different alcohols, indicated a 1 : 1 stoichiometry.

$$PhSO_2NClNa + RCH(OH)CH_3 \rightarrow PhSO_2NH_2 + RCOCH_3 + Na^+ + Cl^- \quad (A)$$

Here Ph is C_6H_5–, and R = $-CH_3$ for 2-propanol, $-CH_2CH_3$ for 2-butanol, $-(CH_2)_2CH_3$ for 2-pentanol, $-(CH_2)_3CH_3$ for 2-hexanol and $-(CH_2)_4CH_3$ for 2-heptanol.

The reaction product benzenesulphonamide ($PhSO_2NH_2$) was detected[7] by TLC and the corresponding ketones were identified by IR, NMR and also quantitatively estimated through their 2,4-dinitrophenylhydrazone derivatives[8]. 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 in a nitrogen atmosphere.

RESULTS

At constant [HCl] and [alcohol]$_0$, plots of log [CAB] vs time are found to be linear (Table I), indicating a first order dependence of rate on [CAB]$_0$. The rate increased with [alcohol]$_0$ (Table I) and plots of log k' vs log [alcohol]$_0$ are linear with unit slope. Further, plots of k' vs [alcohol]$_0$ (r = 0·9900) gave straight lines passing through the origin, confirming the first order dependence on [alcohol]$_0$. The reaction was catalyzed simultaneously by H^+ and Cl^- ions and hence the effect of [H^+] on the rate was studied by keeping [Cl^-] at the highest value (Table II) by adding NaCl. The rate increases with increase in [H^+] were linear with fractional slopes. Plots of k' vs [H^+] (r = 0·989) were also linear with y-intercepts, suggesting a rate law of the type, rate = $a + b[H^+]$. Addition of NaCl to the reaction mixture increased the rate. Plots of log k' vs log [Cl^-] (r = 0·991, Table II) gave straight lines with fractional slopes. The effect of gross [HCl] was also studied at constant [CAB]$_0$ and [alcohol]$_0$, k' values increased with increase in [HCl]. Plots of log k' vs log [HCl] (r = 0·997, Table I) were straight lines with slopes of the orders 0·65 to

Table I

Effect of varying the reactant concentration on the rate of oxidation by secondary alcohols by CAB at 40°C

10^4[CAB]$_0$ mol dm^{-3}	10^2[alcohol]$_0$ mol dm^{-3}	10^2[HCl] mol dm^{-3}	$k' . 10^5, s^{-1}$				
			2-propanol	2-butanol	2-pentanol	2-hexanol[a]	2-heptanol[a]
5·0	4·0	10·0	4·13	6·56	6·01	14·74	15·94
6·0	4·0	10·0	4·00	6·65	5·98	14·85	15·21
7·0	4·0	10·0	4·00	6·80	5·86	14·62	15·12
8·0	4·0	10·0	4·01	6·75	5·77	14·64	15·00
9·0	4·0	10·0	3·86	6·65	5·81	14·54	15·12
7·0	2·0[a](0·6)	10·0	1·99	3·60	2·56	7·47	9·68
7·0	3·0(0·8)	10·0	2·93	5·16	4·02	8·69	13·33
7·0	4·0(1·0)	10·0	4·00	6·80	5·24	14·62	15·27
7·0	6·0(1·2)	10·0	6·11	10·41	8·31	16·48	19·42
7·0	8·0(1·6)	10·0	7·96	13·30	10·72	21·55	26·22
7·0	4·0(1·0)	5·0	2·31	4·16	2·33	6·74	6·68
7·0	4·0(1·0)	8·0	3·44	5·89	4·08	11·38	10·73
7·0	4·0(1·0)	10·0	4·00	6·80	5·41	14·62	15·27
7·0	4·0(1·0)	12·0	4·52	7·58	6·58	18·96	18·33
7·0	4·0(1·0)	15·0	5·40	9·19	8·91	26·11	22·56

[a] [HCl] = $1 . 10^{-2}$ mol dm^{-3}.

1·24, indicating the composite orders of H^+ and Cl^-. The slopes (orders) of all the plots are summarized in Table III.

Addition of the reaction product benzenesulphonamide ($[PhSO_2NH_2] = 0{\cdot}1$ to $0{\cdot}5 \,.\, 10^{-3}$ mol dm^{-3}) had no influence on the rate. Ionic strength (μ, mol dm^{-3}) of the reaction mixture was varied by adding $NaClO_4$ (0·10–0·30 mol dm^{-3}) but no significant effect was noticed. The dielectric constant of the medium (D) was varied by adding different proportions (0 to 30% (v/v)) of methanol to the reaction mixture. Blank experiments were performed and showed that the oxidation of methanol under the present conditions employed was very small (<3%) and the k' obtained after subtracting the blank values in each case. A plot of log k' vs $1/D$ ($r = 0{\cdot}975$) gave a straight line with a positive slope.

Solvent isotope studies were made in D_2O medium for 2-propanol as a probe. Values of $k'(D_2O)$ and $k'(H_2O)$ were $4{\cdot}88 \times 10^{-5}$ and $4{\cdot}00 \times 10^{-5}\,s^{-1}$, giving a solvent isotope effect $k'(H_2O)/k'(D_2O) = 0{\cdot}80$.

The reaction was studied at different temperatures (308 K to 323 K) and from the Arrhenius plots of log k' vs $1/T$ ($r = 0{\cdot}991$) values of activation parameters were calculated (Table III).

DISCUSSION

Chloramine-B ($PhSO_2NClNa$) ionizes in aqueous solution as in Eq. (B) the anion picks up a proton in acid solution to give monochlolamine ($PhSO_2NHCl$), which can undergo disproportionation and/or hydrolysis:

$$PhSO_2NClNa \rightleftarrows PhSO_2NCl^- + Na^+ \tag{B}$$

$$2\,PhSO_2NHCl \rightleftarrows PhSO_2NCl_2 + PhSO_2NH_2 \tag{C}$$

$$PhSO_2NHCl + H_2O \rightleftarrows PhSO_2NH_2 + HOCl \tag{D}$$

Thus, the probable oxidizing species in acidified CAB solutions are $PhSO_2NHCl$, $PhSO_2NCl_2$ and HOCl. If $PhSO_2NCl_2$ were to be the oxidizing species in the oxidation of alcohols, a second order dependence of rate on $[CAB]_0$ should be observed, which is contrary to the experimental observations. Further, the hydrolysis of $PhSO_2NHCl$ is slight[9] ($K_h = 4{\cdot}21 \,.\, 10^{-3}$ at 25°C) and if HOCl is involved, a first order retardation of rate by the added benzenesulphonamide is expected. Since no such effect was noticed, HOCl is ruled out as the oxidizing species. Therefore, the free acid $PhSO_2NHCl$ is responsible for the oxidation of secondary alcohols. Narayanan and Rao[9] have shown the existence of species of the type: $ArSO_2NHCl$ in chloramine-T solutions at pH ≤ 2:

$$ArSO_2NHCl + H^+ \overset{K}{\rightleftarrows} ArSO_2\overset{+}{N}H_2Cl \tag{E}$$

TABLE II

Effect of varying $[H^+]$ and $[Cl^-]$ on the rate of oxidation of secondary alcohols by CAB at 40°C ($[CAB]_0 = 7{\cdot}0 \,.\, 10^{-4}$ mol dm^{-3})

$10^2[H^+]$ mol dm^{-3}	$10^2[Cl^-]$ mol dm^{-3}	$k' \,.\, 10^5$, s^{-1}				
		2-propanol[a]	2-butanol[a]	2-pentanol[a]	2-hexanol[b]	2-heptanol[b]
5·0	15·0	2·99	4·87	4·60	8·37	8·72
8·0	15·0	3·83	5·98	6·75	11·75	13·05
10·0	15·0	4·24	6·39	7·29	14·93	17·33
12·0	15·0	4·93	6·83	7·96	18·04	18·06
15·0	15·0	5·40	7·67	9·31	21·98	22·56
10·0	10·0	4·00	6·80	5·86	14·62	15·27
10·0	15·0	4·24	7·41	7·29	14·93	17·33
10·0	20·0	4·64	7·92	8·77	15·70	18·92
10·0	30·0	4·95	8·86	10·72	17·75	21·29
10·0	40·0	5·20	9·61	13·86	19·82	23·03

[a] $[\text{alcohol}]_0 = 4{\cdot}0 \,.\, 10^{-2}$ mol dm^{-3}; [b] $[\text{alcohol}]_0 = 1{\cdot}0 \,.\, 10^{-2}$ mol dm^{-3}.

TABLE III

Kinetic and thermodynamic parameters and kinetic orders for the oxidation of secondary alcohols by chloramine-B at 40°C ($[HCl] = 1 \,.\, 10^{-2}$ mol dm^{-3}, $[CAB]_0 = 7 \,.\, 10^{-4}$ mol dm^{-3}, $\mu = 0{\cdot}5$ mol dm^{-3})

Parameters	2-Propanol[a]	2-Butanol[a]	2-Pentanol[a]	2-Hexanol[b]	2-Heptanol[b]
k' 10^5, s^{-1}	4·00	6·80	5·86	14·62	15·12
E_{act}, kJ mol^{-1}	71·83	70·12	72·04	83·01	79·91
$\Delta H^{\neq}$, kJ mol^{-1}	69·2	67·5	69·5	80·4	77·0
$\Delta G^{\neq}$, kJ mol^{-1}	103·4 ± 0·1	102·1 ± 0·2	102·9 ± 0·2	100·0 ± 0·1	99·7 ± 0·1
$\Delta S^{\neq}$, JK^{-1} mol^{-1}	−108·5 ± 0·1	−110·0 ± 0·1	−104·9 ± 0·1	−62·3 ± 0·1	−71·9 ± 0·1
log A	9·70	9·60	9·41	13·18	12·64
			Kinetic orders		
$[CAB]_0$	1·00	1·00	1·00	1·00	1·00
$[\text{alcohol}]_0$	1·00	1·00	1·00	1·00	1·00
$[H^+]$	0·55	0·40	0·66	0·89	0·86
$[Cl^-]$	0·20	0·24	0·60	0·29	0·30
$[HCl]$	0·76	0·65	1·24	1·22	1·14

[a,b] See notes in Table II.

It has been found that with Ar = p-$CH_3C_6H_4$–, $K = 1{\cdot}02\,.\,10^2$ at 298 K, while with[10] Ar = C_6H_5–, $K = 61 \pm 5$ at 298 K.

Absence of ionic strength effect on rate indicates that neutral species are involved in the rate limiting step. Addition of the reaction product, benzenesulphonamide has no effect on the rate indicating that it is not involved in an equilibrium before the rate determining step (rds). Further, a plot of $1/k'$ vs $1/[\text{alcohol}]_0$ gives a straight line passing through the origin. This suggests a pathway involving a fast equilibrium formation of an intermediate and its slow decomposition into products.

A plot of $k'/[\text{alc}]_0$ vs $[H^+]$ ($r = 0{\cdot}990$), gives a straight line with an intercept k_0 and hence the $[H^+]$ dependence on the rate is of the type, rate = $k_0 + k_a[H^+]$. The values of k_0 and k_a are computed as follows (Table IV).

The above values (k_0 and k_a) indicate (i) a rapid pre-equilibrium protonated and deprotonated forms (Eq. E) (ii) a small protonation equilibrium constant (iii), that both the forms are reactive and (iv) that the protonated form is more active. Taking into consideration the first order dependence of rate on $[\text{CAB}]_0$, $[\text{alcohol}]_0$ and fractional order in $[H^+]$ the following acid dependent and an acid independent paths have been proposed (Schemes 1 and 2).

$$\text{PhSO}_2\text{NHCl} + \text{H}^+ \overset{K_1}{\rightleftharpoons} \text{PhSO}_2\overset{+}{\text{N}}\text{H}_2\text{Cl} \qquad (i)$$

$$\text{(A)}$$

$$\text{A} + \text{alcohol} \xrightarrow[\text{rds}]{k_2} \text{B} \qquad (ii)$$

$$\text{B} \xrightarrow[\text{fast}]{k_3} \text{products} \qquad (iii)$$

SCHEME 1

$$\text{PhSO}_2\text{NHCl} + \text{alcohol} \xrightarrow[\text{rds}]{k_4} \text{B}' \qquad (i)$$

$$\text{B}' \xrightarrow[\text{fast}]{k_5} \text{products} \qquad (ii)$$

SCHEME 2

The combined rate law can be given as

$$\text{rate} = k_0[\text{CAB}]\,[\text{alc}] + k_a[\text{CAB}]\,[\text{alc}]\,[H^+] \qquad (1)$$

where k_0 is the rate constant for acid independent path, k_a is the rate constant for acid dependent path.

The chloride catalysis observed during the oxidation of secondary alcohols by CAB can be given by Scheme 3.

$$PhSO_2NHCl + Cl^- \overset{K_1'}{\rightleftarrows} \underset{(C)}{PhSO_2NHCl\text{---}Cl} \qquad (i)$$

$$C + \text{alcohol} \xrightarrow[\text{rds}]{k_2'} C' \qquad (ii)$$

$$C' \xrightarrow[\text{fast}]{k_2'} \text{products} \qquad (iii)$$

SCHEME 3

From the Schemes 1 – 3, the rate law (*2*) can be shown to account for the observed Cl^- effect during the oxidation of secondary alcohols.

$$\text{rate} = k_0[\text{CAB}]\,[\text{alc}] + k_a[\text{CAB}]\,[\text{alc}]\,[H^+] + k_{Cl^-}[\text{CAB}]\,[\text{alc}]\,[Cl^-] \quad (2)$$

Negi and Banerji[1] have shown the absence of a primary kinetic isotope effect in the oxidation of alcohols by NBA. This indicated the formation of hypobromite ester in a slow step, while its decomposition to ketone is rapid. The fact that the reaction product $PhSO_2NH_2$ had no effect on the rate clearly supports the formation of hypochlorite ester[11] in the slow step and its decomposition into products by a fast step of the reaction.

Amis[5] has shown that a plot of log k_{obs} vs $1/D$ gives a straight line with a positive slope for positive ion dipole interaction. The positive dielectric effect in the present investigation shows a charge dispersal in the transition state, pointing towards an ion–dipole reaction.

Solvent isotope studies have shown that the rate of reaction is higher in D_2O medium. For pre-equilibrium proton transfer, generally the inverse solvent isotope effect $k'(D_2O)/k'(H_2O) \sim 2 - 3$ is observed but the value of 1·22 obtained with 2-propanol as a probe is a reflection of the fractional order dependence of rate on $[H^+]$ since a part of the reaction takes place by chloride catalysis, and part through an acid independent path.

TABLE IV

Values of k_0 and k_a (in $l\,mol^{-1}\,s^{-1}$) for the oxidation of secondary alcohols by CAB

Alcohol	$k_0 \cdot 10^4$	$k_a \cdot 10^4$
2-Propanol	4·55	61·4
2-Butanol	9·10	67·7
2-Pentanol	54·1	1 200
2-Hexanol	11·1	1 390
2-Heptanol	22·8	1 367

Attempts have been made to correlate rates of oxidation of alcohols with Taft substitution constant σ^* and E_s where σ^* represents the polar substitutent constant and E_s is the steric substituent constant[12]. The following regression equations were obtained when single parameter correlations were made.

$$(\log k' - E_s) = -23{\cdot}0\,\sigma^* - 6{\cdot}45 \tag{3}$$

$$\log k' = -3{\cdot}7\,\sigma^* - 4{\cdot}4 \tag{4}$$

$$\log k' = -0{\cdot}99\,E_s - 4{\cdot}23 \tag{5}$$

A negative value of σ^* $(-3{\cdot}7)$ in Eq. (*4*) shows that electron donating centres increase the rate of reaction. However, it may be inferred from Eq. (*3*) that both electronic and steric effects are important. Attempts were also made to use the Pavelich–Taft equation[13] in the four parameter form $\log(k'/k'_0) = \sigma^*\varrho^* + \delta E_s$. Here ϱ^* and δ are recation constants.

Measuring the susceptibility of the reaction series to polar and steric effects respectively. Using the method of least squares it was found that $\varrho^* = -2{\cdot}40$ and $\delta = -0{\cdot}45$. The plot of $\log(k'/k'_0) - \delta E_s$ against σ^* is approximately linear indicating that the rates of oxidation of alcohols are governed by both polar and steric effects.

The activation enthalpies and entropies of the oxidation of the five alcohols are linearly related by plotting ΔH^{+} vs ΔS^{+}, $(r = 0{\cdot}9996)$. From the slope, the value of isokinetic temperature (β) is computed as 248 K. Further verification of the isokinetic relation has been done by the Exner criterion[14] by plotting $\log k'(323\text{K})$ vs $\log k'(313\text{K})$ which gives a straight line $(r = 0{\cdot}9999)$ for which β is 238 K. Current views do not attach much physical significance to isokinetic temperature[15]. The linear correlation, however, implies that all the alcohols are oxidized by the same mechanism. The values of β from both the plots calculated are lower than the experimental temperature (313 K) indicating entropy as a controlling factor. The large negative entropy of activation also supports the proposed mechanism. When two reacting molecules combine to form a single activated complex, the restrictions on their motion obviously increase, for they can no longer move independently, which results in a large negative entropy of activation.

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REFERENCES

1. Negi S. C., Banerji K. K.: Indian J. Chem., B *21*, 846 (1982).
2. Sharma C. B.: Rev. Roum. Chim. *28*, 967 (1983).

3. Kudesia V. P., Srivatava S. K., Prakash D., Kant S.: Acta Cienc. Indica, (Ser) Chem. *5*(2), 85 (1979).
4. Natarajan M. M., Thiagarajan V.: J. Chem. Soc., Perkin Trans. 2 *1975*, 1590.
5. Mahadevappa D. S., Rangappa K. S., Gowda N. M. M., Gowda B. T.: J. Phys. Chem. *24*, 3651 (1981).
6. Chrzaszewska A.: Bull. Soc. Sci. Lett., Lodz Classe III, *16*, 5 (1952); Chem. Abstr. *49*, 212 (1955).
7. Mahadevappa D. S., Ananda S.: Indian J. Chem., A *24*, 589 (1985).
8. Vogel A. I.: *Text-book of Practical Organic Chemistry* (3rd Ed.), p. 344. ELBS, Longmann Group, London 1973.
9. Narayana S. S., Rao V. R. S.: Radiochimica Acta *32*, 211 (1983).
10. Subhashini M., Subramanian M. S., Rao V. R. S.: Talanta *32*, 1082 (1985).
11. Lewitt L. S., Malinowski E. R.: J. Am. Chem. Soc. *70*, 4517 (1955).
12. Gilliom R. D.: *Introduction to Physical Organic Chemistry*, pp. 156, 168 and 264. Addison--Wesley, London 1970.
13. Pavelich W. A., Taft R. W.: J. Am. Chem. Soc. *79*, 4935 (1957).
14. Exner O.: Collect. Czech. Chem. Commun. *29*, 1904 (1964).
15. Leffler J. E.: J. Org. Chem. *31*, 533 (1966).