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Oxidation of *n*-Propylamine and *n*-Butylamine by Chloramine-B and Chloramine-T in Basic Medium: A Kinetic Study

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The oxidation of aliphatic primary amines, *n*-propylamine (PA) and *n*-butylamine (BA), by chloramine-B (CAB) and chloramine-T (CAT) in aqueous alkaline medium has been kinetically studied at 318 K. The reaction follows the experimental rate law: rate = k' [oxidant] $[amine]^0$ $[OH^-]^x$, where oxidant is CAT or CAB and x is fractional. Additions of chloride ions, the reduction product, sulfonamide, and sodium perchlorate, which is used for changing the ionic strength of the solvent medium, have no effect on the reaction rate. However, the rate varies with change in dielectric constant of the medium. The reaction has been studied in the temperature range, 313–323K, and the activation parameters have been evaluated. A suitable mechanism consistent with the observed kinetic data has been proposed and the rate law derived.

Keywords kinetics, oxidation, amines, *n*-propylamine and *n*-butylamine, Chloramine-T, Chloramine-B, mechanism, rate law

INTRODUCTION

Sodium salts of N-halo derivatives of arylsulphonamide are N-metallo-N-Arylhalosulphonamides. The important members of this class of haloamine compounds are: chloramine-T (p-$CH_3C_6H_4SO_2NClNa.3H_2O$ or CAT) and chloramine-B ($C_6H_5SO_2NClNa$ $1.5H_2O$ or CAB). Bishop and Jennings[1] have reported some important characteristics of CAT solutions. Higuchi and Coworkers[2] have published an extensive study of the concentrations of various species present in aqueous solutions of 0.05 M CAT at different pH values. Both CAT and CAB have been widely used in oxidation studies and mechanisms of their reactions have been investigated.[3–6] Oxidations of amines by oxidants such as N-bromosuccinamide, bromamine, cerium(IV), aqueous chlorine, bromamine-T and Mn(III) have been reported.[7–11] The present paper reports the kinetic studies on the oxidation of aliphatic primary amines, *n*-propylamine (PA) and *n*-butylamine (BA) by CAT and CAB in aqueous sodium hydroxide solutions.

EXPERIMENTAL

Materials

Chloramine-T (Loba) was purified by the method of Morris and coworkers.[12] Chloramine-B was prepared by a standard method.[12] Approximately 0.10 mole dm^{-3} stock solutions of CAT and CAB were prepared and standardized by iodometric method and used. The solutions were stored in amber colored bottles. The two amines used, *n*-propylamine and *n*-butylamine (SD Fine or Sisco Research Chemicals, India), were purified by distillation. All other reagents were of analytical grades of purity. All aqueous solutions were prepared in triply distilled water.

Kinetic Measurement

Kinetic runs were carried out under pseudo first order conditions of $[amine]_o \gg [oxidant]_o$ at a constant temperature.[11] The constant temperature (e.g., 318 ± 0.1 K) was maintained using a water bath. Requisite amounts of solutions of the amine (PA or BA), NaOH, and perchlorate (to maintain a constant ionic strength) were mixed in a stoppered Pyrex glass tube. Required volume of water was added to maintain a known total volume of the reaction mixture. The tube was thermostated at 318 K. The reaction was initiated by adding a measured amount of pre-equilibrated, standard CAB or CAT solution into the above tube and the reaction mixture was shaken periodically. The progress of the reaction was monitored by iodometric titrations of the unreacted oxidant present in aliquots against a standardized $Na_2S_2O_3$ solution at various time periods[12]. The pseudo-first order rate constants, $k^|$, were calculated from plots of ln [ox] *vs.* time or ln (titer) *vs* time (where ox = CAT or CAB). Values of $k^|$ are accurate within ±3%.

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RESULTS

Stoichiometry and Product Analysis

Reaction mixtures containing varying compositions of the amine and oxidant in 0.05 M NaOH were stirred for 24 hrs at 318 K. The unconsumed oxidant was determined iodometrically.[11] Based on these data, the number of moles of CAB or CAT consumed per mole of the amine was calculated, which showed a mole ratio of 1:1. The following general equation represents the reaction stoichiometry:

$$\begin{aligned} &RCH_2NH_2 + ArSO_2NCl^- + H_2O \\ &\quad \rightarrow RCHO + NH_3 + ArSO_2NH_2 + Cl^- \qquad [1] \end{aligned}$$

where R = ethyl or propyl group and Ar = C_6H_5 for CAB and p-$CH_3C_6H_4$ for CAT.

In each case, the oxidation products were identified as the corresponding aldehyde (propionaldehyde or n-butyraldehyde), ammonia, and *p*-toluenesulphonamide (PTS) or benzenesulphonaminide (BSA). The aldehydes were identified by preparing their orange 2,4-dinitrophenylhydrazone (2,4-DNP) derivatives[13,14] and by Tollen's reagent test.[14] Furthermore, the aldehydes were characterized by melting points of 2,4-DNP derivatives, which were consistent with the reported values for 2,4-DNP derivatives of propionaldehyde and *n*-butyraldehyde. Ammonia liberated during the reaction was quantitatively measured using a slightly modified micro-Kjeldahl procedure.[13,15]

The reduction products, benzenesulphonamide (BSA) and *p*-toluene-sulfonamide, in the reaction mixtures were isolated using solvent extraction with diethylether, recrystallized from the dichloromethane-petroleum ether mixture (1:1 v/v) and identified by TLC (PTS, $R_f = 0.26$ with a mobile phase of dichloromethane; BSA, $R_f = 0.88$ with a mixture of petroleum ether, chloroform and *n*–butanol (2:2:1 – v/v/v); and iodine developing agent. Furthermore, mass spectra obtained on a 70 eV Shimadzu GCMS-QP5050 spectrometer showed parent molecular ion peaks at m/z 157 amu and 171 amu for BSA and PTS, respectively, confirming their identities.

Kinetics

The reactions were studied under pseudo-first-order conditions of $[amine]_o \gg [ox]_o$, at several initial concentrations of the oxidant (ox = CAT or CAB) while keeping the other reaction conditions such as $[amine]_0$, $[OH^-]$, ionic strength, solvent and temperature constant.

Plots of ln [ox] *vs.* time were found to be linear (e.g., $r > 0.996$, plots not shown) showing a first-order dependence of the reaction rate on [ox]. Pseudo-first-order rate constants (k′) obtained with varying $[ox]_0$, which are nearly constant, are presented in Table1. Under identical conditions, increase in $[amine]_0$ did not affect the rate. The values of $k^{|}$ at different concentrations of PA and BA are given in Table 2.

TABLE 1
Effects of $[CAT]_0$ and $[CAB]_0$ on the reaction rate
$[PA]_0 = [BA]_0 = 5.00 \times 10^{-2}$ M, $[NaOH] = 5.00 \times 10^{-2}$ M, $\mu = 0.500$ M, T = 318 K

$10^3[CAT]_0$ (M) Or $10^3[CAB]_0$ (M)	10^4 k′ (s^{-1})			
	CAT		CAB	
	PA	BA	PA	BA
3.00	1.05	0.86	1.06	1.23
4.00	1.03	0.87	1.01	1.27
5.00	1.04	0.87	1.05	1.30
6.00	1.06	0.86	1.00	1.32
7.00	1.04	0.86	1.00	1.30

The rate constant increased with an increase in [NaOH] when the other reaction conditions were kept constant (Table 3). The order of the reaction with respect to the hydroxide ion concentration, calculated from the slope of the linear plot of ln $k^{|}$ *vs* ln $[OH^-]$, was found to be fractional, in each case. The orders obtained were: 0.35 and 0.33 for PA and BA, respectively, for the CAT reaction and 0.56 and 0.53, respectively, for the CAB reaction.

Addition of the reduction product, PTS or BSA, to the reaction mixtures had no significant effect on the rate. Also, the addition of sodium chloride and perchlorate did not affect k′ values suggesting that the chloride ions and the ionic strength of the medium (μ) had no effect on the reaction rate. Varying the solvent composition using MeOH (up to 30% (v/v)) showed that the rate increased with increasing concentrations of MeOH (i.e., decreasing dielectric constant D of the medium), as shown in Table 4. Plots of ln k′ *vs* 1/D were linear up to 20% MeOH and with further increase in MeOH content the curve leveled off with CAT and decreased slightly with CAB.

The temperature effect on the reaction rate was studied at different temperatures (313–323 K) by keeping all other conditions the same and the k′ values are listed in Table 5. Based

TABLE 2
Effects of [PA] and [BA] on the reaction rate
$[CAT]_0 = [CAB]_0 = 5.00 \times 10^{-3}$ M, $[NaOH] = 5.00 \times 10^{-2}$ M, $\mu = 0.500$ M, T = 318 K

$10^2[Amine]_0$ (M)	10^4 k′ (s^{-1})			
	CAT		CAB	
	PA	BA	PA	BA
2.50	0.96	0.85	0.97	1.22
5.00	1.04	0.87	1.05	1.30
7.50	1.06	0.87	1.07	1.33
10.0	1.08	0.89	1.09	1.40

TABLE 3
Effect of [NaOH] on the reaction rate
$[PA]_0 = [BA]_0 = 7.50 \times 10^{-2}$ M, $[CAT]_0 = [CAB]_0 = 5.00 \times 10^{-3}$ M, $\mu = 0.500$ M, T = 318 K

	PA		BA	
10^2[NaOH] (M)	CAT $10^4 k' (s^{-1})$	CAB $10^4 k' (s^{-1})$	CAT $10^4 k' (s^{-1})$	CAB $10^4 k' (s^{-1})$
2.50	0.820	0.680	0.680	0.920
5.00	1.04	1.05	0.87	1.30
7.50	1.20	1.26	0.98	1.65
10.0	1.33	1.49	1.07	1.90

on the Arrhenius plot of ln k′ *vs* 1/T and the Eyring plot of ln (k′/T) *vs* 1/T, activation parameters for the composite reaction, namely, energy of activation (E_a), enthalpy of activation ($\Delta H^{\neq}$), and entropy of activation ($\Delta S^{\neq}$) were calculated (Table 6).

Test for Free Radicals

Alkene monomers, acrylonitrile and 10% acrylamide solution, under nitrogen atmosphere, were added to the amine-oxidant reaction mixtures in 0.0500 M NaOH to initiate polymerization in the presence of free radicals formed *in situ* in dark.A suitable control was also run. A lack of turbidity observed in the solutions indicated the absence of *in situ* formation of free radicals.[17]

DISCUSSION

The kinetic data show the following experimental rate law:

$$\text{rate} = -\,d[\text{oxidant}]/dt = k'[\text{oxidant}][OH^-]^X \quad [2]$$

where oxidant = CAB or CAT and x is a fractional value.

In aqueous acid solutions, CAB and CAT behave as electrolytes as shown in the following equilibria [3–10][3,12,16].

$$ArSO_2NClNa \rightleftharpoons ArSO_2NCl^- + Na^+ \quad [3]$$

$$ArSO_2NCl^- + H^+ \rightleftharpoons ArSO_2NHCL \quad [4]$$

$$2ArSO_2NHCl \rightleftharpoons ArSO_2NH_2 + ArSO_2NCl_2 \quad [5]$$

$$ArSO_2NHCl + H^+ \rightleftharpoons ArSO_2NH_2Cl^+ \quad [6]$$

$$ArSO_2NHCl + H_2O \rightleftharpoons ArSO_2NH_2 + HOCl \quad [7]$$

$$ArSO_2NCl_2 + H_2O \rightleftharpoons ArSO_2NHCl + HOCl \quad [8]$$

$$HOCl \rightleftharpoons H^+ + OCl^- \quad [9]$$

$$HOCl + H^+ \rightleftharpoons H_2OCl^+ \quad [10]$$

where $Ar = p - CH_3C_6H_4-$

In alkaline solutions, Hardy and Johnston[3,16] have reported the existence of equilibria (11)-(13) for CAT, which are also applicable to CAB.

$$ArSO_2NCl^- + H_2O \rightleftharpoons ArSO_2NHCl + OH^- \quad [11]$$

$$ArSO_2NCl^- + H_2O \rightleftharpoons ArSO_2NH_2 + OCl^- \quad [12]$$

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \quad [13]$$

The concentration of each species depends on the pH and nature of the medium.[3] As a result, CAB and CAT react with a wide range of functional groups affecting an array of molecular transformations. In acid solutions, the probable oxidizing species are the free acid ($ArSO_2NHCl$), dichloramine-T ($ArSO_2NCl_2$), HOCl and H_2OCl^+. In alkaline solutions of

TABLE 4
Effect of dielectric constant (D) of the medium on the reaction rate
$[PA]_0 = [BA]_0 = 7.50 \times 10^{-2}$ M, $[CAT]_0 = [CAB]_0 = 5.00 \times 10^{-3}$ M, [NaOH] = 5.00×10^{-2} M, $\mu = 0.500$ M, T = 318 K

			PA		BA	
[Me OH] (%, V/V)	D	10^2/D	CAT $10^4 k' (s^{-1})$	CAB $10^4 k' (s^{-1})$	CAT $10^4 k' (s^{-1})$	CAB $10^4 k' (s^{-1})$
0.0	76.72	1.30	1.04	1.05	0.87	1.30
10.0	72.37	1.38	1.24	1.27	1.06	1.49
15.0	69.93	1.43	1.32	1.35	1.10	1.55
20.0	67.48	1.48	1.38	1.51	1.20	1.68
30.0	62.71	1.60	1.44	1.34	1.21	1.38

TABLE 5
Effect of temperature on the reaction rate
$[PA]_0 = [BA]_0 = 7.50 \times 10^{-2}$ M, $[CAT]_0 = [CAB]_0 = 5.00 \times 10^{-3}$ M, $[NaOH] = 5.00 \times 10^{-2}$ M, $\mu = 0.500$ M

	PA		BA	
Temperature (K)	CAT 10^4 k$^{|}$ (s^{-1})	CAB 10^4 k$^{|}$ (s^{-1})	CAT 10^4 k$^{|}$ (s^{-1})	CAB 10^4 k$^{|}$(s^{-1})
313	0.740	0.720	0.580	1.02
316	0.930	0.900	0.770	1.17
318	1.04	1.05	0.870	1.30
321	1.32	1.35	1.15	1.55
323	1.48	1.55	1.38	1.66

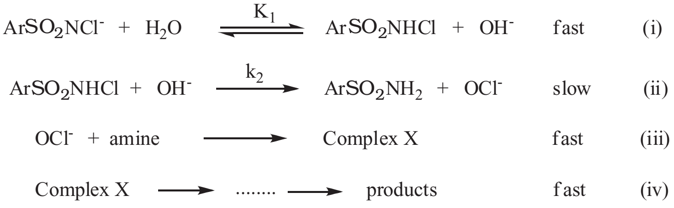
CAB or CAT, $ArSO_2NCl_2$, and H_2OCl^+do not exist. Therefore, the expected reactive species are $ArSO_2NHCl$, HOCl, OCl^- and $ArSO_2NCl^-$. The species $ArSO_2NCl^-$ and OCl^- could be transformed into more reactive oxidizing species $ArSO_2NHCl$ and HOCl through reactions (eqs. 11–13). If HOCl and OCl^- were the primary oxidizing species, as indicated by eqs. (7) and (12), a first-order retardation of the rate by the added $ArSO_2NH_2$ would be expected, which is contrary to the experimental observations. If $ArSO_2NHCl$ were the reactive species, retardation of the rate by $[OH^-]$ would be expected (eq. 11), which is also contrary to the experimental observations. Hence, $ArSO_2NCl^-$ is the first likely oxidizing species as the rate increases with the increase in $[OH^-]$. Under the present experimental conditions, the kinetic results of a first order dependence on [oxidant], zero order on [amine], and fractional order on $[OH^-]$ and zero effect of the added reduction product PTS/BSA can be explained by considering Scheme1 as shown below.

In Scheme 1, the oxidant species $ArSO_2NHCl$ formed in the fast pre-equilibrium (step (i)) interacts with OH^- in the slow step to form the most reactive species OCl^-, which then reacts with the substrate-amine in several fast steps to form the end products as shown in Scheme 2. Scheme 2 shows the detailed electron-pushing mechanism of oxidation of amines. The reactive oxidant species OCl^- formed in the slow step electrophilically attacks the amino N atom in a fast step to form an N-Cl complex anion (X). In another fast step, X undergoes intramolecular rearrangements to give a chloramine intermediate (complex X′) and OH^-. In the next fast step, the chloramine intermediate X′ interacts with a nucleophile (OH^-) and undergoes rearrangements to form an imine intermediate (complex X′′) after eliminating H_2O and Cl^-. The hydrolysis of imine (X′′) forms the intermediate (X′′′), which on intramolecular rearrangements leads to the formation of the aldehyde end-product along with ammonia.

TABLE 6
Activation parameters for the oxidation of PA and BA by CAT and CAB in NaOH medium*

	CAT		CAB	
Activation parameter	PA	BA	PA	BA
E_a/kJ mol^{-1}	58.7	72.3	65.3	42.2
$\Delta H^{\neq}$/kJ mol^{-1}	56.1	69.7	62.6	39.6
log A	5.66	7.82	6.74	3.04
$\Delta S^{\neq}$/JK^{-1} mol^{-1}	−137.1	−95.8	−117.	−187
$\Delta G^{\neq}$/kJ mol^{-1}	99.7	100.	99.6	99.1

*Conditions are as shown in Table 5.



$$ArSO_2NCl^- + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} ArSO_2NHCl + OH^- \quad \text{fast} \quad (i)$$

$$ArSO_2NHCl + OH^- \xrightarrow{k_2} ArSO_2NH_2 + OCl^- \quad \text{slow} \quad (ii)$$

$$OCl^- + \text{amine} \longrightarrow \text{Complex X} \quad \text{fast} \quad (iii)$$

$$\text{Complex X} \longrightarrow \cdots\cdots \longrightarrow \text{products} \quad \text{fast} \quad (iv)$$

SCH. 1.

Based on the slow/rate determining step (ii), the rate law obtained is as follows:

$$\text{rate} = -d[\text{oxidant}]/dt = k_2[ArSO_2NHCl][OH^-] \qquad [14]$$

The total effective concentration of the oxidant is given by,

$$[\text{oxidant}]_{\text{tot}} = [ArSO_2Cl^-] + [ArNSO_2HCl]$$

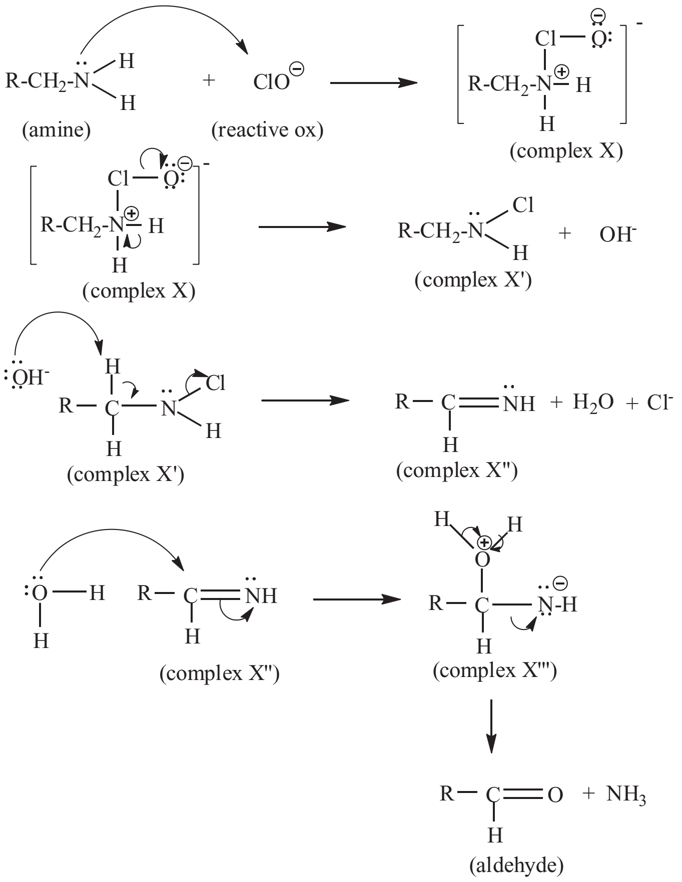
where

$$[\text{oxidant}]_{\text{tot}} = [CAB]_{\text{tot}} \text{ or } [CAT]_{\text{tot}}$$

Or

After substitution for $[ArNSO_2Cl^-]$ from step (i) of Scheme 1 and after proper rearrangements, one gets the derived rate law [eq. (15)].

$$[\text{oxidant}]_{\text{tot}} = \frac{[ArNSO_2HCl][OH]^-}{K_1[H_2O]} + [ArNSO_2HCl]$$



SCH. 2. Mechanism of the amine oxidation by CAB or CAT in basic medium.

Or

$$[\text{oxidant}]_{\text{tot}} = \frac{[\text{ArNSO}_2\text{HCl}][\text{OH}^-] + K_1[\text{H}_2\text{O}][\text{ArNSO}_2\text{HCl}]}{\text{K}_1[\text{H}_2\text{O}]}$$

Or

$$[\text{ArNSO}_2\text{HCl}] = \frac{\text{K}_1[\text{oxidant}]_{\text{tot}}[\text{H}_2\text{O}]}{\text{K}_1[\text{H}_2\text{O}] + [\text{OH}^-]}$$

Or

$$\text{rate} = \frac{\text{K}_1\text{k}_2[\text{oxidant}]_{\text{tot}}[\text{OH}^-][\text{H}_2\text{O}]}{\text{K}_1[\text{H}_2\text{O}] + [\text{OH}^-]} \qquad [15]$$

The rate law [eq. 15] derived from Scheme 1 is thus in agreement with the experimental rate law (eq. (2)). It is also possible to transform eq. (15) into the following equations:

$$\text{k}^{|} = \frac{\text{K}_1\text{k}_2[\text{OH}^-][\text{H}_2\text{O}]}{\text{K}_1[\text{H}_2\text{O}] + [\text{OH}^-]}$$

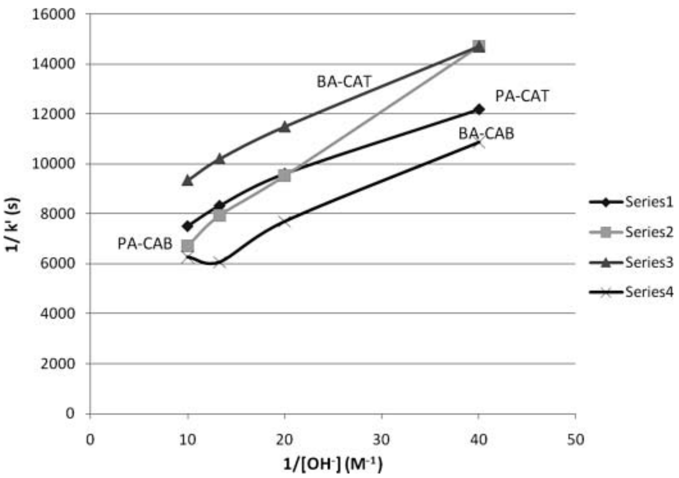


FIG. 1. Double reciprocal plots for the amine-chloramine reactions at 318 K

Or

$$\frac{1}{\text{k}^{|}} = \frac{1}{\text{k}_2[\text{OH}^-]} + \frac{1}{\text{K}_1\text{k}_2[\text{H}_2\text{O}]} \qquad [16]$$

Thus plots of $1/\text{k}^{|}$ vs $1/[\text{OH}^-]$, derived from data in Table 3, were found to be linear, as seen in Figure 1. The values of k_2 $(\text{M}^{-1}\text{s}^{-1})$ evaluated form the slope and intercept are found to be 6.63×10^{-4} and 5.73×10^{-4} for PA and BA, respectively, with CAT as oxidant and 3.8×10^{-4} and 5.45×10^{-4}, respectively, with CAB as oxidant.

The zero effect of BSA or PTS and ionic strength on the reaction rate also supports Scheme 1. The effect of varying solvent composition on the rate has been described by Laidlar[18] and Benson.[19] Amis and Jaffe[20] have derived a relationship for the variation of the rate constant as a function of the dielectric constant (D) of the medium for the interaction between an ion and a dipolar molecule as

$$\log \text{k}_{\text{D}}^{|} = \log \text{k}_{\infty}^{|} + (\text{Ze}\mu/2.303\,\text{k}\,\text{T}\,\text{r}^2\,\text{D}) \qquad [17]$$

It is evident from equation (17) that the rate constant will increase on decreasing D. In the present case, it is found that the rate increases with decrease in D as expected for an ion-dipole interaction in the rate determining step (step (ii)). The values of energy of activation and other activation parameters also support Scheme 1. A probable mechanism of oxidation is given in Scheme 2.

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