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Kinetics and Mechanism of Oxidation of *o*-Toluidine by Sodium-N-Chlorobenzene Sulphonamide (Chloramine-B) in Acid Medium

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The kinetics of the oxidation of *o*-toluidine by chloramine-B [CAB] has been studied in aqueous sulfuric acid at 303 K. The rate shows first order dependence on [CAB], fractional order in [*o*-toluidine] and inverse first order in $[H^+]$. The variation of ionic strength, change in dielectric constant of the medium, addition of the reaction product (benzene sulphonamide) and halide ions had no significant effect on the reaction rate. The oxidation product has been identified as *o*,*o'*-dimethylazobenzene. Thermodynamic parameters were evaluated. The protonation constant of monochloramine-B has been evaluated to be 64.5 ± 3.

INTRODUCTION

The kinetics of oxidation of aliphatic primary amines by N-haloamines as oxidants have been reported from our laboratory[1–3] and oxidation of *o*-toluidine by different oxidants has been reported[4–8]. However, information on reaction of *o*-toluidine by N-haloamines is not reported. Therefore, in the present paper, we report the mechanistic and kinetic aspects of the oxidation of *o*-toluidine by chloramine-B (CAB or $C_6H_5SO_2NClNa\cdot 1.5H_2O$) in sulfuric acid medium at 303 K.

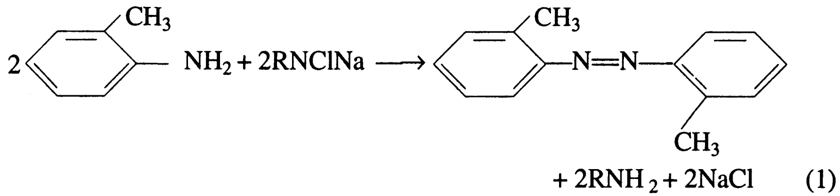
RESULTS AND DISCUSSION

The kinetics of oxidation of *o*-toluidine by CAB was investigated in 10% methanol medium. Blank experiments with methanol, however, showed that there is slight reaction of the solvent (< 2%) under the experimental conditions used. This was allowed in the calculation of the net reaction rate constants for the oxidation of *o*-toluidine.

Reaction stoichiometry

Varying ratios of the oxidant (CAB) to *o*-toluidine under experimental condition were equilibrated at 303 K for 24 h. The mole ratio (number of moles of CAB consumed per mole of *o*-toluidine) was calculated iodometrically and spectrophotometrically.

The stoichiometric reaction can be represented as below:



(1)

Here, R = $C_6H_5SO_2$.

The presence of benzenesulphonamide (BSA) which is the reduction product of CAB, was detected by thin layer chromatography[3]. The oxidation product of *o*-toluidine, *i.e.*, *o*-*o*′-dimethylazobenzene has been identified by the method of pausacker and Scroggie[9].

Effect of reactants

With substrate in excess, at constant [H_2SO_4] and [*o*-toluidine], plots of log [CAB] *vs.* time were linear indicating a first order dependence of rate on $[CAB]_0$. The pseudo-first order rate constants (k^1) obtained are given in Table-1. The rate increased with increase in $[o\text{-toluidine}]_0$. A plot of log k^1 *vs.* log $[o\text{-toluidine}]_0$ was linear with a fractional slope (0.44) indicating fractional order dependence on the *o*-toluidine concentration (Table-1).

TABLE-1

EFFECT OF VARYING CAB, *o*-TOLUIDINE AND H_2SO_4 CONCENTRATIONS ON THE RATE OF REACTION

10^4 [CAB] (mol dm^{-3})	10^3 [*o*-toluidine] (mol dm^{-3})	10^2 [H_2SO_4] (mol dm^{-3})	$k^1 \times 10^4$ (S^{-1})
5.0	10.0	2.0	4.62
7.5	10.0	2.0	4.60
10.0	10.0	2.0	4.60
15.0	10.0	2.0	4.72
20.0	10.0	2.0	4.68
10.0	1.0	2.0	1.72
10.0	2.5	2.0	2.50
10.0	5.0	2.0	3.52
10.0	10.0	2.0	4.60
10.0	15.0	2.0	5.62
10.0	20.0	2.0	6.42
10.0	10.0	1.0	9.67
10.0	10.0	1.5	6.28
10.0	10.0	2.0	4.60
10.0	10.0	3.0	3.16
10.0	10.0	4.0	2.32
10.0	10.0	5.0	1.85
10.0	10.0	8.0	1.01

$\mu = 0.3$ mol dm^{-3}; Temperature = 303 K.

Effect of varying [H_2SO_4] on the rate

The rate of reaction decreased with increase in [H_2SO_4]. The plot of log k^1 *vs.* log [H_2SO_4] was linear indicating an inverse first order dependence on [H_2SO_4] (Table-1). Further the addition of SO_4^{2-} ions in the form of Na_2SO_4 (0.005–0.1 mol dm^{-3}) had no effect on the rate of reaction. Hence, the dependence of the rate on [H_2SO_4] reflected the effect of [H^+] only on the reaction.

Pryde and Soper[10], Morris *et al.*[11] and Bishop and Jennings[12] have shown the existence of similar equilibria in acid and alkaline solutions of N-metallo-N-haloarylsulphonamides. Chloramine-B, being analogous to CAT, behaves as a strong electrolyte in aqueous solutions forming different species as shown in Eqns. (2)–(6).

$$RNClNa \rightleftharpoons RNCl^- + Na^+ \quad (2)$$

$$RNCl^- + H^+ \rightleftharpoons RNHCl \quad (3)$$

$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl \quad (4)$$

$$2RNHCl \rightleftharpoons RNH_2 + RNCl_2 \quad (5)$$

$$HOCl + H^+ \rightleftharpoons H_2OCl^+ \quad (6)$$

In acid solutions, the probable oxidizing species are the free acid (RNHCl), $RNCl_2$, HOCl and H_2OCl^+. The involvement of $RNCl_2$ in the mechanism leads to a second order rate dependence on $[CAB]_0$, according to equation (5), which is contrary to the experimental observations. As Eqn (4) indicates a slow hydrolysis, if HOCl were the primary oxidizing species of first order, a retardation of the rate by the added RNH_2 would be expected. However, no such effect was noticed in this study. Narayan and Rao[13] and Subhashini *et al.*[14] have reported that monohaloamines can be further protonated at pH < 2, as in Eqns. (7) and (8) for chloramine-T and chloramine-B, respectively:

$$p\text{-}CH_3C_6H_4SO_2NHCl + H^+ \rightleftharpoons p\text{-}CH_3C_6H_4SO_2N^+H_2Cl \quad (7)$$

$$C_6H_5SO_2NHCl + H^+ \rightleftharpoons C_6H_5SO_2N^+H_2Cl \quad (8)$$

Therefore in higher acidic conditions, for CAB, RNHCl is expected to be protonated as follows:

$$RNHCl + H^+ \rightleftharpoons RN^+H_2Cl \quad (9)$$

In the present investigations, the retardation of the rate by H^+ ion indicates deprotonation of the species RN^+H_2Cl to monoprotonated oxidant RNHCl which is the active oxidizing species and Scheme-I is proposed for the oxidation of *o*-toluidine by CAB.

If $[CAB]_t$ represents the total concentration of the oxidant.

$$[CAB]_t = RN^+H_2Cl + RNHCl + X \quad (16)$$

Then, Scheme-I leads to the rate law:

$$\text{Rate} = \frac{k_3K_2K_1[CAB]_t[S]}{[H^+] + K_1\{1 + K_2[S]\}} \quad (17)$$

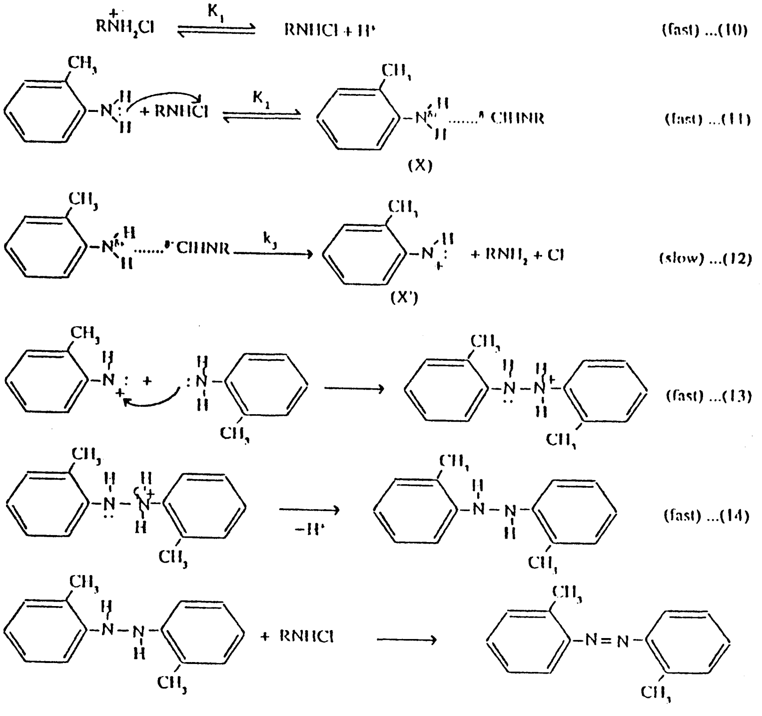
where [S] represents concentration of *o*-toluidine which is in agreement with the experimental results.

Since rate = $k^1[\text{CAB}]_t$, Eqn. (17) can be transformed into Eqns. (18) and (19).

$$\frac{1}{k^1} = \frac{1}{k_3K_1K_2[S]} \cdot [H^+] + \left\{\frac{1}{k_3K_2[S]} + \frac{1}{k_3}\right\} \tag{18}$$

$$\frac{1}{k^1} = \frac{1}{k_3} + \frac{1}{k_3K_2[S]}\left\{\frac{[H^+]}{K_1} + 1\right\} \tag{19}$$

Based on Eqns. (18) and (19), a plot of $1/k^1$ *vs.* $[H^+]$ at constant [S] and a plot of $1/k^1$ *vs.* $1/[S]$ at constant $[H^+]$ was found to be linear (Fig. 1). The values of K_1, K_2 and k_3 were calculated from the slope and intercept of the plots for the standard runs with $[\text{CAB}]_0 = 1 \times 10^{-3}$ mol dm^{-3}, [*o*-toluidine]$_0$ = 1×10^{-2} mol dm^{-3} and $[H^+] = 2 \times 10^{-2}$ mol dm^{-3} at 303 K.



Scheme-I

The value of the deprotonation constant (K_1) is found to be 0.015. Therefore the value of protonation constant (K_p) of RNHCl is given by:

$$K_p = \frac{1}{K_1} = 64.5$$

Furthermore, the value of K_1 is compared with the values obtained for the oxidation of different substrates by chloramine-B[13–15]. The constancy of the K_1 or K_p value is a strong indirect evidence for the formation of the reactive species RNHCl from RN^+H_2Cl supporting the proposed mechanism of oxidation of *o*-toluidine by CAB (Scheme-I).

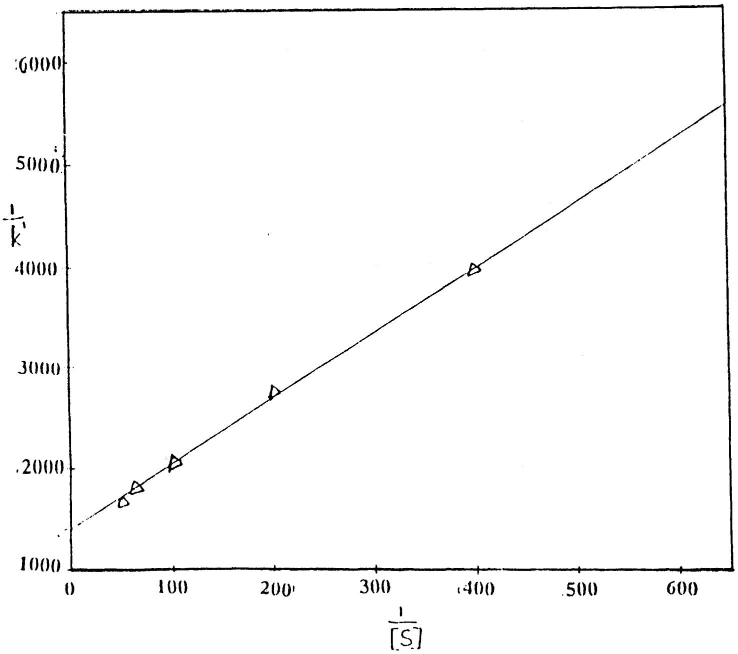


Fig. 1

The activation parameters have been evaluated using Arrhenius and Eyring's equations. The calculated values of energy of activation E_a, enthalpy of activation $\Delta H^{\#}$, free energy of activation $\Delta G^{\#}$ and entropy of activation $\Delta S^{\#}$ are 65.6 kJ mol^{-1}, 63.0 kJ mol^{-1}, 93.8 kJ mol^{-1} and –100.5 JK^{-1} mol^{-1} respectively.

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