

# Kinetics of Oxidation of Benzyl Alcohol by Sodium *N*-Chloro-*p*- Toluenesulfonamide\*

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## Abstract

The kinetics of oxidation of benzyl alcohol and substituted benzyl alcohols by sodium *N*-chloro-*p*-toluenesulfonamide (chloramine-T, CAT) in  $\text{HClO}_4$  (0.1–1 mol/dm<sup>3</sup>) containing  $\text{Cl}^-$  ions, over the temperature range of 30–50°C have been studied. The reaction is of first order each with respect to alcohol and oxidant. The fractional order dependence of the rate on the concentrations of  $\text{H}^+$  and  $\text{Cl}^-$  suggests a complex formation between  $\text{RNCl}^-$  and  $\text{HCl}$ . In higher acidic chloride solution the rate of reaction is proportional to the concentrations of both  $\text{H}^+$  and  $\text{Cl}^-$ . The observed solvent isotope effect ( $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$ ) is 1.43 at 30°C. The reaction constant ( $\rho = -1.66$ ) and thermodynamic parameters are evaluated. Rate expressions and probable mechanisms for the observed kinetics have been suggested.

## Introduction

*N*-Halogeno compounds are known to oxidize alcohols [1]. The kinetics and the mechanism of oxidation of alcohols by chloramine-T (sodium salt of *N*-chloro-*p*-toluenesulfonamide) to carbonyl compounds have been reported [2–6]. The results are rationalized by the formation of molecular chlorine, or  $\text{HOCl}$ ,  $\text{H}_2\text{OCl}^+$ , or protonated forms of chloramine-T, followed by the interaction with the alcohol. A review of the literature shows that the mineral acids other than  $\text{HCl}$  are poor catalysts for the oxidation of many substrates by chloramine-T.

Since benzyl alcohol is an industrially important substance, it has been oxidized by many oxidizing agents [7–9]. The present investigation deals with the kinetics and the mechanism of oxidation of benzyl alcohol by chloramine-T in  $\text{HClO}_4$  solution containing chloride ions with a view to elucidate the nature of the oxidizing species and the reaction mechanism.

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## Experimental

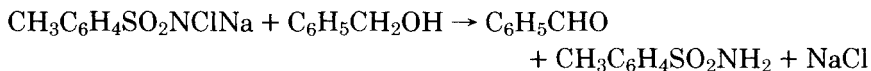
All chemicals used were of A.R. grade.  $\text{HClO}_4$  (E. Merck) was used without any further purification. Solutions were prepared using triply distilled water.

### *Kinetic Measurements*

Kinetic experiments were carried out under pseudo-first-order conditions at  $30^\circ\text{C}$ . The reaction was initiated by adding chloramine-T (CAT) solution (maintained at the same temperature) to a solution containing benzyl alcohol (BA),  $\text{HClO}_4$ , and NaCl. The unreacted CAT was estimated iodometrically at different time intervals. The pseudo-first-order rate constant was evaluated graphically and was reproducible within  $\pm 3\%$ . The detailed experimental procedure has been given elsewhere [6].

### *Stoichiometry*

The reaction mixture containing a slight excess of CAT in comparison with alcohol was kept at  $30^\circ\text{C}$  in  $\text{HClO}_4$  ( $0.1\text{--}1\text{ mol/dm}^3$ ) containing NaCl ( $0.1\text{ mol/dm}^3$ ). Estimation of the unreacted CAT after 48 hr showed that 1 mol of alcohol reacted with 1 mol of CAT according to the stoichiometric equation



The product isolated from the reaction mixture with CAT was identified as benzaldehyde,  $\gamma_{\text{max}}$ -2720, 1700, and  $727\text{ cm}^{-1}$  (Carl Zeiss Specord 75IR spectrophotometer, smear). Benzaldehyde was also isolated as its 2:4 dinitrophenyl hydrazone (mp  $224^\circ\text{C}$ ) [10].

## Results

### *Dependence of Rate on [CAT] and [BA]*

The oxidation of BA by CAT in various concentrations ( $0.1\text{--}1\text{ mol/dm}^3$ ) of  $\text{HClO}_4$  containing  $0.1\text{ mol/dm}^3$  NaCl was studied at  $30^\circ\text{C}$ . The reaction was found to follow the first-order kinetics with respect to [CAT]. From the linear plots of  $\log a/(a-x)$  versus time, the first-order rate constants  $k$  were evaluated and found to be independent of the initial concentration of CAT (Table I) in the concentration range of  $0.002\text{--}0.01\text{ mol/dm}^3$ .

The dependence of the rate on the concentration of BA is summarized in Table I. An increase in [BA] without change in [CAT] increased the rate of the reaction. A plot of  $\log k$  vs.  $\log [\text{BA}]$  gives a straight line with unit slope, indicating first-order dependence on [BA].

TABLE I Effect of concentration of reactants at 30°C.

| $[BA] \times 10^{-3}$<br>mol dm <sup>-3</sup> | $[CAT] \times 10^3$<br>mol dm <sup>-3</sup> | $k^a \times 10^4$<br>sec <sup>-1</sup> | $k^b \times 10^4$<br>sec <sup>-1</sup> |
|---|---|--|--|
| 0.50  | 2.5   | 1.07                                   | 3.98                                   |
| 0.75  | 2.5   | 1.78                                   | 6.09                                   |
| 1.00  | 2.5   | 2.39                                   | 8.02                                   |
| 1.25  | 2.5   | 3.02                                   | 9.66                                   |
| 1.00  | 1.0   | 2.44                                   | 7.93                                   |
| 1.00  | 5.0   | 2.21                                   | 7.84                                   |
| 1.00  | 7.5   | 2.14                                   | 8.12                                   |
| 1.00 <sup>c</sup>                             | 2.5   | 2.40                                   | 8.01                                   |
| 1.00 <sup>d</sup>                             | 2.5   | 2.38                                   | 7.45                                   |
| 1.00 <sup>e</sup>                             | 2.5   | 3.43                                   | 11.46                                  |

<sup>a</sup>  $[H^+] = 0.3$  mol/dm<sup>3</sup>.

<sup>b</sup>  $[H^+] = 0.8$  mol/dm<sup>3</sup>.

<sup>c</sup> At ionic strength of 0.5.

<sup>d</sup> In the presence of *p*-toluenesulfonamide ( $5 \times 10^3$  mol/dm<sup>3</sup>).

<sup>e</sup> Deuterium oxide as solvent,  $[Cl^-] = 0.1$  mol/dm<sup>3</sup>.

### Dependence on $[H^+]$ and $[Cl^-]$

The reactions were carried out with  $2.5 \times 10^{-3}$  mol/dm<sup>3</sup> CAT and 0.1 mol/dm<sup>3</sup> BA in the presence of various concentrations (0.1–1 mol/dm<sup>3</sup>) of HClO<sub>4</sub> containing a constant concentration (0.1 mol/dm<sup>3</sup>) of Cl<sup>-</sup> ions. The rate constant increased with the increase in acid concentration (Table II). A plot of  $\log k$  vs.  $\log [H^+]$  (Fig. 1) gives straight lines with different slopes

TABLE II. Effect of  $[H^+]$  at 30°C.<sup>a</sup>

| $[H^+]$<br>mol dm <sup>-3</sup> | $k \times 10^4$<br>sec <sup>-1</sup> | $[H^+]$<br>mol dm <sup>-3</sup> | $k \times 10^4$<br>sec <sup>-1</sup> |
|---------------------------------|--------------------------------------|---------------------------------|--------------------------------------|
| 0.1                             | 1.29                                 | 0.6                             | 5.69                                 |
| 0.2                             | 1.94                                 | 0.7                             | 6.91                                 |
| 0.3                             | 2.36                                 | 0.8                             | 8.02                                 |
| 0.4                             | 2.81                                 | 0.9                             | 8.91                                 |
| 0.5                             | 4.67                                 | 1.0                             | 9.77                                 |

<sup>a</sup>  $[CAT] = 2.5 \times 10^{-3}$  mol/dm<sup>3</sup>;  $[BA] = 0.1$  mol/dm<sup>3</sup>;  $[Cl^-] = 0.1$  mol/dm<sup>3</sup>.

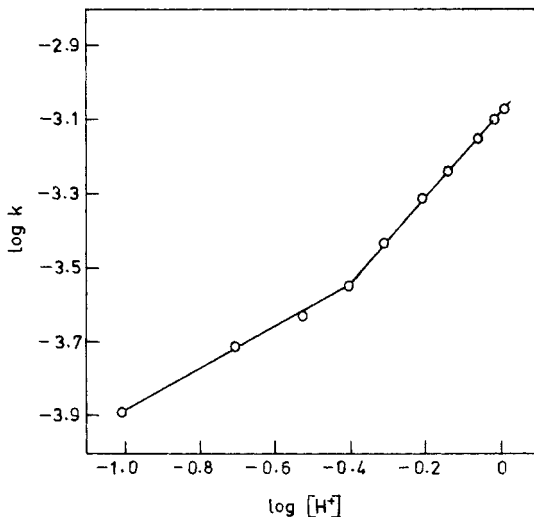


Figure 1. Plot of  $\log k$  vs.  $\log [H^+]$  for the oxidation of BA with CAT at 30°C.  $[BA] = 0.1 \text{ mol/dm}^3$ ;  $[CAT] = 2.5 \times 10^{-3} \text{ mol/dm}^3$ ;  $[Cl^-] = 0.1 \text{ mol/dm}^3$ .

( $[H^+] < 0.4 \text{ mol/dm}^3$ , slope = 0.6,  $[H^+] > 0.4 \text{ mol/dm}^3$ , slope = 1).

A detailed investigation on the kinetics of oxidation of BA by CAT at two different concentrations of  $HClO_4$  (0.3 and 0.8  $\text{mol/dm}^3$ ) containing various amounts (0.1–1  $\text{mol/dm}^3$ ) of  $Cl^-$  ions was made to know the dependence of the rate on the  $[Cl^-]$  ions. The rate of oxidation was affected by the addition of  $Cl^-$  ions. The rate constants at 30°C with different  $[Cl^-]$  ions are given in Table III. The kinetic data in 0.3  $\text{mol/dm}^3$   $HClO_4$  containing  $Cl^-$  ions in the form of a double reciprocal plot of  $1/k'$  vs.  $1/[Cl^-]$  ( $k'$ , being the second-order rate constant) give a linear relationship with a definite Y intercept (Fig. 2), indicating the fractional order dependence on  $[Cl^-]$ . However, at high  $[H^+]$  ( $>0.4 \text{ mol/dm}^3$ ) there exists a clear first-order dependence on  $[Cl^-]$ .

TABLE III. Effect of  $[Cl^-]$  at 30°C.<sup>a</sup>

| $[Cl^-]$                           | 0.0   | 0.1  | 0.2  | 0.3  | 0.4  |
|------------------------------------|-------|------|------|------|------|
| $k^b \times 10^4 \text{ sec}^{-1}$ | 0.032 | 2.34 | 4.16 | 5.62 | 7.24 |
| $k^c \times 10^3 \text{ sec}^{-1}$ | 0.005 | 0.80 | 1.51 | 2.39 | 3.31 |

<sup>a</sup>  $[CAT] = 2.5 \times 10^{-3} \text{ mol/dm}^3$ ;  $[BA] = \text{mol/dm}^3$ .

<sup>b</sup>  $[H^+] = 0.3 \text{ mol/dm}^3$ .

<sup>c</sup>  $[H^+] = 0.8 \text{ mol/dm}^3$ .

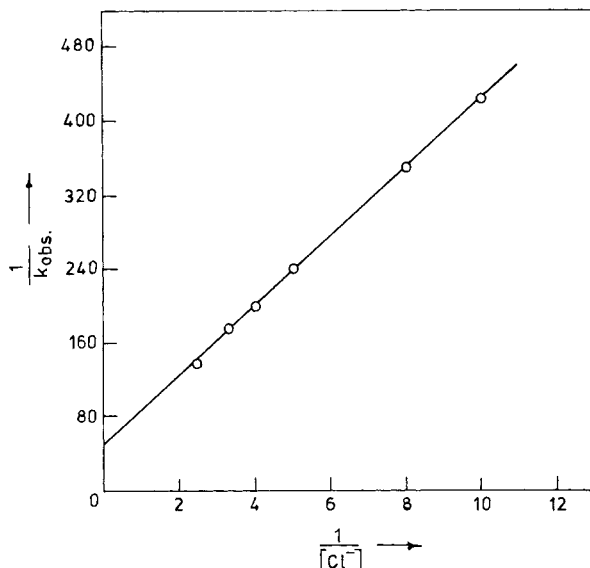


Figure 2. Double reciprocal plot of  $1/k'$  vs.  $1/[Cl^-]$  at  $30^\circ C$ .  $[BA] = 0.1 \text{ mol/dm}^3$ ;  $[CAT] = 2.5 \times 10^{-3} \text{ mol/dm}^3$ ,  $[H^+] = 0.3 \text{ mol/dm}^3$ .


### Effect of Temperature

The effect of temperature on the rate of oxidation of BA ( $0.1 \text{ mol/dm}^3$ ) by CAT ( $2.5 \times 10^{-3} \text{ mol/dm}^3$ ) in the presence of  $0.3$  and  $0.8 \text{ mol/dm}^3 \text{ HClO}_4$  containing  $0.2 \text{ mol/dm}^3 \text{ Cl}^-$  ions was studied. From the Arrhenius plots ( $\log k$  vs.  $1/T$ ), all of which are linear, the activation energies  $E_a$ , entropies  $\Delta S^\ddagger$ , and free energies  $\Delta G^\ddagger$  of activation have been evaluated. The values of these kinetic parameters in  $0.3 \text{ mol/dm}^3 \text{ HClO}_4$  containing  $0.2 \text{ mol/dm}^3 \text{ Cl}^-$  ions are given in Table IV. Similar results were also obtained in  $0.8 \text{ mol/dm}^3 \text{ HClO}_4$  containing  $0.2 \text{ mol/dm}^3 \text{ Cl}^-$  ions.

### Effect of Substituents

The oxidation of substituted benzyl alcohols by CAT was also carried out at  $30^\circ C$ . The order of the reaction with reference to the substrate was found to be unity, even in the presence of substituents. The rate constant values for the oxidation of substituted benzyl alcohols are summarized in Table V. The table indicates that electron releasing substituents in the benzene ring of BA in the para position accelerate the oxidation, whereas electron withdrawing substituents retard it. Hammett treatment of the present data using  $\sigma$  constants [11] yields a  $\rho$  value of  $-1.66$  at  $30^\circ C$  in  $0.3 \text{ mol/dm}^3 \text{ HClO}_4$  containing  $0.2 \text{ mol/dm}^3 \text{ Cl}^-$  ions. The same type of results were obtained in higher  $[H^+]$ .

TABLE IV. Thermodynamic parameters.

|  | $E_a$<br>KJ mol <sup>-1</sup> | $\Delta S^\ddagger$<br>JK <sup>-1</sup> mol <sup>-1</sup> | $\Delta G^\ddagger$<br>KJ mol <sup>-1</sup> |
|---|-------------------------------|---|---|
| H   | 80.2                          | 53.5  | 81.2  |
| p-OCH <sub>3</sub>  | 74.5                          | 64.3  | 76.2  |
| p-CH <sub>3</sub>   | 77.2                          | 57.7  | 78.5  |
| p-Cl  | 86.4                          | 41.3  | 86.6  |
| p-NO <sub>2</sub>   | 96.5                          | 26.6  | 95.8  |

No attempt was made to maintain constant ionic strength during oxidation. However, the effect of the change of the ionic strength of the medium (0.1–0.5) on the reaction rate was found to be negligible in both 0.3 and 0.8 mol/dm<sup>3</sup> HClO<sub>4</sub>. The reaction was carried out at 30°C with initially added toluene *p*-sulfonamide (TPS) in both 0.3 and 0.8 mol/dm<sup>3</sup> HClO<sub>4</sub>. The rate of oxidation was not affected in 0.3 mol/dm<sup>3</sup> HClO<sub>4</sub>, but a slight retardation was noticed in a higher [H<sup>+</sup>] range. The effect of the dielectric constant on the kinetics of oxidation was also studied by adding *tert*-butanol to the reacting system. A slight decrease in the rate constant was noticed on decreasing the dielectric constant of the medium in 0.3 mol/dm<sup>3</sup> HClO<sub>4</sub> (Fig. 3). However, there was no effect of the dielectric constant on the rate constant in 0.8 mol/dm<sup>3</sup> HClO<sub>4</sub>.

TABLE V. Effect of substituents.<sup>a</sup>

| Substituents       | $k^b \times 10^4$<br>sec <sup>-1</sup> | $\sigma$ |
|--------------------|--|----------|
| H                  | 1.496                                  | 0.0      |
| p-OCH <sub>3</sub> | 3.981                                  | -0.268   |
| p-CH <sub>3</sub>  | 2.985                                  | -0.170   |
| p-Cl               | 0.562                                  | +0.227   |
| p-NO <sub>2</sub>  | 0.061                                  | +0.778   |

<sup>a</sup> [CAT] = 2.5 × 10<sup>-3</sup> mol/dm<sup>3</sup>; [BA] = 0.1 mol/dm<sup>3</sup>.

<sup>b</sup> [H<sup>+</sup>] = 0.3 mol/dm<sup>3</sup>; [Cl<sup>-</sup>] = 0.2 mol/dm<sup>3</sup>.

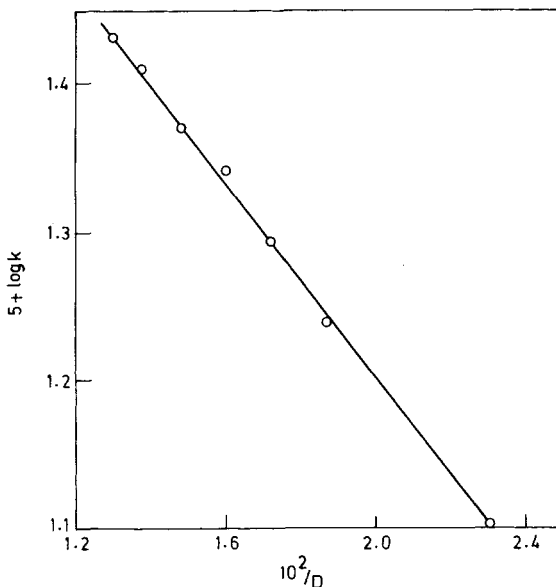


Figure 3. Plot of  $\log k$  vs.  $1/D$  in *tert*-butanol–water system,  $[H^+] = 0.3 \text{ mol/dm}^3$ ,  $[Cl^-] = 0.1 \text{ mol/dm}^3$ ,  $[BA] = 0.1 \text{ mol/dm}^3$ ,  $[CAT] = 2.5 \times 10^{-3} \text{ mol/dm}^3$ .

### Discussion

CAT gives several oxidizing species [12,13], namely,  $RNHCl$ ,  $RNCl_2$ ,  $HOCl$ , and  $H_2OCl^+$ . The relative concentration of each species depends on the concentration of CAT, the nature and the pH of the medium. In aqueous appreciable acidic chloride solution, the participation of  $HOCl$  or  $H_2OCl^+$  as kinetic intermediates is unlikely [12,13]. The first-order dependence on CAT rules out the possibility of  $RNCl_2$  as an oxidizing agent [4]. It is known [14] that in higher acidic chloride solution  $RNHCl$  gives  $Cl_2$ . Both  $H^+$  and  $Cl^-$  ions suppress the hydrolysis of  $Cl_2$  [15]. Hence in the present system one can expect  $RNHCl$  or  $Cl_2$  as the effective oxidizing species. Some experiments are carried out with  $Cl_2$  water under identical experimental conditions. It is found that kinetic data with  $Cl_2$  water are identical with those of CAT (Fig. 4) in higher acidic solution. Therefore  $RNHCl$  is the oxidizing agent in lower acidic solution.

The oxidation of alcohol, under nitrogen atmosphere, failed to induce polymerization of acrylonitrile. Thus formation of free radicals in this reaction is unlikely. The dependence of the rate on the  $[H^+]$  (Fig. 1) suggests different oxidation mechanisms in lower and higher acidic solutions. In lower acidic solution the deprotonation of  $RNHCl$  is predominant [16]. The fractional order dependence on  $[Cl^-]$  ions (Fig. 2) is indicative of the intermediacy of a complex between CAT and  $Cl^-$  ions. The observed results lead to the view that the rate of reaction is governed by the rate of

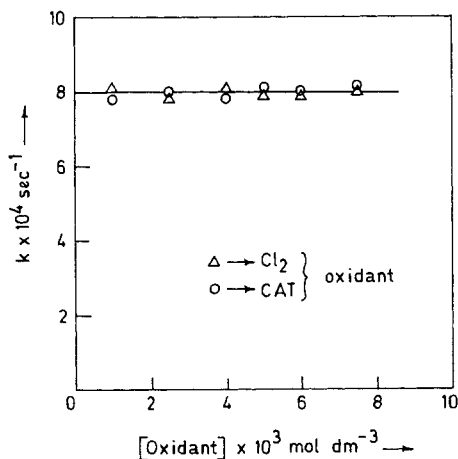
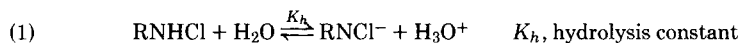


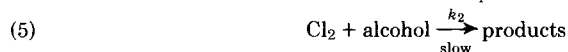
Figure 4. Relationship between  $k_{\text{CAT}}$  and  $k_{\text{Cl}_2}$  at 30°C.  $[\text{H}^+] = 0.8 \text{ mol/dm}^3$ ;  $[\text{Cl}^-] = 0.1 \text{ mol/dm}^3$ ;  $[\text{CAT}] = 1.75 \times 10^{-3} \text{ mol/dm}^3$ ;  $[\text{BA}] = 0.1 \text{ mol/dm}^3$ ;  $[\text{Cl}_2] = 1.75 \times 10^{-3} \text{ mol/dm}^3$ .

interaction between substrate and complex, whereas in higher acidic solution the oxidation proceeds through molecular  $\text{Cl}_2$  interacting in a slow step with the substrate. Based on these facts, kinetically distinguishable schemes 1 and 2 for the oxidation of BA by CAT in lower and higher acidic chloride solutions may be written:

scheme 1:



scheme 2:



Assuming total concentration of CAT as  $[\text{CAT}]_T = [\text{RNCl}^-] + [\text{RNHCl}] + [\text{X}]$  with  $[\text{Cl}^-]_T \gg [\text{CAT}]_T$ , one could obtain from scheme 1:

$$(6) \quad [\text{X}] = \frac{K[\text{CAT}]_T[\text{H}_3\text{O}^+][\text{Cl}^-]}{K_h + [\text{H}_3\text{O}^+] + K[\text{H}_3\text{O}^+][\text{Cl}^-]}$$

since

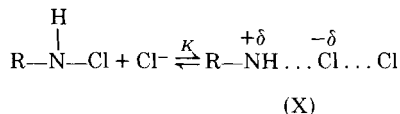
$$\frac{-d[\text{CAT}]_T}{dt} = k_1[\text{Alc}][\text{X}]$$

Substituting the value of  $[\text{X}]$  and rearranging,



$$(7) \quad \frac{1}{k'} = \frac{1}{k_1} + \frac{1}{Kk_1[\text{Cl}^-]} + \frac{K_h}{Kk_1[\text{H}_3\text{O}^+][\text{Cl}^-]}$$

where  $k'$  is the second-order rate constant. This equation predicts a linearity between  $1/k'$  and  $1/[\text{Cl}^-]$  with constant  $[\text{H}^+]$ . This is realized experimentally (Fig. 2).  $K$  and  $K_h$  calculated from this relationship are 1.38 and 0.029, respectively. The structure of the complex (X) is not known. However, a similar type of complex has been proposed for the oxidation of secondary alcohols by *N*-chlorosuccinamide [16].

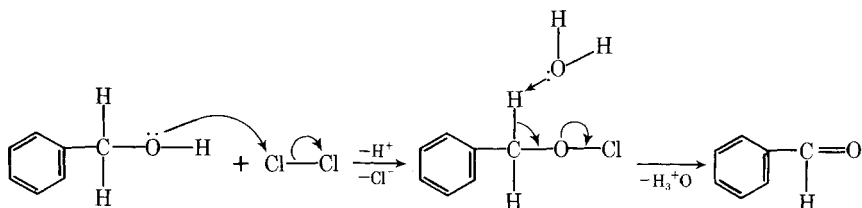


In scheme 2, applying a steady-state condition to  $\text{Cl}_2$  and assuming  $k_{-1}[\text{RNH}_2] \gg k_2[\text{Alc}]$ , one could derive the rate equation (8) for higher acidic chloride solution:

$$(8) \quad \frac{-d[\text{CAT}]}{dt} = \frac{k_1 k_2 [\text{Alc}] [\text{RHNCl}] [\text{H}^+] [\text{Cl}^-]}{k_{-1} [\text{RHN}_2]}$$

Equation (8) is in agreement with the observations. A first-order retardation by  $\text{RNH}_2$  is not noticed. However, the observed retardation (Table I) in rate by added  $\text{RNH}_2$  is probably due to a reaction between  $\text{Cl}_2$  and  $\text{RNH}_2$  becoming significant, thus decreasing the concentration of  $\text{Cl}_2$ .

From the results, a mechanism involving the formation of a hypochlorite ester is suggested. However, hydride transfer is unlikely in view of the observed low solvent isotope effect [ $k_{(\text{D}_2\text{O})}/k_{(\text{H}_2\text{O})} = 1.43$ ]. The electron flow during oxidation is depicted as follows:



The results at high acidity when subjected to a Bunnett plot [17] gave 3.89 for  $W$ , indicating that the water molecule functions only as a proton transfer agent. The negative value of the reaction constant ( $\rho = -1.66$ ) points to an electron-deficient carbon center in the transition state. The negative entropy of activation (Table IV) probably indicates the formation of the compact hypochlorite species. The observed neutral salt effect and the slight dielectric constant effect on the reaction rate in lower acidic so-

lution are probably in support of the proposed mechanism (scheme 1). The mechanism of oxidation of BA by CAT in acidic chloride solution is partly analogous to the oxidations of secondary alcohols by *N*-chlorosuccinamide [16] and *N*-bromosuccinamide [18,19].

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