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# Kinetics and Mechanism of Ruthenium(III) Catalysed Oxidation of Phenyl Acetic Acid by Sodium-N-Chlorobenzene Sulphonamide (Chloramine-B) in Acid Solution

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The kinetics of oxidation of phenyl acetic acid by chloramine-B (CAB) has been studied in hydrochloric acid solution at 303 K. In the absence of Ru(III) the rate shows a first order dependence on [CAB], independent with respect to [substrate] and first order dependence on [$H^+$]. In presence of Ru(III), the rate is first order with respect to [CAB], independent with respect to [substrate], first order dependence on [$H^+$] and fractional order dependence on [Ru(III)]. The variation of the ionic strength, dielectric constant of the medium and addition of chloride ion, the reaction product of CAB (benzene sulphonamide) do not have significant effect on the reaction rate. The rate of oxidation of phenyl acetic acid by CAB has been studied for various concentrations of [Ru(III)] at different temperatures and the catalytic constants have been calculated. Activation parameters have been evaluated from Arrhenius plot. A mechanism consistent with experimental results has been proposed.

**Key words: Kinetics, Mechanism, Ruthenium(III), Oxidation, Phenyl acetic acid, Chloramine-B.**

## INTRODUCTION

The chemistry of aromatic sulphonyl haloamines in general and of the sodium salt of N-chlorobenzene sulphonamide (chloramine-B, CAB) in particular has received considerable attention. Phenyl acetic acid (α-toluic acid or PAA) is commonly used as a starting material in the manufacture of synthetic perfumes. Literature survey reveals that no work has been done on the kinetic investigations of PAA oxidations. The present studies were undertaken to investigate the kinetic aspects of oxidation of PAA by N-metallo-N-halo aryl sulphonamides. We now report a detailed investigation of the kinetics of oxidation of PAA by CAB in acid solution both in absence and presence of catalyst Ru(III) at 303 K.

## RESULTS AND DISCUSSION

The kinetics of oxidation of phenylacetic acid by CAB was investigated in 25% methanol medium. Blank experiments with methanol, however, showed that there is a slight reaction of the solvent (less than 3%) under the experimental conditions used. This was allowed in the calculation of the net reaction rate constants for the oxidation of phenylacetic acid. Solution of ruthenium(III) chloride in 0.5 mol $dm^{-3}$ hydrochloric acid was used as catalyst. Allowance was made for the amount of hydrochloric acid present in the catalyst solution while preparing solution for kinetic runs.

**Stoichiometry and Product Analysis:** Reaction mixtures containing varying compositions of CAB and phenylacetic acid were kept at 303 K in presence of 0.1 mol $dm^{-3}$ hydrochloric acid for 24 h. The iodometric determination of unreacted CAB in the reaction mixture showed that one mole of CAB was consumed per mole of the phenylacetic acid and given by equation (1).

$$C_6H_5CH_2COOH + C_6H_5SO_2NClNa + H_2O \longrightarrow$$
$$C_6H_5SO_2NH_2 + C_6H_5CHO + NaCl + HCOOH \qquad (1)$$

The reaction product benzene sulphonamide ($C_6H$[illegible]$H_2$) was detected by thin layer chromatography using a petroleum eth[illegible]orofor[illegible]utanol (2 : 2 : 1 v/v) as the solvent with iodine as the developing reagent[illegible] 0.88). The presence of aldehyde among the reaction products was detected by preparing its 2,4-dinitrophenyl hydrazone derivative and by using Tollen's and chromic acid tests[1]. The presence of formic acid was detected by chromotrophic acid tests[1].

**Effect of Reactants:** With the substrate in excess and constant [HCl], [phenylacetic acid], plots of log [CAB] *vs.* time were linear indicating a first-order dependence of the reaction rate on [CAB] both in presence and absence of catalyst. The pseudo-first order rate constants [k'] obtained are given in Table-1. The reaction rate was independent of [substrate].

TABLE-1
EFFECT OF VARYING REACTANT CONCENTRATION ON THE RATE

$[H^+] = 10 \times 10^{-2}$ mole $dm^{-3}$
$[Ru(III)] = 19.28 \times 10^{-6}$ mol $dm^{-3}$, $\mu = 0.2$ mol $dm^{-3}$, Temp. = 303 K

| [CAB] $\times 10^{-4}$ mole $dm^{-3}$ | [Phenyl acetic Acid] $\times 10^{-2}$ mole $dm^{-3}$ | $k' \times 10^4$ ($s^{-1}$) |
|---|---|---|
| 3.0 | 10.0 | 4.17 (1.81) |
| 4.0 | 10.0 | 3.82 (1.83) |
| 5.0 | 10.0 | 3.74 (1.88) |
| 7.0 | 10.0 | 3.69 (1.89) |
| 10.0 | 10.0 | 3.98 (1.90) |
| 5.0 | 2.5 | — (2.11) |
| 5.0 | 5.0 | 3.47 (1.92) |
| 5.0 | 7.5 | 3.44 (2.08) |
| 5.0 | 10.0 | 3.74 (1.88) |
| 5.0 | 12.5 | 3.83 (2.06) |
| 5.0 | 15.0 | 3.83 (1.74) |

The values in parentheses are for the uncatalysed oxidation of phenyl acetic acid by CAB in HCl medium.

**Effect of $[H^+]$:** At fixed $[CAB]_0$ and [substrate] the rate of reaction increased with increase in [HCl] both in presence and absence of Ru(III). The plot of k′ *vs.* log $[H^+]$ was linear with a slope equal to unity (Table-2).

TABLE-2
EFFECT OF VARYING HYDROGEN ION CONCENTRATION ON THE REACTION RATE

$[CAB]_0 = 5.0 \times 10^{-4}$ mole $dm^{-3}$
[phenyl acetic acid] = $10 \times 10^{-2}$ mole $dm^{-3}$
[Ru(III)] = $19.28 \times 10^{-6}$ mol $dm^{-3}$, Temp. = 303 K

| $[H^+] \times 10^{-2}$ mole $dm^{-3}$ | $k \times 10^4$ $(s^{-1})$ |
|---|---|
| 5.0 | 1.87 (0.950) |
| 7.5 | 2.81 (1.405) |
| 10.0 | 3.74 (1.880) |
| 12.5 | 4.67 (2.365) |
| 15.0 | 5.62 (2.800) |
| 17.5 | 6.60 — |
| 20.0 | 7.48 (3.790) |
| 25.0 | 9.54 (4.750) |

The values in parentheses are for the uncatalysed oxidation of phenyl acetic acid by CAB in HCl medium.

**Effect of [Ru(III)]:** The reaction rate increased with increase in Ru(III) and plot of log k′ vs. log [Ru(III)] was linear with a fractional slope (Table-3).

TABLE-3
EFFECT OF VARYING [Ru(III)] CATALYST CONCENTRATION ON THE REACTION RATE AT DIFFERENT TEMPERATURES

$[CAB]_0 = 5.0 \times 10^{-4}$ mole $dm^{-3}$
[phenyl acetic acid] = $10 \times 10^{-2}$ mole $dm^{-3}$
$[H^+]$ = $10 \times 10^{-2}$ mol $dm^{-3}$, $\mu = 0.2$ mol $dm^{-3}$

| [Ru(III)] $\times 10^{-6}$ mol $dm^{-3}$ | $k \times 10^4$ $(s^{-1})$ | | | |
|---|---|---|---|---|
| | 298 K | 303 K | 308 K | 313 K |
| 4.82 | — | 1.90 | — | 4.11 |
| 14.46 | 2.05 | 3.23 | 4.26 | 6.58 |
| 19.28 | 2.43 | 3.74 | 4.90 | 7.51 |
| 24.10 | 2.68 | 4.16 | 5.51 | 8.44 |
| 38.58 | 3.38 | 5.28 | 7.03 | 10.79 |
| 48.20 | 3.77 | 5.75 | 7.82 | — |
| 57.84 | 4.14 | 6.30 | 8.63 | — |

**Effect of [Cl⁻]:** The addition of [Cl⁻] in the form of sodium chloride keeping $[H^+]$ constant had no effect on the rate of reaction.

**Effect of benzene sulphonamide on the rate:** The addition of the reaction product benzene sulphonamide ($C_6H_5SO_2NH_2$) ($1 \times 10^{-4}$ to $5 \times 10^{-4}$ mol dm$^{-3}$) had no effect on the rate both in presence and absence of Ru(III).

**Effect of ionic strength and dielectric constant of the medium:** Variation of ionic strength of the medium by adding $NaClO_4$ (0.1–0.5 mol. dm$^{-3}$) had no effect on the rate. The reaction was studied in aqueous methanol of different composition (5–20%) had no effect on the rate both in presence and absence of the catalyst.

**Effect of temperature:** The reaction was studied at different temperatures in the range 298–313 K and values of k′ were determined for both presence and absence of Ru(III) (Table-4). The activation parameters, *viz.*, energy of activation $E_a$, enthalpy of activation $\Delta H^{\#}$, entropy of activation $\Delta S^{\#}$ and free energy of activation $\Delta G^{\#}$ were obtained from the Arrhenius plot of log k′ *vs.* 1/T.

TABLE-4
AVERAGE CATALYTIC CONSTANT AT DIFFERENT TEMPERATURES

| Temperature (K) | $K_c$ | Activation parameter |
|---|---|---|
| 298 | 4.85 | $E_a$ = 51.04 (59.32) kJ mol$^{-1}$ |
| 303 | 8.82 | $\Delta H^{\#}$ = 48.52 (56.80) kJ mol$^{-1}$ |
| 308 | 10.48 | $\Delta S^{\#}$ = −150.33 (−128.93) J K mol$^{-1}$ |
| 313 | 17.70 | $\Delta G^{\#}$ = 94.13 (95.87) kJ mol$^{-1}$ |

The values in parentheses are for the uncatalysed oxidation of phenyl acetic acid by CAB in HCl medium.

Pryde and Soper[2], Morries *et al.*[3] and Bishop and Jennings[4] have shown the existence of similar equilibrium in acid and alkaline solutions of N-metallohaloaryl sulphonamides. Chloramines-B ($PhSO_2NClNa$), like chlorine analogue chloramines-T, behaves as a strong electrolyte in aqueous solution forming different species as shown in equations (2)–(6).

$$PhSO_2NClNa \rightleftharpoons PhSO_2NCl^- + Na^+ \quad (2)$$

$$PhSO_2NCl^- + H^+ \rightleftharpoons PhSO_2NHCl \quad (3)$$

$$PhSO_2NHCl + H_2O \rightleftharpoons PhSO_2NH_2 + HOCl \quad (4)$$

$$2PhSO_2NHCl \rightleftharpoons PhSO_2NH_2 + PhSO_2NCl_2 \quad (5)$$

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

In acidic solution, the probable oxidizing species are the free acid ($PhSO_2NHCl$), dichloramine-B ($PhSO_2NCl_2$), HOCl and $H_2OCl^+$. The involvement of $PhSO_2NCl_2$ in the mechanism leads to a second-order rate dependence on $[CAB]_0$, according to eqn. (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 added $RNH_2$ would be expected. However, no such effect was noticed in this study. Hardy and Johnston[5] who have studied the pH dependence of relative concentrations of the species present in acidified chloramine-T solution of comparable molarities, have shown that $PhSO_2NHCl$ is the likely oxidizing species in acid medium. Narayanan and Rao[6] and Subhashini *et al.*[7] have reported that monohaloamines can be further protonated at $pH < 2$ as shown in the following equations (7) and (8) for chloramine-T and chloramine-B, respectively.

$$p\text{-}CH_3C_6H_4SO_2NHCl + H^+ \rightleftharpoons p\text{-}CH_3C_6H_4SO_2N^+H_2Cl \tag{7}$$

$$C_6H_5SO_2NHCl + H^+ \rightleftharpoons C_6H_5SO_2N^+H_2Cl \tag{8}$$

The second protonation constant for chloramine-T and chloramine-B are 102 $mol^{-1}$ and 61 ± 5 $mol^{-1}$ respectively at 298 K.

Based on the preceding discussion a mechanism in Scheme-1 is proposed for the reaction.

$$RNCl^- + H^+ \overset{K_2}{\rightleftharpoons} RNHCl \qquad \text{(i) Fast}$$

$$RNHCl + H_2O \xrightarrow{k_2} RNH_2 + HOCl \qquad \text{(ii) Slow}$$

$$HOCl + S \longrightarrow \text{products} \qquad \text{(iii) Fast}$$

Scheme I

Then

$$\text{Rate} = k_2[RNHCl][H_2O] \tag{9}$$

$$K_1 = \frac{[RNHCl]}{[H^+][RNCl^-]} \tag{10}$$

$$[RNHCl] = K_1[H^+][RNCl^-] \tag{11}$$

Substituting eqn. (11) in eqn. (9),

$$\text{Rate} = K_1k_2[H^+][CAB]$$

The rate law is in good agreement with the experimental results such as first order in [CAB] and $[H^+]$.

$$\frac{1}{k_{obs}} = \frac{1}{K_1k_2[H^+]} \tag{12}$$

Plottings $\frac{1}{k_{obs}}$ *vs.* $\frac{1}{[H^+]}$ were linear passing through the origin.

Cady and Connick[8] and Connick and Fine[9] have determined the formula of aqueous ruthenium(III) complex species using the ion exchange resin properties and UV spectral studies. These studies have shown that the octahedral complex species such as $[RuCl_5(H_2O)]^{2-}$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^+$ do not exist in aqueous solutions of $RuCl_3$. Other studies have shown that the following equilibrium exists for $RuCl_3$ in acidic solutions[10–12].

$$[RuCl_6]^{3-} + H_2O \rightleftharpoons [RuCl_5(H_2O)]^{2-} + Cl^- \qquad (13)$$

Singh *et al.*[13, 14] used the above equilibrium in the ruthenium(III) chloride catalyzed oxidation of primary alcohols by BAB and of ethylene glycols by N-bromoacetamide in $HClO_4$ medium. In the present study, however, the chloride ion has no effect on the rate which indicates that the complex ion $[RuCl_6]^{3-}$ is the reactive catalyst species that interacts with the oxidant to form a complex intermediate. Similar results were observed in the Ru(III) catalyzed oxidation of chloroacetic acids by bromamine-T[15] and bromamine-B[16] and aliphatic primary amines by bromamine-T[17].

Furthermore, ultraviolet spectral measurements showed that a sharp absorption band was noticed at 210 nm for Ru(III), 264 nm for CAB solution and broad band around 297 nm for phenyl acetic acid in presence of $10 \times 10^{-2}$ mol dm$^{-3}$ HCl. A mixture of CAB and Ru(III) solution in presence of $10 \times 10^{-2}$ mol dm$^{-3}$ HCl showed an absorption band at 319 nm while for the mixture phenyl acetic acid and Ru(III) solutions there was no change in the $\lambda_{max}$ at 297 nm, indicating that complex formation has taken place only between Ru(III) and oxidant. Based on the preceding discussion, a mechanism (Scheme-II) is proposed for the reaction

$$RNHCl + Ru(III) \overset{K_1}{\rightleftharpoons} X \qquad (14)\ \text{Fast}$$

$$X^+ + H^+ \xrightarrow{k_2} X^I \qquad (15)\ \text{Slow}$$

$$X^I + S \xrightarrow{k_3} X^{II} \qquad (16)\ \text{Fast}$$

$$X^{II} \xrightarrow{k_4} \text{Products} \qquad (17)\ \text{Fast}$$

From the slow step of the preceding Scheme-II,

$$\text{Rate} = k_2[X][H^+] \qquad (18)$$

If $[CAB]_t$ represents the total [CAB], then

$$[CAB]_t = [RNHCl] + [X] \qquad (19)$$

By substituting [RNHCl] from equilibrium steps (14) in Scheme-II into eqn. (19), one obtains

$$[CAB]_t = [X]\left\{\frac{1 + K_1[Ru(III)]}{K_1[Ru(III)]}\right\}$$

$$\therefore \qquad [X] = \frac{[CAB]_t K_1[Ru(III)]}{1 + K_1[Ru(III)]}$$

Substituting for [X] in equation (18), one obtains the rate law equation (20).

$$\text{Rate} = \frac{k_2K_1[CAB]_t[Ru(III)][H^+]}{1 + K_1[Ru(III)]} \qquad (20)$$

The rate law is in good agreement with the experimental results such as first order in [CAB] and fractional order in [Ru(III)] and first order in $[H^+]$.

$$\frac{1}{k_{obs}} = \frac{1}{k_2K_1[Ru(III)][H^+]} + \frac{1}{k_2[H^+]} \tag{21}$$

The values of $K_1$ ($41.6 \times 10^3$) and $k_2$ ($7.69 \times 10^{-3}$) were calculated by using slope and intercept of the plot

$$\frac{1}{k_{obs}}\ vs.\ \frac{1}{Ru(III)}$$

It has been pointed out by Moelwyn and Hughes[18] that in the presence of the catalyst, the uncatalyzed and catalyzed reactions proceed simultaneously so that

$$k_1 = k_0 + K_c[\text{Catalyst}]^x$$

Successive addition of the catalyst brings about proportionate increase in the observed velocity. 'x' is unity and $K_c$ becomes a bimolecular constant. In the present study it has been found that the value of the rate constant is directly proportional to the concentration of the catalyst Ru(III) ion and therefore 'x' is unity and the relation will be

$$k_1 = k_0 + K_c[Ru(III)]$$

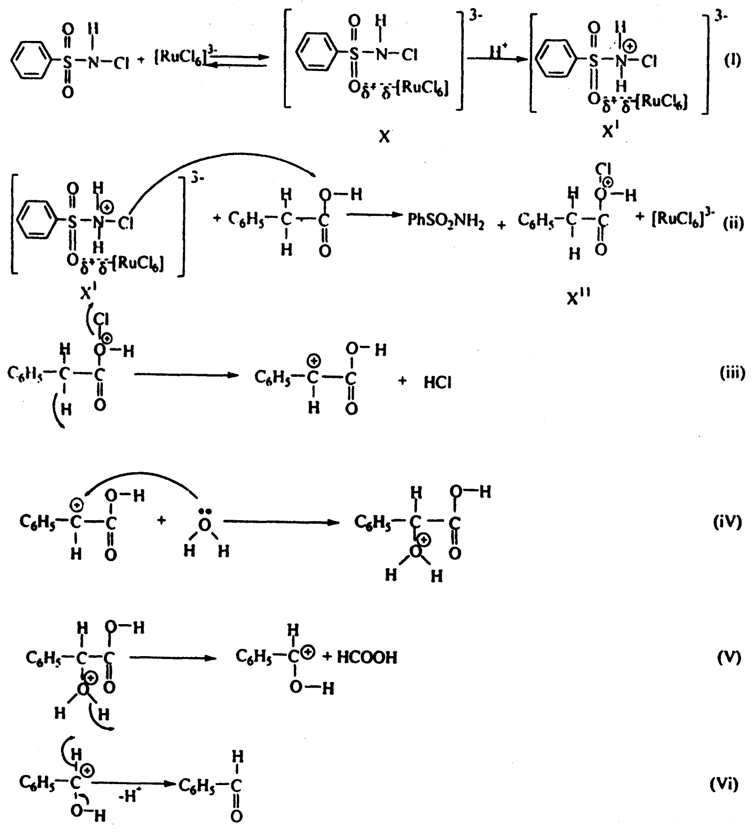
where $k_1$ is the observed pseudo-first order rate constant in the presence of the catalyst Ru(III), $k_0$ is the pseudo-first order rate constant for the uncatalyzed reaction and $K_c$ is the catalytic constant. The value of $K_c$ is obtained from

$$K_c = \frac{k_1 - k_0}{[Ru(III)]}$$

The experiments were conducted for different concentrations of [Ru(III)] at different temperatures. The values of $K_c$ were calculated at each temperature for different concentrations of [Ru(III)]. The values of $K_c$ were found to vary for different temperatures. The average values of $K_c$ for different [Ru(III)] at each temperature were calculated (Table-4). log $K_c$ values were plotted against 1/T and a linear graph was obtained from which $E_a$ value was calculated. Thermodynamic parameters were computed.

A detailed mechanism of the oxidation of phenyl acetic acid by CAB in HCl solution in presence of Ru(III) catalyst is given in Scheme-III.

An initial step involves equilibrium, the oxygen atom of the oxidant coordinates to the metal centre of the active catalyst species $[Ru(Cl_6)]^{3-}$ to form a loosely bound metal complex X (step (i) in Scheme-III) trapped in a solvent cage. This is similar to an associative interchange mechanism involving a fast pre-equilibrium in a ligand substitution reaction of metal complexes. The intermediate X undergoes protonation forming the intermediate $X^I$ (step (i) in Scheme-III). Then an electrophilic attack by $X^I$ at the oxygen atom of phenyl acetic acid to form the intermediate species $X^{II}$ (step (ii) in Scheme-III) and releasing $[Ru(Cl_6)]^{3-}$ and $PhSO_2NH_2$. The intermediate $X^{II}$ undergoes intramolecular rearrangements (Steps (iii–vi) in Scheme-III) forming formic acid and benzaldehyde as products.



Scheme-III

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