# Ruthenium(III) Catalyzed Kinetics of Chloroacetic Acids Oxidation by Sodium N-Bromobenzenesulfonamide in Hydrochloric Acid Medium

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#### Abstract

Kinetics of uncatalyzed and Ru(III)-catalyzed oxidations of mono-, di-, and tri-chloroacetic acids by the title compound (bromamine-B or BAB) in HCl medium has been studied at 40°C. The uncatalyzed reaction shows a first-order dependence of the rate on [BAB], and fractional and zero orders in [acid] at low and high [HCl] ranges, respectively. The Ru(III)-catalyzed reaction, on the other hand, shows a first-order behavior on each of [BAB] and [substrate], second-order dependence on [Ru(III)], and inverse fractional and inverse first orders in [acid] at low and high [HCl] ranges. Addition of halide ions and the reduction product of BAB, benzenesulfonamide, has no effect on the reaction rate. Variation of ionic strength of the medium has no influence on the reaction. Solvent isotope effect was studied using  $D_2O$ . Activation parameters have been evaluated from the Arrhenius plots. Mechanisms consistent with the above kinetic data have been proposed. The protonation constant of monobromamine-B evaluated from the uncatalyzed reaction is 12.4 while that evaluated from Ru(III) catalyzed reaction is 12.7. A Taft linear free-energy relationship is noted for the catalyzed reaction with  $ho^* = 1.2$  and 0.07 indicating that electron withdrawing groups enhance the rate. An isokinetic relation is observed with  $\beta = 338$  K indicating that enthalpy factors control the reaction rate. © 1993 John Wiley & Sons, Inc.

#### Introduction

Generally halogenated fatty acids are unaffected by mild oxidants unless a metal catalyst is employed. Kinetics of oxidation of chloroacetic acids by acid permanganate has been studied by Reddy et al. [1]. Although, iridium(III) and vanadium(IV) catalyzed oxidations of chloroacetic acids by chloramine-T in acid medium have been investigated by Ramakrishna and Kandlikar [2,3], there is no information available on the oxidation by bromamines. As a part of our mechanistic studies on the oxidation of substrates by aromatic-N-bromamines [4,5], we herein report the kinetics of oxidation of monochloroacetic acid (MCA), dichloroacetic acid (DCA), and trichloroacetic acid (TCA) with bromamine-B (PhSO<sub>2</sub>NBrNa 1.5 H<sub>2</sub>O herein

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International Journal of Chemical Kinetics, Vol. 25, 755–770 (1993) © 1993 John Wiley & Sons, Inc. CCC 0538-8066/93/090755-16 after abbreviated as BAB) in HCl medium. The catalytic effect of Ru(III) is also investigated.

## **Experimental**

Bromamine-B was prepared using a standard method [6] and its purity checked iodometrically and through IR and <sup>13</sup>C NMR spectral data [6]. An aqueous solution of BAB was prepared, standardized by iodometric method, and preserved in an amber colored bottle, until use, to prevent its photochemical deterioration.

Aqueous solutions of Analar grade chloroacetic acid (E. Merck), dichloroacetic acid (Aldrich Chem. Co.), and trichloroacetic acid (Thomas Baker, Bombay) were prepared and used. A solution of RuCl<sub>3</sub> (Arora, Matthey) in 0.50 M HCl was prepared and used as the stock catalyst solution. Allowance was made for the amount of HCl present in the catalyst solution while preparing reaction mixtures for kinetic runs. All other chemicals used were of acceptable grades of purity. A constant ionic strength of the reaction mixture was maintained at 0.60 M by adding required amount of a concentrated NaClO<sub>4</sub> solution. Triply distilled water was employed for preparing aqueous solutions. Heavy water (99.2%) was obtained from the Bhabha Atomic research Centre, Trombay, India.

### Kinetic Measurement

Mixtures containing requisite amounts of substrate, NaClO<sub>4</sub>, Ru(III) (in the case of catalyzed reactions only) and HCl were taken in stoppered pyrex glass tubes whose outer surfaces were coated black. Required amount of water was added to maintain a constant total volume. The tube was thermostated in a water bath to a given temperature (40°C for most runs). To this solution was added a measured amount of preequilibrated BAB solution to give a known concentration. The reaction mixture was shaken for uniform concentration. The progress of the reaction was monitored iodometrically for two half lives by withdrawing aliquots of the reaction mixture at regular time intervals. Under pseudo-first-order conditions, rate constants, k', were reproducible within  $\pm 3\%$ . Since the total ionic strength maintained was 0.6 M, concentrations were used in the expression of rate constants instead of activities, in first approximation, neglecting the activity coefficients. Regression analysis of experimental data was carried out on an EC-72 Statistical Calculator.

# Stoichiometry and Product Analysis

Preliminary investigations of oxidation of the substrates in HCl medium showed the reaction stoichiometry to be 1 mol BAB: 1 mol substrate. The reactions are represented by the following eqs. (1-3).

(1) 
$$ClCH_2COOH + PhSO_2NBr^- + H_2O \longrightarrow PhSO_2NH_2 + CO_2 + HCHO$$
  
+  $H^+ + Cl^- + Br^-$ 

(2) 
$$Cl_2CHCOOH + PhSO_2NBr^- + 2H_2O \longrightarrow PhSO_2NH_2 + CO_2 + HCOOH + 2H^+ + 2Cl^- + Br^-$$

(3) 
$$Cl_3CCOOH + PhSO_2NBr^- + 2H_2O \longrightarrow PhSO_2NH_2 + 2CO_2 + 3H^+ + 3Cl^- + Br^-$$

The reduction product of BAB, PhSO<sub>2</sub>NH<sub>2</sub>, was identified by TLC using petroleum ether-chloroform-1-butanol (2:2:1 V/V) solvent system for ascending irrigation and iodine as developing reagent ( $R_f = 0.88$ ). Formalde-hyde and formic acid were identified by the chromotropic acid procedure [7]. The later was reduced by Mg/HCl reaction to formaldehyde before applying the test. The evolved CO<sub>2</sub> was detected by the conventional lime water test. Attempts to quantitatively measure the amount of CO<sub>2</sub> evolved were unsuccessful.

#### Results

## Uncatalyzed Reaction

Under pseudo-first-order conditions of [substrate]<sub>o</sub>  $\gg$  [BAB]<sub>o</sub>, plots of log [BAB] vs. time were linear (r > 0.9986, s < 0.02) indicating a first-order dependence of the reaction rate on [oxidant] (plots not shown). The pseudo-first-order rate constants obtained at 40°C are given in Table I. Increase in [substrate] had no effect on the rate showing that it was independent of substrate concentration (Table I). At constant [BAB]<sub>o</sub> and [substrate]<sub>o</sub>, the rate increased with increase in [HCl] at 40°C. At lower acid concentration range (0.04–0.30 M), the plots of log k' vs. log [HCl] were linear (r > 0.9996) with fractional slopes indicating fractional orders

TABLE I. Effect of varying reactant concentrations on the reaction rate.<sup>a</sup>

		$k^\prime  imes 10^4/{ m s}^{-1}$		
$10^3  \mathrm{[BAB]}_{\mathrm{o}}/M$	$[substrate]_o/M$	MCA	DCA	TCA
0.60	0.100	5.88 (0.33)	6.44 (0.33)	7.33 (0.35)
0.80	0.100	5.67 (0.32)	6.31 (0.34)	7.29 (0.34)
1.00	0.100	5.75 (0.32)	6.40 (0.33)	7.34 (0.34)
1.50	0.100	5.90 (0.32)	6.46 (0.33)	7.38 (0.35)
2.00	0.100	5.72(0.32)	6.28 (0.34)	7.30 (0.34)
3.00	0.100	5.80 (0.32)	6.38 (0.33)	7.35 (0.35)
1.00	0.020	1.28 (0.32)	1.53 (0.34)	1.65 (0.34)
1.00	0.040	2.50 (0.33)	2.95 (0.33)	3.20 (0.35)
1.00	0.060	3.80 (0.33)	4.50 (0.34)	4.90 (0.35)
1.00	0.080	4.90 (0.32)	5.40 (0.34)	6.31 (0.34)
1.00	0.120	7.76 (0.33)	8.30 (0.34)	9.33 (0.35)
1.00	0.150	10.00 (0.32)	11.00 (0.34)	12.20 (0.35)

<sup>a</sup> [HCl] = 0.10 M; [Ru(III)] =  $2.41 \times 10^{-5}$  M; temp.  $40 \pm 0.1^{\circ}$ C;  $\mu = 0.60$  M; k' values in parenthesis are for the uncatalyzed reaction.

		$k' imes 10^4/{ m s}^{-1}$	
[HCl]/ <i>M</i>	MCA	DCA	TCA
0.040	9.25 (0.20)	10.15 (0.21)	11.40 (0.21)
0.060	7.70 (0.24)	8.35 (0.24)	9.80 (0.25)
0.080	6.76 (0.28)	7.36 (0.28)	8.50 (0.29)
0.100	5.75 (0.32)	6.40 (0.35)	7.35(0.34)
0.120	5.25 (0.35)	5.63 (0.36)	6.61 (0.37)
0.150	4.66 (0.39)	5.01 (0.40)	5.75 (0.41)
0.200	3.74 (0.46)	4.22 (0.47)	4.80 (0.48)
0.300	3.00 (0.47)	3.60 (0.51)	3.90 (0.53)
0.400	2.51 (0.48)	2.85 (0.53)	3.00(0.54)
0.500	1.80 (0.48)	2.07 (0.54)	2.35 (0.55)
0.700	1.31	1.53	1.68
0.800	1.16	1.29	1.42
1.00	0.95	1.07	1.18

TABLE II. Effect of varying hydrochloric acid concentration on the reaction rate.<sup>a</sup>

<sup>a</sup> [BAB]<sub>o</sub> = 1.00 × 10<sup>-3</sup> M; [substrate]<sub>o</sub> = 0.100 M; [Ru(III)] = 2.41 × 10<sup>-5</sup> M; temp. 40 ± 0.1°C;  $\mu = 0.60$  M; k' values in the parenthesis are for the uncatalyzed reaction.

of approximately 0.4 in [acid] (Table II) (plots not shown). The rate leveled off at higher  $[H^+]$  ( $\geq 0.30$  M) indicating a zero order in  $[H^+]$ .

Addition of Cl<sup>-</sup> or Br<sup>-</sup> ions in the form of NaCl or NaBr at fixed [H<sup>+</sup>] and ionic strength did not affect the rate. Hence, the rate dependence on [HCl] reflected the effect of [H<sup>+</sup>] only. Addition of the reaction product, benzenesulfonamide or PhSO<sub>2</sub>NH<sub>2</sub> ( $2 \times 10^{-4} - 9 \times 10^{-4}$  M), or variation of ionic strength of medium (0.12–0.60 M) had no effect on the reaction rate.

Solvent isotope studies were performed in D<sub>2</sub>O medium at 40°C using the substrate MCA as the probe. The values of  $k'_{\rm D2O}$  and  $k'_{\rm H2O}$  were found to be  $3.20 \times 10^{-5} \, {\rm s}^{-1}$  and  $3.22 \times 10^{-5} \, {\rm s}^{-1}$ , respectively, showing the inverse isotope effect,  $k'_{\rm D_2O}/k'_{\rm H_2O}$ , to be almost unity.

The reaction was studied at varying temperatures 308 K to 323 K to obtain Arrhenius plots of log k' vs. reciprocal of temperature which were linear (r > 0.9997, s < 0.023) (plots not shown). Activation parameters computed are presented in Table IV.

Addition of the reaction mixtures to aqueous acrylamide monomer solutions did not initiate polymerization indicating the absence of free radical species in the reaction sequence (proper control experiments were also run simultaneously).

#### Ru(III) Catalyzed Reaction

The reaction performed in the presence of Ru(III), under pseudo-firstorder conditions of [substrate]<sub>o</sub>  $\gg$  [BAB]<sub>o</sub>, gave linear plots of log [BAB] vs. time (r > 0.9975, s < 0.02) indicating a first-order dependence of the reaction rate on [BAB], as in the uncatalyzed reaction (plots not shown). The values of k' are given in Table I. When other variables were kept constant, the rate increased with increase in [substrate]. The linear plots of log k' vs. log [substrate] (r > 0.9985, s < 0.018) obtained indicated a first-order rate dependence on the substrate concentration (Table I). At constant [substrate]<sub>o</sub>, [BAB]<sub>o</sub>, and [Ru(III)], the reaction was studied with varying concentrations of HCl at 40°C (Table II). At lower [HCl] range (0.040-0.40 M), the plots of log k' vs. log [HCl] were linear (r > 0.9996, s <0.025) with negative fractional slopes indicating an inverse fractional order (approx. -0.6) dependence of the rate on H<sup>+</sup> ion concentration (plots not shown). However, at higher [HCl] range (0.50-1.0 M), the linear log-log plots (r > 0.9989, s < 0.018) had a unit negative slope indicating an inverse first-order dependence on H<sup>+</sup> ion concentration (Table II).

Runs performed with increasing [Ru(III)], keeping other conditions constant, showed an increase in the rate (Table III). Slopes of the linear plots of log k' vs. log [Ru(III)] indicated a second-order dependence of the rate on Ru(III) concentration (plots not shown).

As with uncatalyzed reaction, addition of Cl<sup>-</sup>, Br<sup>-</sup>, PhSO<sub>2</sub>NH<sub>2</sub> (2 ×  $10^{-4} - 9 \times 10^{-4}$  M), NaClO<sub>4</sub> (to effect ionic strength change, 0.12–0.60 M) had no influence on the rate in the presence of Ru(III) catalyst (2.41 ×  $10^{-5}$  M) (results not shown).

Solvent isotope studies were carried out in D<sub>2</sub>O medium at 40°C using the substrate MCA as the probe. The values of  $k'_{\rm D_2O}$  and  $k'_{\rm H_2O}$  were found to be  $4.13 \times 10^{-4} \, {\rm s}^{-1}$  and  $5.75 \times 10^{-4} \, {\rm s}^{-1}$ , respectively, showing an inverse isotope effect,  $k'_{\rm D_2O}/k'_{\rm H_2O}$ , of 0.72. Activation parameters computed from Arrhenius plots, in the 308 K to 323 K range, are presented in Table IV.

Tests performed using aqueous acrylamide monomer for the presence of free radicals in the reaction mixture were found to be negative.

#### Discussion

Bromamine-B (PhSO<sub>2</sub>NBrNa) analogous to chloramine-T behaves as a strong electrolyte [8] in aqueous solutions dissociating as

(4) 
$$PhSO_2NBrNa \implies PhSO_2NBr^- + Na^+$$

In acidic medium, protonation of the anion forms the free acid monobromamine-B, PhSO<sub>2</sub>NHBr, the ionization constant  $K_a$  of which is  $1.12 \times 10^{-5}$  at 25°C [9].

The free acid has not been isolated, but in analogy to the N-chloro derivatives, experimental evidence for its formation in acid solutions can

	$k^\prime  imes 10^4/{ m s}^{-1}$		
10 <sup>5</sup> [Ru(III)]/ <i>M</i>	MCA	DCA	TCA
0.964	0.813	1.06	1.18
1.205	1.25	1.55	1.70
1.440	1.86	2.16	2.75
1.928	3.44	3.77	4.72
2.410	5.75	6.40	7.34
2.893	7.94	8.75	10.65
3.616	11.36	13.24	15.70

TABLE III. Effect of varying catalyst concentrations on the reaction rate.<sup>a</sup>

<sup>a</sup> [BAB]<sub>o</sub> =  $1.00 \times 10^{-3}$  M; [substrate]<sub>o</sub> = 0.100 M; [HCl] = 0.100 M; temp.  $40 \pm 0.1^{\circ}$ C; and  $\mu = 0.60$  M.

I ADLE 1V.	I emperatur		iu acuvation par			acids by DAR III Under		catalyst.
		<i>R'</i> × 1	- s/s		$^{+H_{\ddagger}}$	$\Lambda S^{\ddagger}$	$VG^{\ddagger}$	$E_{a}$
Substrate	308 K	313 K	318 K	323 K	$(kJ mol^{-1})$	$(JK^{-1} mol^{-1})$	$(kJ mol^{-1})$	(kJ mol <sup>-1</sup> )
MCA	3.84	5.75	8.61	12.38	62.1	-109.0	96.5	64.8
	(0.21)	(0.32)	(0.51)	(0.78)	(10.0)	(-108.1)	(104.0)	(72.6)
DCA	4.55	6.40	9.55	13.40	57.6	-122.3	96.2	60.3
	(0.22)	(0.33)	(0.51)	(0.78)	(68.3)	(-112.9)	(104.0)	(11.0)
TCA	5.20	7.35	10.47	14.30	53.47	-134.6	96.0	51.1
	(0.23)	(0.34)	(0.52)	(0.79)	(65.65)	(-121.2)	(103.9)	(68.3)
k' values in t	he parenthesi	is are for the u	ncatalyzed react	ion.				

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be visualized [10]. It could undergo disproportionation forming benzenesulfonamide and dibromamine-B as follows:

(5) 2PhSO<sub>2</sub>NHBr 
$$\rightleftharpoons^{k_d}$$
 PhSO<sub>2</sub>NH<sub>2</sub> + PhSO<sub>2</sub>NBr<sub>2</sub>  
( $k_d = 1.13 \times 10^{-2}$  at 25<sup>o</sup>C)

Dibromamine-B and monobromamine-B on hydrolysis form hypobromous acid as in eqs. (6) and (7) below:

(6) 
$$PhSO_2NBr_2 + H_2O \implies PhSO_2NHBr + HOBr$$

(7) PhSO<sub>2</sub>NHBr + H<sub>2</sub>O 
$$\rightleftharpoons k'_h$$
 PhSO<sub>2</sub>NH<sub>2</sub> + HOBr  
( $k'_h = 4.21 \times 10^{-3}$  at 25°C)

The weak electrolyte HOBr ionizes in aqueous solutions as,

(8) HOBr 
$$\rightleftharpoons k'_a$$
 H<sup>+</sup> + OBr<sup>-</sup>  $(k'_a = 2.0 \times 10^{-9} \text{ at } 25^{\circ}\text{C})$ 

The possible reactive oxidizing species in acidified BAB solutions are, therefore, PhSO<sub>2</sub>NHBr, PhSO<sub>2</sub>NBr<sub>2</sub>, HOBr, and OBr<sup>-</sup> ion. Since the involvement of PhSO<sub>2</sub>NBr<sub>2</sub> in the mechanism leads to a second-order rate law according to eq. (5), this compound can not be the reactive species responsible for the substrate oxidation. As eq. (7) indicates a slow hydrolysis, if HOBr were to be primarily involved, a first-order retardation of the rate by the added  $PhSO_2NH_2$  is expected, which is contrary to experimental observation. Hardy and Johnston [9] have determined the pH dependent relative concentrations of the species, the conjugate acid PhSO<sub>2</sub>NHBr, HOBr, and OBr<sup>-</sup> ion, in aqueous BAB solutions ( $6 \times 10^{-3}$  M) in the pH range of 7-13. According to these results, [PhSO<sub>2</sub>NHBr] is high at pH 7  $(4.1 \times 10^{-5} \text{ M})$  where [HOBr] and [OBr<sup>-</sup>] are  $6.0 \times 10^{-6} \text{ M}$  and  $1.0 \times 10^{-6} \text{ M}$  $10^{-7}$  M, respectively. A comparison with the relative concentrations of species present in acidified chloramine-T solutions of comparable molarities [8] would indicate that PhSO<sub>2</sub>NHBr is the likely oxidizing species in acid medium. Recently Narayanan and Rao [11] and Subhashini et al. [12] have reported that monohaloamines can be further protonated at pH < 2 as shown in eqs. (9) and (10) below:

(9) 
$$CH_3C_6H_4SO_2NHCl + H^+ \xrightarrow{K''} CH_3C_6H_4SO_2NH_2Cl$$

(10) 
$$PhSO_2NHBr + H^+ \rightleftharpoons^{\Lambda_1} PhSO_2NH_2Br$$

The values of these second protonation constants, K'' and  $K_1$ , are 102 and 61  $\pm$  5 at 25°C, respectively. Gupta [13], however, feels that the above values could be lower.

## Uncatalyzed Reaction

Since the rate of reaction is independent of [substrate] in the absence of the Ru(III) catalyst, further protonation of  $PhSO_2NHBr$  is likely in acid

solutions leading to the formation of  $PhSO_2 \overset{\oplus}{N}H_2Br$  which is the reactive oxidizing species. Based on this and other results discussed earlier, the following mechanism (Scheme I) is proposed for the uncatalyzed reaction:

$$\begin{array}{rcl} PhSO_2NHBr + H^+ & \stackrel{K_1}{\longleftarrow} & PhSO_2\overset{\bigoplus}{N}H_2Br & (i) \text{ fast} \\ PhSO_2\overset{\bigoplus}{N}H_2Br + H_2O & \stackrel{k_2}{\longrightarrow} & H_2OBr^+ + PhSO_2NH_2 & (ii) \text{ slow} \\ & H_2OBr^+ + S & \stackrel{k_3}{\longrightarrow} \text{ products} & (iii) \text{ fast} \end{array}$$

where S is the substrate, MCA or DCA or TCA

Scheme I

Absence of solvent isotope effect clearly supports Scheme I. Since  $D_3O^+$  ion is a stronger acid than  $H_3O^+$ , it is normally expected that for a fast preequilibrium proton transfer, the solvent isotope effect is  $k'_{H_2O}/k'_{D_2O} < 1$  as shown in step (i). But the protonation is followed by the slow (r.d.s.) hydolysis step (ii) where O—H and O—D bond dissociations lead to the primary isotope effect,  $k'_H/k'_D > 1$ . Thus, the observed isotope effect is a composite of the counter acting effects making  $k'_{H_2O}/k'_{D_2O}$  ca. 1.

The total effective concentration of BAB, from Scheme I, is as follows:

(11) 
$$[BAB]_{t} = [PhSO_{2}NHBr] + \left[PhSO_{2}\overset{\bigoplus}{NH_{2}}Br\right]$$

Substitution for  $[PhSO_2NHBr]$  from equilibrium (i) in eq. (11) leads to eq. (12):

(12) 
$$\left[\operatorname{PhSO}_{2}\overset{\bigoplus}{\mathrm{NH}}_{2}\mathrm{Br}\right] = K_{1}[\mathrm{BAB}]_{t}[\mathrm{H}^{+}]/(1 + K_{1}[\mathrm{H}^{+}])$$

This on substitution into eq. (13), obtained from the slow step (ii) (r.d.s.), gives the rate law (eq. (14)).

(13) 
$$\operatorname{rate} = -d[\operatorname{BAB}]_t/dt = k_2 \left[\operatorname{PhSO}_2 \overset{\bigoplus}{\operatorname{NH}}_2 \operatorname{Br}\right] [\operatorname{H}_2 \operatorname{O}]$$

(14) 
$$-d[BAB]_t/dt = \frac{K_1 k_2 [BAB]_t [H^+]}{1 + K_1 [H^+]}$$

(since the water concentration is constant, it is omitted)

This rate law (eq. (14)) is in agreement with the experimental observations of first-order in [BAB], and fractional and zero orders in  $[H^+]$  at lower and higher [acid] ranges.

Equation (14) can be transformed into the following forms (eqs. (15) and (16)):

(14) 
$$-d[BAB]_t/dt = k'[BAB]_t = \frac{K_1k_2[BAB]_t[H^+]}{1 + K_1[H^+]}$$

(15) 
$$k' = \frac{K_1 k_2 [\mathrm{H}^+]}{1 + K_1 [\mathrm{H}^+]}$$

 Substrate	$K_1/M^{-1}$	$k_2  imes 10^{-5}/M^{-1}~{ m s}^{-1}$
MCA	12.5	5.93
DCA	12.2	6.11
TCA	12.5	6.18

TABLE V. Equilibrium and rate constant data from eq. (16)<sup>a</sup>.

<sup>a</sup>Calculated from a double reciprocal plot of 1/k' vs.  $1/[H^+]$ .

(16) 
$$\frac{1}{k'} = \frac{1}{K_1 k_2 [\mathrm{H}^+]} + \frac{1}{k_2}$$

The values of  $K_1$  and  $k_2$  were calculated from the slope and intercept of the double reciprocal plot of 1/k' vs.  $1/[H^+]$  which was linear (r > 0.9987, s < 0.02). The values obtained at 313 K are presented in Table V. The near constant values of  $K_1$  and  $k_2$  support the proposed mechanism of oxidation of the substrates by BAB. Furthermore, at higher  $[H^+]$  the condition  $K_1[H^+] \gg 1$  holds good in eq. (14) consistent with the observed independence of the rate on  $[H^+]$ .

A detailed mechanistic interpretation of uncatalyzed oxidation of chloroacetic acids by BAB in HCl medium is presented in Scheme II, using MCA oxidation as an example. Steps (i) and (ii) are similar to all three substrates, MCA, DCA, and TCA. Since DCA and TCA form some products different from those of MCA, the final step (iiia) applies only for MCA, while steps (iiib) and (iiic) are substituted to represent the products of oxidation of DCA and TCA, respectively.

## Ru(III) Catalyzed Reaction

Electronic spectral studies by Cady and Connick [14] and Connick and Fine [15] have shown that coordination species such as  $[RuCl_5(H_2O)]^{-2}$ ,  $[RuCl_4(H_2O)_2]^-$ ,  $[RuCl_3(H_2O)_3]$ ,  $[RuCl_2(H_2O)_4]^+$ , and  $[RuCl(H_2O)_5]^{+2}$  do not exist in aqueous solutions of RuCl<sub>3</sub>. Ruthenium(III), however, exists in the following ligand substitution equilibrium in acid medium [16–18]:

(17) 
$$[\operatorname{RuCl}_6]^{-3} + \operatorname{H}_2O \rightleftharpoons [\operatorname{RuCl}_5(\operatorname{H}_2O)]^{-2}, + Cl$$

Singh et al. [19,20] have employed the above equilibrium in ruthenium(III) chloride catalyzed bromamine-T oxidation of primary alcohols and in the ruthenium(III) chloride catalyzed oxidation of diethylene glycol and methyldiethyl glycol by N-bromoacetamide in HClO<sub>4</sub> medium. In the present study, however, addition of chloride ion in the form of NaCl at constant [H<sup>+</sup>] and ionic strength had no effect on the rate indicating that [RuCl<sub>6</sub>]<sup>-3</sup> is the most likely catalyzing species which interacts with the substrate to form a complex intermediate. The inverse fractional order in [H<sup>+</sup>] at lower acid concentration range (0.04–0.40 M) indicates that the deprotonation of PhSO<sub>2</sub>NH<sub>2</sub>Br results in the reformation of PhSO<sub>2</sub>NHBr which is likely to be the active oxidizing species involved in the mechanism of oxidation of the substrates. In the proposed mechanism (Scheme III), the Ru(III)-substrate complex (X) reacts with PhSO<sub>2</sub>NHBr in a slow step (r.d.s.) to form the intermediate (X') which then disproportinates to the products.



FOR DCA







$$PhSO_2NH_2Br \xrightarrow{K'_1} PhSO_2NHBr + H^+$$
 (i) fast

$$S + 2Ru(III) \xrightarrow{K_2} X$$
 (ii) fast  
(complex)

$$PhSO_2NHBr + X \xrightarrow{k'_3} X' + PhSO_2NH^-$$
(iii) slow  
(complex)

$$PhSO_2NH^- + H^+ \xrightarrow{k_4} PhSO_2NH_2$$
 (iv) fast

 $X' + H_2O \xrightarrow{k_5'}$  products (v) fast

Scheme III

Here S represents the substrate anion  $RCOO^-$ , and X and X' represent the complex intermediate species,  $[S(RuCl_6)_2]^{-7}$  and  $[(Br)S(RuCl_6)_2]^{-6}$ , respectively, as shown in Scheme IV.

The following rate law (eq. (18)), consistent with experimental results, is derived from Scheme III:

(18) 
$$rate = \frac{K_1' K_2' k_3' [BAB]_t [S] [Ru(III)]^2}{[H^+] + K_1'}$$

Inverse first-order in [H<sup>+</sup>] at higher acid concentration range is expected as  $[H^+] \gg K'_1$ . Similarly, at lower acid concentration range,  $K'_1$  and  $[H^+]$ are of the same order of magnitude leading to an inverse fractional order in  $[H^+]$  as observed experimentally.

A detailed mechanistic scheme of Ru(III) catalyzed oxidation of chloroacetic acids by BAB in HCl medium is presented in Scheme IV, using MCA oxidation as an example. Steps (i), (ii), and (iii) are similar to all three substrates, MCA, DCA, and TCA. Since DCA and TCA form some products different from those of MCA, the final step (iva) of MCA is to be replaced by steps (ivb) and (ivc) for the oxidation of DCA and TCA, respectively.

Ultraviolet spectrophotometric measurements showed that aqueous MCA solutions have a sharp absorption maximum ( $\lambda_{max}$ ) at 218 nm. Ru(III) solutions showed a  $\lambda_{max}$  around 204 nm while BAB solutions exhibited a peak around 233 nm in the presence of 0.10 M HCl. A mixture of MCA and Ru(III) solutions in the presence of 0.10 M HCl showed a  $\lambda_{max}$  at 224 nm while for a mixture of BAB and Ru(III) solutions there was no change in the  $\lambda_{max}$  at 233 nm indicating that the complex formation occurred only between the substrate (S) and Ru(III).

Since rate = k' [BAB], the rate law (eq. (18)) can be transformed into eqs. (19) and (20).

(19) 
$$k' = \frac{K_1' K_2' k_3' [S] [Ru(III)]^2}{[H^+] + K_1'}$$

(20) 
$$\frac{1}{k'} = \frac{[\mathrm{H}^+]}{K_1' K_2' k_3' [\mathrm{S}] [\mathrm{Ru}(\mathrm{III})]^2} + \frac{1}{K_2' k_3' [\mathrm{S}] [\mathrm{Ru}(\mathrm{III})]^2}$$

A plot of 1/k' vs.  $[H^+]$  at constant [S] and [Ru(III)] was found to be linear (Figure 1; r > 0.9989). From the intercept and slope of the plot,  $K'_1$ and product of  $K'_2k'_3$  were determined at 313 K. The protonation constant  $K_1$  ( $K_1 = 1/K'_1$ ) of PhSO<sub>2</sub>NHBr was also evaluated. The data obtained are presented in Table VI. The near constant values of ( $K'_2k'_3$ ) and  $K'_1$ support the proposed mechanism of oxidation of the substrates by BAB in the presence of the Ru(III) catalyst. Furthermore, the values of  $K_1$ obtained from eq. (20) are in very good agreement with those calculated from Scheme I (eq. (16)), and, thus, form a strong indirect evidence for the existence of the species, PhSO<sub>2</sub>NH<sub>2</sub>Br, supporting the proposed Schemes I and III.

## FOR MCA



Scheme IV





Scheme IV (continued)

Since  $D_3O^+$  ion is a stronger acid than  $H_3O^+$  [19], a further rate retardation is expected in  $D_2O$  medium. This has been confirmed as the inverse solvent isotope effect,  $k'_{D_2O}/k'_{H_2O}$ , was found to be 0.72. Attempts were made to arrive at a linear free-energy relation [20] for the oxidation of chloroacetic acids by BAB. Tests of the complete Taft equation as well as single correlations with polar substitution constant  $\sigma^*$  and steric substitution constant  $E_s$  were made by the plots,  $(\log k' - E_s)$  vs.  $\sigma^*$ ,  $\log k'$ vs.  $\sigma^*$ , and  $\log k'$  vs.  $E_s$ . The following regression equations were found:

(21) 
$$(\log k' - E_s) = 1.2\sigma^* - 4.2$$
  $(r = 0.9871)$ 

(22) 
$$\log k' = 0.07\sigma^* - 3.3$$
  $(r = 0.9904)$ 

(23) 
$$\log k' = -0.05E_s - 3.2$$
  $(r = 0.9504)$ 

A good correlation of  $\log k'$  with  $\sigma^*$  in eq. (22) implies that electronic effects play a dominant role in determining the rate. However, the correlation in eq. (21) shows that both steric and electronic effects influence in determining the rate. The positive values of polar constant  $\rho^*$ , although small (1.2 and 0.07), indicate that electron withdrawing groups increase the rate of reaction.

It is seen from Table IV that the rate of oxidation of chloroacetic acids by BAB increases in the order: MCA < DCA < TCA, showing the regular operation of the inductive effect due to the chlorine substituent. The largest activation energy for the slowest reaction of MCA and vice versa for TCA, indicate that the reactions are enthalpy controlled. The activation



Figure 1. Plots of 1/k' vs. [H<sup>+</sup>]: (a) MCA; (b) DCA; and (c) TCA. [BAB]<sub>o</sub> =  $1.00 \times 10^{-3}$  M; [substrate]<sub>o</sub> = 0.100 M; [Ru(III)] =  $2.41 \times 10^{-5}$  M; temp. 40 ± 0.1°C; and  $\mu$  = 0.60 M.

enthalpies  $(\Delta H^{\ddagger})$  and entropies  $(\Delta S^{\ddagger})$  for the oxidation of chloroacetic acids are linearly related. From the slope of the plot of  $\Delta H^{\ddagger}$  vs.  $\Delta S^{\ddagger}$  (Figure 2a, r = 0.9982), the isokinetic temperature ( $\beta$ ) was calculated to be 338 K. This was further verified by employing the Exner criterion [21] by plotting log  $k'_{308\,\mathrm{K}}$  vs. log  $k'_{323\,\mathrm{K}}$ , which is linear (Figure 2b, r = 0.9995). The Exner slope ( $\beta$ ) was found to be 337.7 K. The value of  $\beta$ , which is higher than the temperature range employed in the present study, indicates that the substrate oxidation is enthalpy controlled. The fairly negative values of entropy of activation indicate the formation of a rigid transition state. The constant values of free energy of activation ( $\Delta G^{\ddagger}$ ) indicate that the three chloroacetic acids undergo oxidation via the same mechanism.

Substrate	$K_2' k_3'  imes 10^{-7}/M^{-3}~{ m s}^{-1}$	$K_1'  imes 10^2/M$	$K_1/M^{-1}$
MCA	2.26	7.91	12.63
DCA	2.53	7.90	12.64
TCA	2.91	7.81	12.79

TABLE VI. Data calculated using eq.  $(20)^a$ .

<sup>a</sup>Calculated from a plot of 1/k' vs. [H<sup>+</sup>] at constant [S] and [Ru(III)].



Figure 2. (a) A Plot of  $\Delta H^{\ddagger}$  vs.  $\Delta S^{\ddagger}$  and (b) Exner plot of log  $k'_{323}$  vs. log  $k'_{308}$ .

# Acknowledgment

One of the authors (BMV) acknowledges the award of a Project Assistantship from the Department of Science and Technology, Government of India, New Delhi. The authors are thankful to Professor J. S. Prasad, Department of Physics, University of Mysore, Mysore for his encouragement and interest.

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Received January 19, 1993 Accepted March 30, 1993