Asian Journal of Chemistry Vol. 4, No. 2 (1992), 338–347

Ruthenium(III) Catalysed Oxidation of Aliphatic Amines by N-Bromosuccinimide in Perchloric Acid Medium

RASHMI SAXENA and S. K. UPADHYAY*

Department of Chemistry
Harcourt Butler Technological Institute, Kanpur–208 002, India

The kinetics of ruthenium(III) catalysed oxidation of aliphatic amines viz. ethylamine, diethylamine and triethylamine by N-bromosuccinimide (NBS) have been investigated in perchloric acid medium and in presence of mercuric acetate. The order of reaction in NBS varies between one and two. A first order dependence of rate with respect to each substrate and catalyst and an inverse first order dependence of rate with respect to acid has been observed. A retarding effect of succinimide and acetic acid on the rate of reaction was also observed in each case. A suitable mechanism is proposed and discussed.

INTRODUCTION

The investigations on the oxidation of amines with various oxidants like hexacyanoferrate(III)[1], chloramine-T[2] etc. have shown that reactions are very slow in absence of the catalyst while in presence of transition metal ions *viz.* osmium(VIII), ruthenium(III), etc. the reactions follow a complex kinetics. The oxidation of amines by N-bromosuccinimide (NBS), which has been used as a potent oxidant in acidic media during the oxidation of alcohols[3,4], esters[5], ketones[6,7] etc. has not received attention. The present communication incorporates the results of the kinetices of ruthenium(III) catalysed oxidation of ethylamine, diethylamine and triethylamine by NBS in perchloric acid medium and in presence of mercuric acetate. The suitable mechanism consistent with kinetic data has been proposed for the oxidation process.

EXPERIMENTAL

The reagents employed were ethylamine, diethylamine and triethylamine (all AR grade), ruthenium trichloride (Johnson M. Atthey), N-bromosuccinimide (Emerck, GR grade). Other reagents used were of AR grade. All the solutions were praepared in doubly distilled water.

An aqueous solution of NBS was prepared fresh each day and its strength was checked by iodometric method[7]. The solution of ruthenium trichloride was prepared by dissolving the sample in very dilute HCl. The final strengths of ruthenium(III) chloride and HCl were kept at 19.2×10^{-3} mol dm^{-3} and 16.4×10^{-2} mol dm^{-3} respectively. The stock solution of ruthenium trichloride was stored in a black coated bottle to prevent photochemical decomposition.

A thermostatic water bath was used to maintain the desired temperature within ± 0.1°C. The reactions were initiated by addition of NBS solution to other reagents, although the order of addition had no effect on the rate. The progress of reaction was followed by determining NBS iodometrically in aliquots withdrawn after suitable time intervals. The iodine liberated by ruthenium(III) was taken into account.

RESULTS AND DISCUSSION

The kinetic investigations were carried out at several initial concentrations of the reactants. The kinetic results of oxidation of ethylamine, diethylamine and triethylamine were similar. The interesting feature of the oxidation of amines by NBS is the effect of NBS on the rate of reaction. The log [NBS] versus time and $[NBS]^{-1}$ versus time plots at various initial NBS concentrations (Fig. 1a and Fig. 1b, taking the case of ethylamine) showed that order of reaction in NBS is one only at very low NBS concentration (Fig. 1a). At higher, initial NBS concentrations a second order dependence of rate with respect to NBS is clearly indicated by $[NBS]^{-1}$ versus time plots (Fig. 1b). Therefore pseudo second rate constants in NBS (k_{obs}) were evaluated from the slopes of the $[NBS]^{-1}$ versus time plots at various initial concentrations of the reactants. Further an increase in the initial

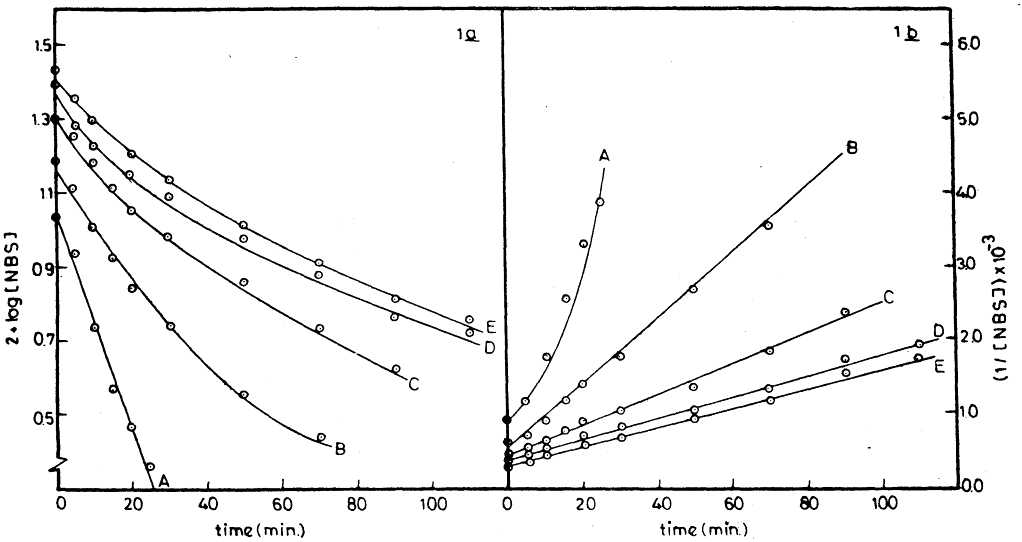


Fig. 1 (a) Pseudo first order plots in NBS at 35°C. (b) Pseudo-second order plots in NBS at 35°C. [Ethylamine] = 2.0×10^{-2} mol dm^{-3}, $[HClO_4]$ = 2.0×10^{-2} mol dm^{-3}, [Ru(III)] = 9.6×10^{-5} mol dm^{-3}, $[Hg(OAc)_2]$ = 2.0×10^{-3} mol dm^{-3} and [NBS] = 1.0, 1.5, 2.0, 2.5 and 3.0×10^{-3} mol dm^{-3} for A, B, C, D and E respectively

NBS concentration *i.e.* $[NBS]_0$ resulted in a decrease (Table 1) in the

TABLE 1
EFFECT OF [NBS] ON THE RATE CONSTANTS AT 35°C

$[NBS] \times 10^3$ mol dm^{-3}	$(k_{obs}) \times 10$ mol^{-1} litre sec^{-1}		
	Ethylamine	Diethylamine	Triethylamine
1.5	5.50	1.04	1.50
2.0	3.45	0.65	0.85
2.5	2.50	0.31	0.52
3.0	2.08	0.21	0.40

$[Amine] = 2.0 \times 10^{-2}$ mol dm^{-3}, $[HClO_4] = 2.0 \times 10^{-2}$ mol dm^{-3}, $[Hg(OAC)_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[Ru(III)] = 9.6 \times 10^{-5}$ mol dm^{-3} for ethylamine and diethylamine and 19.2×10^{-5} mol dm^{-3} for triethylamine.

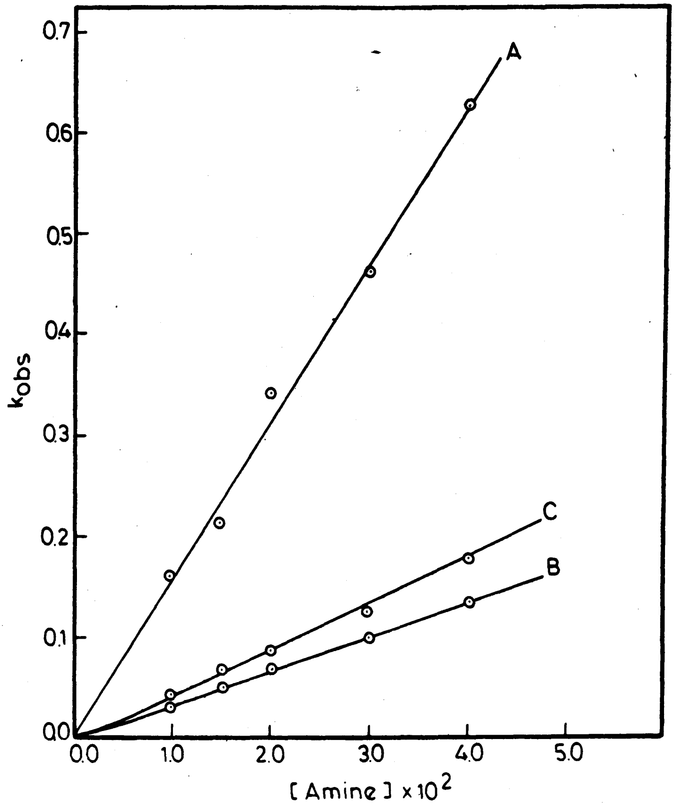


Fig. 2 Plots of k_{obs} versus [Amine] at 35°C. $[HClO_4] = 2.0 \times 10^{-2}$ mol dm^{-3} $[Hg(OAc)_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[Ru(III)]_T = 9.6 \times 10^{-5}$ mol dm^{-3} for A and B and 19.2×10^{-5} mol dm^{-3} for C and $[NBS] = 2.0 \times 10^{-3}$ mol dm^{-3}. A, Ethylamine, B, diethylamine and C, triethylamine

pseudo-second order rate constant (k_{obs}). The plot of k_{obs} versus $1/[NBS]_0$ was also linear in each case.

The plots of k_{obs} versus [Amine] (Fig. 2) and k_{obs} versus $[Ru(III)]_T$ (Fig. 3) were linear passing through the origin suggesting first order

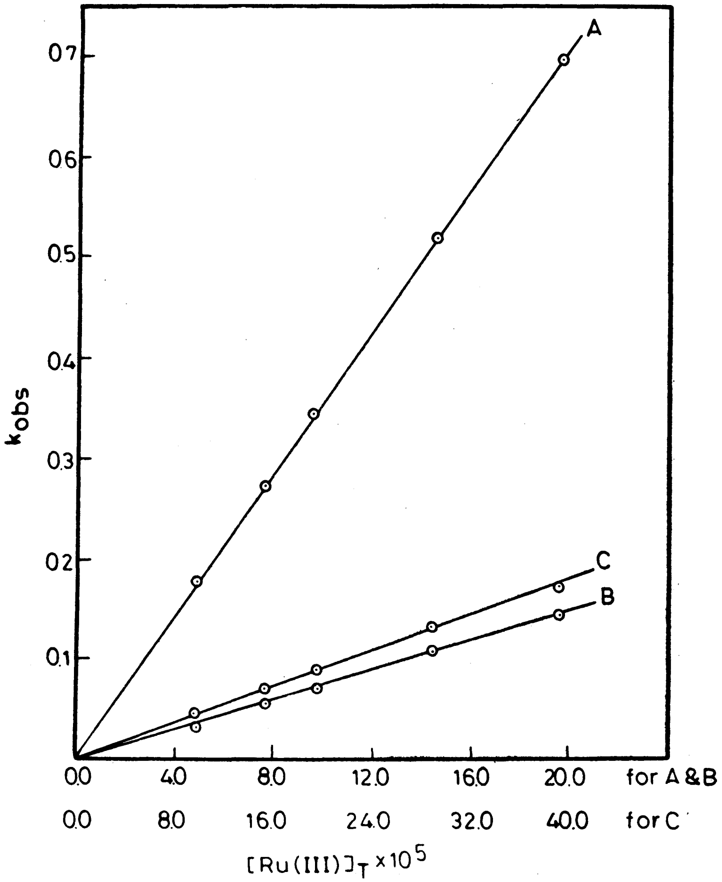


Fig. 3 Plots of k_{obs} versus $[Ru(III)]_T$ at 35°C. [Amine] = 2.0×10^{-3} mol dm^{-3}; other conditions are same as in Fig. 2

dependence of rate with respect to each, the substrate and the catalyst. It is also clear from Fig. 3 that the rate of uncatalysed oxidation of amines under the presented experimental conditions is negligible.

The effect of $[H^+]$ on the reaction rate was studied at a fixed ionic strength ($\mu = 0.04$ mol dm^{-3}) maintained by sodium perchlorate. The amount of acid already present in the catalyst was taken into account. A plot of k_{obs} versus $1/[HClO_4]$ was linear passing through the origin (Fig. 4) in each case suggesting that rate $\propto 1/[H^+]$.

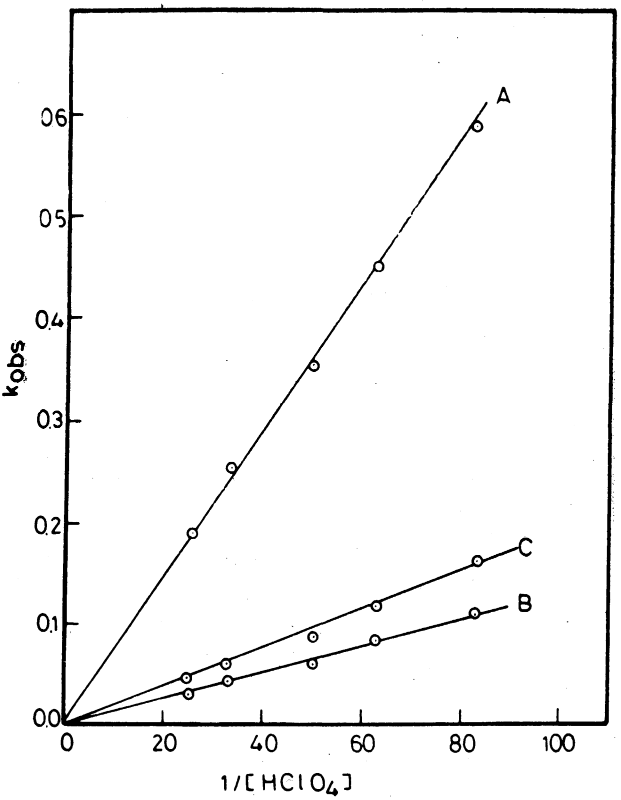


Fig. 4 Plots of k_{obs} versus $1/[HClO_4]$ at 35°C. [Amine] = 2.0×10^{-2} mol dm^{-3}, $\mu = 0.04$ mol dm^{-3} maintained by $NaClO_4$, other conditions are same as in Fig. 2

Successive addition of acetic acid and succinimide (reaction product of NBS) decreased the observed rate constant (Table 2). The plots of $1/k_{obs}$ versus [Succinimide] were linear with intercepts. An insignificant effect of addition of mercuric acetate and sodium perchlorate (ionic strength variation) on the reaction rate was observed in each case. The addition of sodium chloride in the reaction mixture resulted in an increase in the observed rate constant. It was also observed that at high Cl^- concentrations the reactions were no more second order in NBS (order of reaction in NBS changes from 2 to 1 on increasing Cl^- concentrations in the reaction mixture).

The kinetics were also made at different temperatures *viz.* 35, 40, 45, and 50°C, and the values of energy of activation obtained from Arrhenius plot were as 75.0 ± 1.0, 85.0 ± 2.0 and 105.0 ± 2.0 k J mol^{-1} for the oxidation of ethylamine, diethylamine and triethylamine respectively.

In acidic medium NBS is known to exist[3-7] in the following equilibria :

$$>NBr + H^+ \rightleftharpoons >N^+HBr \qquad (1)$$

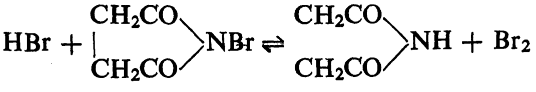
$$>NBr + H^+ \rightleftharpoons >NH + Br^+ \qquad (2)$$

Thus NBS itself, protonated NBS *i.e.* $>N^+HBr$ and Br^+ are the possible reactive species of NBS in acidic media. Insignificant effect of mercuric acetate on the reaction rate rules out its involvement in NBS oxidation and acts as a scavenger (exists as $HgBr_4^{2-}$ or unionised $HgBr_2$) for any Br^- formed in the reaction. The addition of mercuric acetate suppresses completely the oxidation by Br_2 which would have been formed as a result of interaction between NBS and HBr (eq. 3) and ensures that oxidation study is pure NBS oxidation.

TABLE 2
EFFECT OF [SUCCINIMIDE] AND [ACETIC ACID] ON THE RATE CONSTANT AT 35°C

[Succinimide] × 10^3 mol dm^{-3}	[Acetic acid] v/v	(k_{obs}) × 10 mol^{-1} liter sec^{-1}		
		Ethylamine	Diethylamine	Triethylamine
Nil	—	3.45	0.65	0.85
0.5	—	3.12	0.52	0.75
1.0	—	2.70	0.40	0.55
1.5	—	2.08	0.35	0.41
2.0	—	1.94	0.29	0.38
—	5%	2.50	0.63	0.58
—	10%	1.87	0.58	0.42
—	15%	1.66	0.50	0.38
—	20%	1.45	0.45	0.34

[NBS] = 2.0×10^{-3} mol dm^{-3}, [Amine] = 2.0×10^{-2} mol dm^{-3}, [$HClO_4$] = 2.0×10^{-2} mol dm^{-3}, [$Hg(OAc)_2$] = 2.0×10^{-3} mol dm^{-3} and [Ru(III)] = 9.6×10^{-5} mol dm^{-3} for ethyl and diethylamine and 19.2×10^{-5} mol dm^{-3} for triethylamine.



$$HBr + \left|\begin{array}{l} CH_2CO \\ CH_2CO \end{array}\right\rangle NBr \rightleftharpoons \begin{array}{l} CH_2CO \\ CH_2CO \end{array}\rangle NH + Br_2 \qquad (3)$$

A retarding effect of acid (inverse first order) on the rate of reaction ruled out possibility of protonated NBS *i.e.* $>N^+HBr$ protonated amines as the reactive species.

A negligible effect of ionic strength suggests involvement of at least a neutral molecule in the rate determining step. Further retarding effect of acetic acid (+ve dielectric effect) indicate an anion dipole interaction in the rate determining step. Involvement of Br^+ in the rate determining step seems to be unreasonable as its involvement in the rate determining step should give a negative dielectric constant effect. Thus NBS itself seems to be the reactive species under the experimental conditions.

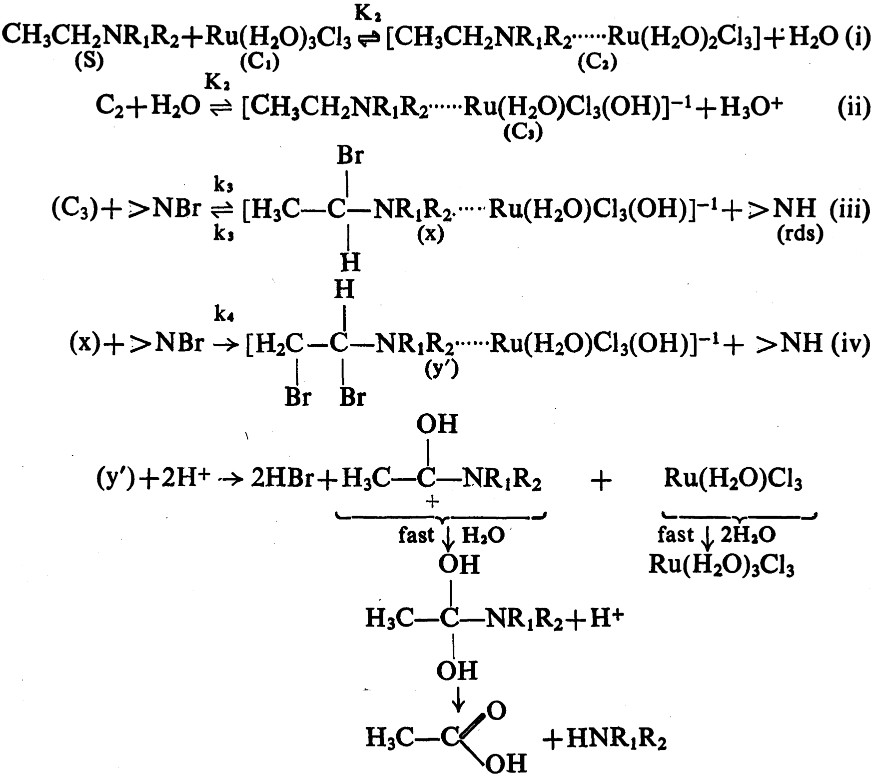
In acidic solutions ruthenium trichloride exists[9] as $[Ru(H_2O)_6]^{3+}$, $[RuCl(H_2O)_5]^{2+}$ and *cis* and *trans* $[RuCl_2(H_2O)_4]^+$. These species have been identified by their electronic spectra. This existence of $RuCl_3$, $RuCl_2^+$ and $RuCl^{++}$ in dilute HCl solution of $RuCl_3$ has also been shown by Connick and Fine[10]. The following equilibrium may be considered between these species.

$$RuCl_3 \rightleftharpoons RuCl_2^+ + Cl^- \qquad (4)$$

$$RuCl_2 \rightleftharpoons RuCl^{++} + Cl^- \qquad (5)$$

A positive effect of Cl^- on the rate of reaction suggests that the neutral species *i.e.* $[Ru(H_2O)_2Cl_3]$ is the reacting species of the catalyst in the present case. The transition metal ion catalyst oxidation of amines by other oxidants[1,2] have shown that the oxidation proceeds via a complex formation between the substrate and the reactive species of the catalyst. On the basis of above facts and experimental results, the mechanism for the oxidation of amines by NBS in presence of ruthenium(III) as catalyst in general may be proposed as given in scheme 1.

SCHEME 1



$$\underset{(S)}{CH_3CH_2NR_1R_2} + \underset{(C_1)}{Ru(H_2O)_3Cl_3} \overset{K_1}{\rightleftharpoons} \underset{(C_2)}{[CH_3CH_2NR_1R_2\cdots\cdots Ru(H_2O)_2Cl_3]} + H_2O \qquad (i)$$

$$C_2 + H_2O \overset{K_2}{\rightleftharpoons} [CH_3CH_2NR_1R_2\cdots\cdots \underset{(C_3)}{Ru(H_2O)Cl_3(OH)}]^{-1} + H_3O^+ \qquad (ii)$$

$$(C_3) + {>}NBr \underset{k_3}{\overset{k_3}{\rightleftharpoons}} [H_3C-\underset{\underset{H}{|}}{\overset{\overset{Br}{|}}{C}}-\underset{(x)}{NR_1R_2}\cdots\cdots Ru(H_2O)Cl_3(OH)]^{-1} + \underset{(rds)}{{>}NH} \qquad (iii)$$

$$(x) + {>}NBr \xrightarrow{k_4} [\underset{\underset{Br}{|}}{H_2C}-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-\underset{(y')}{NR_1R_2}\cdots\cdots Ru(H_2O)Cl_3(OH)]^{-1} + {>}NH \qquad (iv)$$

$$(y') + 2H^+ \rightarrow 2HBr + \underbrace{H_3C-\underset{+}{\overset{\overset{OH}{|}}{C}}-NR_1R_2}_{\text{fast}\downarrow H_2O} + \underbrace{Ru(H_2O)Cl_3}_{\text{fast}\downarrow 2H_2O}$$

$$Ru(H_2O)_3Cl_3$$

$$H_3C-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-NR_1R_2 + H^+$$

$$\downarrow$$

$$H_3C-C\begin{matrix}{\nearrow}O\\ \searrow OH\end{matrix} + HNR_1R_2$$

where R_1 and R_2 represent H in case of ethylamine, H and CH_3CH_2- in case of diethylamine and CH_3CH_2- in case of triethylamine. $>$NH represents succinimide.

An inverse fractional order dependence of rate with respect to $[H^+]$ has also been explained on the basis of the deprotonation equilibrium involving complex between the substrate and $Ru(H_2O)_3Cl_3$. Such reasoning have also been invoked in earlier studies on transition metal ion catalysed reactions[11-13].

The spontaneous conversion of tetrameric ruthenium(III) chloride to polymeric ruthenium(III) chloride in perchloric acid medium is reported[14] in the literature. The mechanism (scheme 1) is also supported by the stoichiometric results which showed that in excess of oxidant (NBS) nearly two moles, four moles and more than four moles of NBS are consumed for each mole of ethylamine, diethylamine and triethylamine respectively. The presence of acetic acid as product was detected by usual spot tests. Acetic acid as the end product of oxidation of amines in absence[15] as well as in presence of catalyst[1-2] is also reported in the literature.

According to the mechanism the rate law equation may be given as:

$$-\frac{d[NBS]}{dt} = k_3[C_3]\,[NBS] - \underline{k}_3[X]\,[>NH] + k_4[X]\,[NBS]$$

$$= 2\,k_4[X]\,[NBS] \tag{6}$$

where [X] is given as

$$[X] = \frac{k_3[C_3]\,[NBS]}{\underline{k}_3[\geqslant NH] + k_4[NBS]} \tag{7}$$

Further the total concentration of the catalyst at any time is given by

$$[Ru(III)]_T = [C_1] + [C_2] + [C_3] \tag{8}$$

where

$[C_2] = K_1[S]\,[C_1]$ from step (i)

and

$[C_3] = K_1K_2[S]\,[C_1]/[H_3O^+]$ from step (i) and (ii)

Thus finding C_3 in terms of $[Ru(III)]_T$ and substituting in equation (7), [X] in terms of $[Ru(III)_T$ is obtained as

$$[X] = \frac{k_3K_1K_2[S]\,[Ru(III]_T\,[NBS]}{\{\underline{k}_3[>NH] + k_4[NBS]\}\,\{[H_3O^+] + K_1[S](K_2 + [H_3O^+])\}} \tag{9}$$

where K_1 and K_2 also include water molecule and, therefore, the rate law equation (6) becomes

$$-\frac{d[NBS]}{dt} = \frac{2k_3k_4K_1K_2[S]\,[Ru(III)]_T\,[NBS]^2}{\{\underline{k}_3[>NH] + k_4[NBS]\}\,\{[H_3O^+] + K_1[S](K_2 + [H_3O^+])\}} \tag{10}$$

By taking $[H_3O^+] \gg K_2$ and $1 \gg K_1[S]$ assuitable approximation, the rate law equation is reduced to

$$-\frac{d[NBS]}{dt} = \frac{2k_3k_4K_1K_2[S]\,[Ru(III)]_T\,[NBS]^2}{\{k_3[>NH] + k_4(NBS]\}\,[H_3O^+]}$$

which explain all the experimental results *i.e.* first order dependence of rate with respect to both substrate and catalyst, an inverse first order dependence of rate with respect to acid, second order dependence of rate with respect to NBS during a particular kinetic run and a retarding effect of succinimide.

Further by taking $k_3 \approx k_4$, the rate law equation (11) converts to

$$-\frac{d[NBS]}{dt} = \frac{2k_3K_1K_2[S]\,[Ru(III)]_T\,[NBS]^2}{[NBS]_0\,[H_3O^+]} \qquad (12)$$

where $[NBS]_0 = [NBS] + [>NH]$ at any time.

The rate law equation (12) is in agreement with the experimental results i.e. rate $\propto 1/[NBS]_0$.

At very low concentrations of NBS (in comparison to substrate), it seems that intermediate (X) formed in step (iii) of the mechanism reacts with H^+ to give the products, which will result in a first order dependence of rate with respect to NBS.

The nature of reactive species of ruthenium(III) chloride in acidic medium depends upon the variation of $[Cl^-]$ on the reaction rate. In high concentrations of Cl^-, ruthenium(III) chloride is exists[7] as $[RuCl_6]^{3-}$. Therefore it is likely that in presence of Cl^- the mechanism of the oxidadation process may be different.

The order of reactivity in the present case is

ethylamine > diethylamine > triethylamine.

ACKNOWLEDGEMENT

The authors wish to thank Prof. A. K, Vasishtha, Director and Prof. R. S. Tewari, Head, Chemistry Deptt., HBTI, Kanpur for their keen interest in the work.

REFERENCES

1. (a) S. K. Upadhyay and M. C. Agarwal, *Indian J. Chem.*, **18A**, 34 (1975); (b) A. K. Awasthi, B. S. Rawat and S. K. Upadhyay, *Indian J. Chem.*, **24A**, 109 (1985).
2. Sushma Gupta, Vazid Ali and S. K. Upadhyay, *Int. J. Chem. Kinetics*, **21**, 315 (1989).
3. M. Venkatsubramanian and V. Thiagarajan, *Tetrahedron Lett.*, **35**, 3349; (1967) *Canad. J. Chem.*, **47**, 694 (1969).
4. J. P. Sharma, R. N. P. Singh, A. K. Singh and Bharat Singh, *Tetrahedron*, **42**, 2739 (1986).
5. P. S. Radhakrishnamurti and S. C. Pati, *J. Indian Chem. Soc.*, **66**, 847 (1969).
6. K. Singh, J. N. Tewari and S. P. Mushran, *Int. J. Chem. Kinetics*, **10**, 995 (1978).

7. Bharat Singh, L. Pandey, J. P. Sharma and S. M. Pandey, *Tetrahedron*, **38**, 169 (1982).

8. M. Z. Barakat and M. F. Wahab Abdel, *Anal. Chem.*, **26**, 1973 (1954).

9. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd Edition, Wiley Eastern Ltd., New Delhi, p. 1007 (1984).

10. R. E. Connick and D. A. Fine. *J. Am. Chem. Soc.*, **83**, 3114 (1961).

11. N. Okada, T. Noma, Y. Katsuyama and H. Hashimoto. *Bull. Chem. Soc. Japan*, **41**, 1395 (1968).

12. P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964).

13. H. P. Panda and B. D. Sahu, *Indian J. Chem.*, **28A**, 323 (1989).

14. R. M. Vallace and R. C. Propst, *J. Am. Chem. Soc.*, **91**, 3779 (1969).

15. G. Galliani and B. Rindone; *Nouv. J. Chem.*, **7**, 639 (1983).

[*Received*: 14 July 1990; *Accepted*: 22 March 1991] AJC–275