

Kinetics and mechanism of ruthenium(III) catalysed oxidation of aminoalcohols by N-bromosuccinimide in perchloric acid medium

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The kinetics of ruthenium(III) catalysed oxidation of aminoalcohols (primary, secondary and tertiary) by N-bromosuccinimide (NBS) have been investigated in perchloric acid medium. A first order dependence of rate in [NBS] in case of primary aminoalcohols and a second order dependence of rate in [NBS] in case of secondary/tertiary aminoalcohols have been observed. The order in [substrate] is zero in the case of primary aminoalcohols. The order reduces from unity at lowest [substrate] to zero at higher concentrations in the case of secondary and tertiary aminoalcohols. Retarding effect of acid on the rate of reaction has also been observed in the case of diethanol and triethanolamine. The rate of reaction is proportional to [Ru(III)] and $\{k' + k''[\text{Ru(III)}]\}$ in case of primary and secondary/tertiary aminoalcohols respectively (k' and k'' are rate constants for uncatalysed and catalysed paths respectively). A suitable mechanism is proposed in each case and discussed.

Kinetic studies on the oxidation of aminoalcohols^{1,2} with oxidants like hexacyanoferrate(III), cerium(IV), chloramine-T, etc. in the presence and absence of transition metal ions, have shown that the reactions follow a complex kinetics. Oxidation of aminoalcohols by N-bromosuccinimide (NBS) has not received much attention and the present communication incorporates the results of the title investigation.

Materials and Methods

The reagents, viz. 2-aminoethanol, 3-aminopropanol, diethanolamine, triethanolamine, ruthenium trichloride (Johnson Matthey) and N-bromosuccinimide were of AR grade. All solutions were prepared in doubly distilled water.

Solution of NBS was always prepared fresh. Ruthenium trichloride solution was prepared in dilute HCl and stored in the dark. The final strength of ruthenium(III) chloride and HCl were kept at $19.2 \times 10^{-3} \text{ mol dm}^{-3}$ and $16.4 \times 10^{-2} \text{ mol dm}^{-3}$ respectively.

The reaction was initiated by addition of NBS solution to a mixture of other reactants. Before addition all solutions/mixtures were equilibrated at the desired temperature ($\pm 0.1^\circ\text{C}$). The progress of reaction was followed by determining NBS iodometrically in aliquots withdrawn after regular time intervals. The iodine liberated by ruthenium(III) was taken into consideration.

Stoichiometry

The reaction mixtures containing a known excess of [NBS] over [aminoalcohol] were kept in the pres-

ence of perchloric acid, mercuric acetate and ruthenium(III) at 35°C for 72 hrs. Estimation of unreacted NBS showed that one mole of ethanolamine, diethanolamine and triethanolamine consumed one, two and three moles of NBS to give formaldehyde, succinimide, ammonia and HBr (quantitative estimation of HCHO has not been made).

The presence of aldehyde and succinimide as the products was detected by usual spot-test³. The presence of formaldehyde was further confirmed by converting it into 2,4-dinitrophenylhydrazone and comparing it with an authentic sample (mmp and Co-TLC). In the case of 3-aminopropanol both formaldehyde and acetaldehyde were observed as end products.

Results

The $\log(a-x)$ versus time plots were linear in the case of primary alcohols and pseudo-first order rate constants (k_1) were evaluated from the slopes of these plots. The observed rate constants (k_1) remained nearly identical at several initial [NBS] (Table 1) which further confirmed first order dependence in [NBS].

The effect of varying $[\text{H}^+]$ on the reaction rate was studied at a fixed ionic strength ($\mu = 0.04 \text{ mol dm}^{-3}$) maintained by the addition of sodium perchlorate. The amount of acid already present in the catalyst was taken into account. It is clear from the data in Table 1 that the effect of varying $[\text{HClO}_4]$ or [substrate] on the rate was negligible in the case of primary aminoalcohols.

Table 1—Effect of [reactants] on the rate constant at 35°C

$[\text{Ru(III)}] = 9.63 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{Hg(OAc)}_2] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ Effect of $[\text{H}^+]$ was studied at a fixed ionic strength (0.04 mol dm^{-3} maintained by NaClO_4)

[NBS] $\times 10^3$ (mol dm^{-3})	[Substrate] $\times 10^2$ (mol dm^{-3})	[H ⁺] $\times 10^2$ (mol dm^{-3})	$k_1 \times 10^4 \text{ (s}^{-1}\text{)}$		$k_2 \text{ (mol}^{-1} \text{ dm}^3 \text{ sec}^{-1}\text{)}$	
			2-Aminoethanol	3-Aminopropanol	Diethanolamine	Triethanolamine
1.2	2.0	2.0	11.9	6.0	3.31	2.22
2.0	2.0	2.0	11.9	5.7	1.62	1.12
2.4	2.0	2.0	11.7	5.7	1.20	0.71
2.8	2.0	2.0	11.5	5.3	0.90	0.53
2.0	1.2	2.0	12.9	6.0	0.90	0.60
2.0	1.6	2.0	11.7	5.7	1.31	0.81
2.0	2.0	2.0	11.4	6.0	1.62	1.12
2.0	3.0	2.0	11.6	6.4	2.52	1.53
2.0	4.0	2.0	11.6	—	3.23	1.69
2.0	2.0	1.2	11.5	5.6	2.11	1.51
2.0	2.0	1.6	12.1	5.7	1.90	1.34
2.0	2.0	2.0	11.9	5.7	1.63	1.12
2.0	2.0	3.0	11.7	5.4	1.01	0.63
2.0	2.0	4.0	11.9	5.9	0.72	0.43

The plots of k_1 versus $[\text{Ru(III)}]_T$ were linear passing through the origin (Fig. 1A and B) suggesting first order dependence of rate in [ruthenium(III) chloride] and that the rate of uncatalysed oxidation of primary aminoalcohols is negligible.

The kinetics of oxidation of secondary aminoalcohol (diethanolamine) and tertiary aminoalcohol (triethanolamine) were similar but different from those of oxidation of primary aminoalcohols. The $\log(a-x)$ versus time plots were not linear. However, $[\text{NBS}]^{-1}$ versus time plots were linear with an intercept, suggesting a second order dependence of rate in [NBS]. In the case of diethanolamine and triethanolamine, therefore, the pseudo-second order rate constants (k_2) were evaluated from the plots of $[\text{NBS}]^{-1}$ versus time at various initial [reactant] (Table 1). However, with increase in initial [NBS] k_2 decreased and the plot of k_2 versus $1/[\text{NBS}]_0$ was linear.

The plots of k_2 versus [substrate] showed a deviation from linearity while the plots of $1/k_2$ versus $1/[\text{substrate}]$ were linear with intercepts.

The plots of k_2 versus $[\text{Ru(III)}]_T$ were linear with intercept (Fig. 1C and D) suggesting that the oxidations of diethanolamine and triethanolamine also proceed in absence of the catalyst. The second order plots in the absence of the catalyst were also linear.

Increase in $[\text{HClO}_4]$ at a fixed ionic strength ($= 0.04 \text{ mol dm}^{-3}$) in the reaction decreased k_2 in the case of diethanolamine and triethanolamine

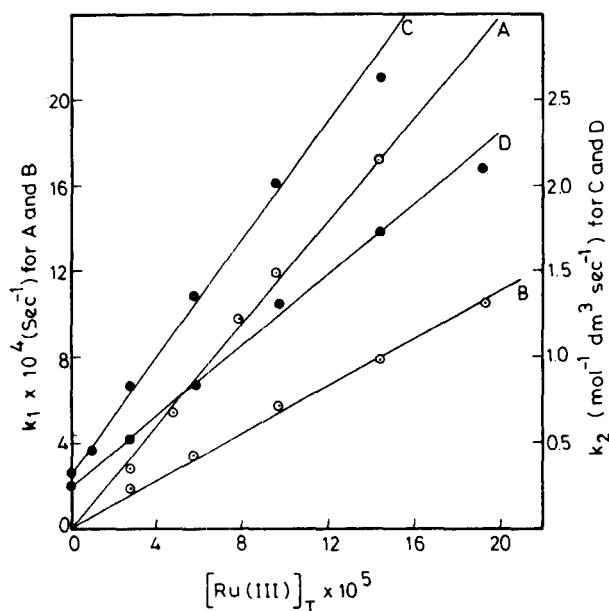


Fig. 1—Plots of k_{obs} versus $[\text{Ru(III)}]_T$ at 35°C ($[\text{NBS}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{S}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$, A, 2-aminoethanol, B, 3-aminopropanol; C, diethanolamine and D, triethanolamine)

(Table 1). The retarding effect of acid was more significant at higher [acid].

The effect of added mercuric acetate and sodium perchlorate (ionic strength variation) on the rate constants was negligible in each case. Successive addition of acetic acid and succinimide (reaction product of NBS) decreased the observed rate constants,

Table 2—Effect of addition of succinimide, acetic acid and chloride ions on rate constants at 35°C

[NBS] = 2.0×10^{-3} mol dm⁻³, [S] = 2.0×10^{-2} mol dm⁻³, [H⁺] = 2.0×10^{-2} mol dm⁻³ [Ru(III)] = 9.63×10^{-5} mol dm⁻⁵
and [Hg(OAc)₂] = 2.0×10^{-3} mol dm⁻³

[Succinimide] × 10 ³ (mol dm ⁻³)	[Acetic acid] % v/v	[NaCl] × 10 ³ (mol dm ⁻³)	$k_1 \times 10^4$ (s ⁻¹)		k_2 (mol ⁻¹ dm ³ s ⁻¹)	
			2-Aminoethanol	3-Aminopropanol	Diethanolamine	Triethanolamine
Nil	—	—	11.9	5.7	1.62	1.12
1.0	—	—	10.5	5.0	0.83	0.63
2.0	—	—	10.0	4.6	0.62	0.45
3.0	—	—	8.3	3.9	0.50	0.32
4.0	—	—	7.2	3.5	0.40	0.25
—	Nil	—	11.9	5.7	1.62	1.12
—	10	—	8.5	5.1	1.03	0.70
—	20	—	7.7	4.6	0.82	0.51
—	30	—	6.9	4.0	0.60	0.39
—	—	Nil	11.9	5.7	1.62	1.12
—	—	2.0	—	6.1	3.33	2.01
—	—	4.0	12.5	—	4.72	3.22
—	—	5.0	15.0	8.7	6.43	4.21

while addition of sodium chloride increased the rate constant (Table 2).

Discussion

In acidic media NBS, protonated NBS (i.e. $>N^+HBr$) and Br^+ are the possible reactive species of NBS. Added mercuric acetate acts as a scavenger for any Br^- formed in the reaction and its insignificant effect on reaction rate rules out its involvement in NBS oxidation. Increase in $[H^+]$ either retarded the reaction or has negligible effect ruling out the possibility of $>N^+HBr$ as the reactive species.

Negligible ionic strength effect suggests involvement of at least a neutral molecule in the rate-determining step. Further rate retardation by added acetic acid (+ve dielectric effect) indicates anion-dipole interaction or dipole-dipole interaction in the rate-determining step. Involvement of Br^+ in the rate-determining step also 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 exists⁴ as $[Ru(H_2O)_6]^{3+}$, $[RuCl(H_2O)_5]^{2+}$ and *cis* and *trans* $[RuCl_2(H_2O)_4]^+$. The existence of $RuCl_3$, $RuCl_2^+$ and $RuCl^{2+}$ in dilute HCl solution of $RuCl_3$ has also been shown by Connick and Fine⁵. A positive effect of Cl^- on the rate of reaction clearly suggests that the neutral species i.e. $[Ru(H_2O)_3Cl_3]$ is the reactive catalyst species. The presence of Michaelis-Menton reciprocal relationship⁶ in the case of diethanolamine and triethanolamine suggests a complex for-

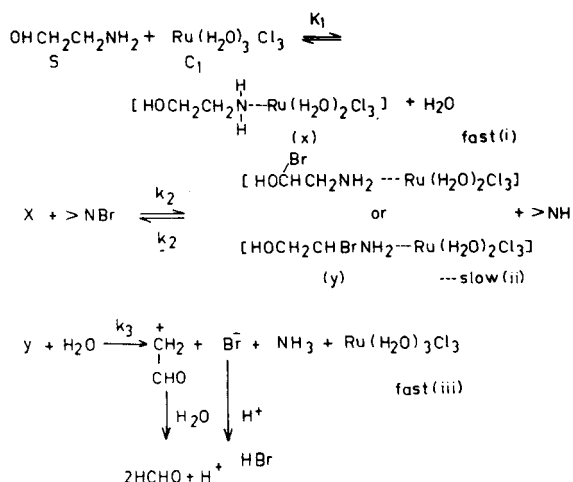
mation between the substrate and the catalyst, in conformity with the earlier observation of complex formation between ruthenium(III) and aminoalcohols.

On the basis of above facts and experimental results the mechanism for the oxidation of primary aminoalcohols (taking case of 2-aminoethanol) by NBS may be proposed as given in Scheme 1.

Scheme 1 leads to rate law (1)

$$-\frac{d[NBS]}{dt} = \frac{K_1 k_2 k_3 [S] [Ru(III)]_T [NBS]}{\{1 + K_1 [S]\} \{k_3 + k_{-2} [>NH]\}} \quad \dots (1)$$

Since step (1) is a fast step, $K_1 [S] \gg 1$ may be taken as a suitable approximation (in case of primary aminoalcohols) and therefore Eq. (1) reduces to Eq. (2)



Scheme 1

$$-\frac{d[\text{NBS}]}{dt} = \frac{k_2 k_3 [\text{Ru(III)}]_{\text{T}} [\text{NBS}]}{\{k_3 + k_{-2} [> \text{NH}]\}} \dots (2)$$

Rate law (2) explains all the experimental results in the case of primary aminoalcohols. According to rate law (2) the plot of 1/(rate constant) versus [succinimide] should be linear with an intercept which has also been observed experimentally.

The inverse fractional order dependence in $[\text{H}^+]$ in the case of diethanolamine and triethanolamine can be explained on the basis of the deprotonation equilibrium involving the complex between the substrate and $\text{Ru}(\text{H}_2\text{O})_3\text{Cl}_3$. Such reasoning has also been invoked in earlier studies⁷⁻⁹. Thus the mechanism of oxidation of diethanolamine may be proposed as given in Scheme 2. However, Y' species in the case of triethanolamine may further react with another molecule of $> \text{NBr}$ to give products in a fast step.

The proposed mechanism (Scheme 2) also explains the observed 1:2 and 1:3 stoichiometry be-

tween substrate and NBS in the case of diethanolamine and triethanolamine respectively.

Scheme 2 leads to rate law (3) for the oxidation of diethanolamine and triethanolamine.

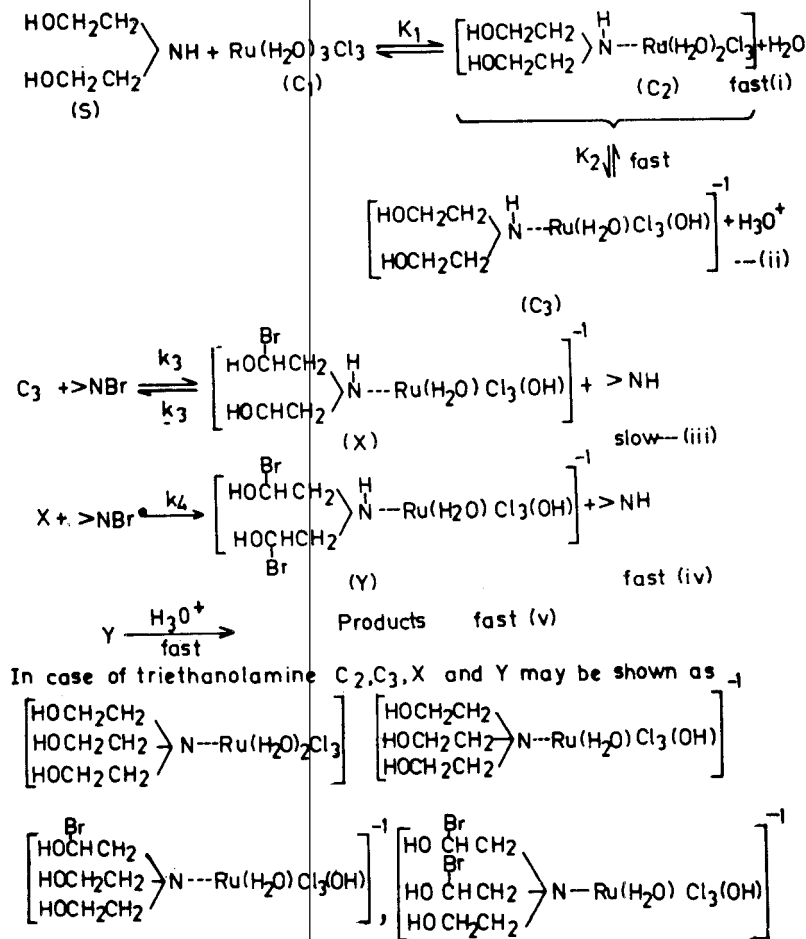
$$-\frac{d[\text{NBS}]}{dt} = \frac{n k_3 k_4 K_1 K_2 [\text{Ru(III)}]_{\text{T}} [\text{S}] [\text{NBS}]^2}{\{k_3 [> \text{NH}] + k_4 [\text{NBS}]\} \{ (1 + K_1 [\text{S}]) [\text{H}_3\text{O}^+] + K_1 K_2 [\text{S}] \}} \dots (3)$$

where $n=2$ and 3 respectively for diethanolamine and triethanolamine, K_1 and K_2 also involve the water molecule.

Further, assuming $k_3 \approx k_4$, rate law (3) becomes

$$-\frac{d[\text{NBS}]}{dt} = \frac{n k_3 K_1 K_2 [\text{Ru(III)}]_{\text{T}} [\text{S}] [\text{NBS}]^2}{[\text{NBS}]_0 \{ (1 + K_1 [\text{S}]) [\text{H}_3\text{O}^+] + K_1 K_2 [\text{S}] \}} \dots (4)$$

where $[\text{NBS}]_0 = [> \text{NH}] + [\text{NBS}]$ at any time.



Scheme 2

The experimental results in the case of diethanolamine and triethanolamine, i.e. linearity (with an intercept) of the plot of $1/(\text{rate constant})$ versus $1/[S]$, linearity of plot of rate constant versus $1/[NBS]_0$, second order dependence of rate in $[NBS]_0$, the linearity of the plot of $1/(\text{rate constant})$ versus $[>NH]$ and retarding effect of acid on the reaction rate are in agreement with the rate laws (3) and (4). The above rate laws do not reflect the intercept obtained in the plot of k_2 versus $[Ru(III)]_T$, because the steps responsible for uncatalysed oxidation of diethanolamine and triethanolamine are not included in the mechanism.

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