Ru(III) catalysed oxidation of diethanolamine and triethanolamine by Br(V) in presence of perchloric acid

Ashok Kumar Singh*, Ajaya Kumar Singh[a], Vineeta Singh, Shahla Rahmani, Ashish and Bharat Singh

Department of Chemistry, University of Allahabad, Allahabad, India

[a]Department of Chemistry, Govt. College, Utai, Durg, Chhattishgarh, India

Kinetics and mechanism of oxidation of diethanolamine (DEA) and triethanolamine (TEA) by potassium bromate in presence of ruthenium(III) chloride as homogeneous catalyst in perchloric acid medium have been investigated. First order kinetics with respect to each of [KBrO$_3$] and [Ru(III) chloride] was observed in the oxidation of both DEA and TEA. With about eight-fold variation in [DEA] and 10-fold variation in [TEA], first order kinetics in [substrate] was observed up to nearly 3-fold variation in [DEA] and 5-fold variation in [TEA]. Kinetics with negative effect of [substrate] became more complex in both cases when a significant decrease in pseudo first order rate constant was observed at their higher concentrations. Inverse fractional order in [H$^+$] was noted throughout its 10-fold variation. Variation in [Hg(OAc)$_2$], [Cl$^-$] and ionic strength (μ) of the medium did not bring about any significant change on the rate of reaction. The values of rate constants observed at four different temperatures were utilised to calculate the activation parameters. Acetic acid and ammonia have been identified as main oxidation products of the reactions. A suitable mechanism involving the formation of a complex between [Ru(III)–aminoalcohol] complex and bromate ion prior to the rate-determining step is proposed.

Potassium bromate [Br(V)] is a powerful oxidising agent with redox potential[1] 1.44V which has been used in the oxidation of many organic substrates.[2,3] Although potassium bromate is a powerful oxidising agent in acidic medium, it was used also as a source of bromine in the presence of Br$^-$ ion. In the study of bromate oxidation, since the product Br$^-$ ion formed in the reaction reacts with Br(V) to generate bromine which, on accumulation, oxidises the substrate and thus sets parallel Br$_2$ oxidation, hence in order to eliminate the parallel bromine oxidation (to ensure pure bromate oxidation) which is much faster than the oxidation by bromate ion, the product bromide ion has been scavenged by mercuric acetate.[4-6a] The use of transition metal ions such as Os(VIII), Ru(III), Ru(VIII), Ir(III) and Pd(II) as homogeneous catalysts in the oxidation of several organic compounds by various oxidants is of recent greater interest. The mechanism of the reaction depends upon the nature of the substrate and oxidant as well as upon the ways in which transition metal complex ions play their role in order to promote the reactant molecules to the activated state before finally changing into products under experimental conditions. DEA and TEA are widely used in a number of personal care industrial products such as cosmetics and pharmaceuticals. Since reports on a potassium bromate oxidation of organic compounds with special reference to transition metal complex ions as homogeneous catalyst are scanty, hence in order to probe reactive species of potassium bromate and to arrive at a definite conclusion about the participation of transition metal complex ion in the activated state, the present study, which includes Ru(III) catalysed oxidation of DEA and TEA by acidic solution of potassium bromate, has been undertaken.

Experimental

The reagents employed were DEA (BDH), TEA (BDH), Ru(III) chloride (Loba chemicals Ltd.) and potassium bromate (E. Merck) and all other reagents used were A.R. Grade. All the solutions were prepared in doubly-distilled water.
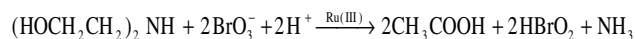
The stock solution of ruthenium(III) chloride was prepared in a dilute solution of hydrochloric acid and was stored in a black coated bottle to prevent photochemical decomposition. The solution of KBrO$_3$ was prepared by dissolving directly the desired weighed amount in double-distilled water and standardised iodometrically. The reaction vessels were also coated on the outside with black varnish to avoid any photochemical effect. Sodium perchlorate and perchloric acid solutions were used to maintain the required ionic strength and [H$^+$], respectively.
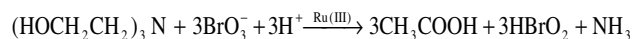
Appropriate volumes of solutions of all the reactants were taken in the reaction vessel which was placed in a thermostatic water bath to maintain the desired temperature (± 0.1°C). The reaction mixture was allowed to attain the temperature of the bath. The reaction was initiated by adding the requisite volume of KBrO$_3$ solution, placed separately in the same bath, to the reaction vessel. The reaction was monitored by iodometric determination of unconsumed amount of KBrO$_3$ up to two half lives under pseudo first-order conditions in which concentration of the substrate was taken in large excess over the concentration of potassium bromate.

Stoichiometry and product analysis

Varying [KBrO$_3$]: [substrate] ratios were equilibrated at 40°C for 72 h with experimental conditions [KBrO$_3$] >> [substrate]. Estimation of unconsumed [KBrO$_3$] in different sets shows that 2 and 3 moles of KBrO$_3$ were consumed by one mole of each of DEA and TEA, respectively. Accordingly, the following stoichiometric equations can be formulated

$$(\text{HOCH}_2\text{CH}_2)_2\,\text{NH} + 2\text{BrO}_3^- + 2\text{H}^+ \xrightarrow{\text{Ru(III)}} 2\text{CH}_3\text{COOH} + 2\text{HBrO}_2 + \text{NH}_3$$

(DEA)

$$(\text{HOCH}_2\text{CH}_2)_3\,\text{N} + 3\text{BrO}_3^- + 3\text{H}^+ \xrightarrow{\text{Ru(III)}} 3\text{CH}_3\text{COOH} + 3\text{HBrO}_2 + \text{NH}_3$$

(TEA)

Acetic acid and ammonia were identified as the main oxidation products in the oxidation of both amino alcohols. TLC[6b] using n-butanol-dimethylamine-water in the ratio of 85:1:14 as the developing solvent was used to verify the presence of acetic acid as product in the oxidation of both DEA and TEA. The R_F value was found to be 0.44 which is very close to the reported R_F value, 0.45 for acetic acid in the aforesaid solvent system. On the basis of equivalence and kinetic studies as well as TLC experiment performed for the confirmation of acetic acid, it is concluded that NH$_3$ is the other oxidation product in the oxidation of both DEA and TEA.

* Correspondent. E-mail: ashokeks@rediffmail.com

Results and discussion

Oxidation kinetics of DEA and TEA by potassium bromate has been investigated in the presence of acidic solution of ruthenium(III) chloride at different concentrations of reactants. The rate *i.e.* $(-dc/dt)$ in each kinetic run was calculated by the slope of the tangent drawn at fixed concentration of potassium bromate which is written as $[KBrO_3]^*$. The first order velocity constant (k_1) was calculated as $k_1 = (-dc/dt)/[KBrO_3]^*$.

Uniform first order rate constant throughout the variation of $[BrO_3^-]$ indicates that the reaction is first order with respect to bromate ion concentration (Table 1, Figure 1). In order to study the effect of substrate concentration on the rate of reaction, the reactions have been studied with 8-fold variation in [DEA] and 10-fold variation in [TEA] at constant concentration of all other reactants and at constant temperature, 35°C. First order kinetics in [substrate] was observed up to nearly 3-fold variation in [DEA] and 5-fold variation in [TEA]. A significant decrease in pseudo-first order rate constant was observed at higher concentrations of both DEA and TEA (Table 2). Figure 2 shows the plots between pseudo-first order rate constant (k_1) and [substrate] along with mathematical fits joining the data for the oxidation of both DEA and TEA. Figure 2 also contains the mathematical equations corresponding to the polynomal fits of DEA and TEA. Linear proportionality between (k_1) and [Ru(III)] was observed throughout the variation of [Ru(III)] in both aminoalcohols (Table 3, Fig. 3). The rate of reaction, which decreases with increase in [H+], shows a small change at higher concentration of H+ ions in oxidation of both amino alcohols (Table 4, Fig. 4). Variation of $[Hg(OAc)_2]$, [Cl−] and ionic strength of the medium (affected by variation of concentration of sodium perchlorate) did not bring about any significant change in k_1 values under the constant experimental conditions. The reactions were also studied at 30°, 35°, 40° and 45°C (Table 5) and with the help of the rate constant k_r, the energy of activation

and other activation parameters were calculated for the oxidation of both aminoalcohols. The following two forms (α) and (β) of the rate law, valid for the conditions under which temperature dependence has been measured, were used to calculate the activation parameters in the oxidation of DEA and TEA respectively.

$$\frac{-d[BrO_3^-]}{dt} = k_r[BrO_3^-][DEA][Ru(III)]_T[H^+]^{-0.74} \qquad (\alpha)$$

$$\frac{-d[BrO_3^-]}{dt} = k_r[BrO_3^-][TEA][Ru(III)]_T[H^+]^{-0.34} \qquad (\beta)$$

Fig. 1 Plot between $(-dc/dt)$ and $[KBrO_3]$ for both DEA and TEA under the conditions of Table 1.

Fig. 2 Plot between k_1 and [substrate] for both DEA and TEA under the conditions of Table 2.

Table 1 Effect of variation of $[KBrO_3]$ on the rate constant at 35°C

$[KBrO_3] \times 10^4$ mol dm⁻³	$k_1 \times 10^4$ s⁻¹	
	DEA[a]	TEA[b]
2.00	4.05	1.67
4.00	4.19	1.63
6.00	4.11	1.74
8.00	3.87	1.99
10.00	4.16	1.83
12.00	4.36	–
14.00	–	1.77
16.00	3.98	1.73

Under the condition of [a][DEA]= 1.0×10^{-2} mol dm⁻³, [H+] = 1.0×10^{-2} mol dm⁻³, [Ru(III)]= 4.58×10^{-5} mol dm⁻³, $[Hg(OAc)_2]$= 4.0×10^{-3} mol dm⁻³, μ=0.02 mol dm⁻³. [b][TEA] = 5.0×10^{-2} mol dm⁻³, [H+]= 4.80×10^{-1} mol dm⁻³, [Ru(III)]=2.30×10^{-5} mol dm⁻³, $[Hg(OAc)_2]$ = 4.96×10^{-3} mol dm⁻³, μ = 0.51 mol dm⁻³.

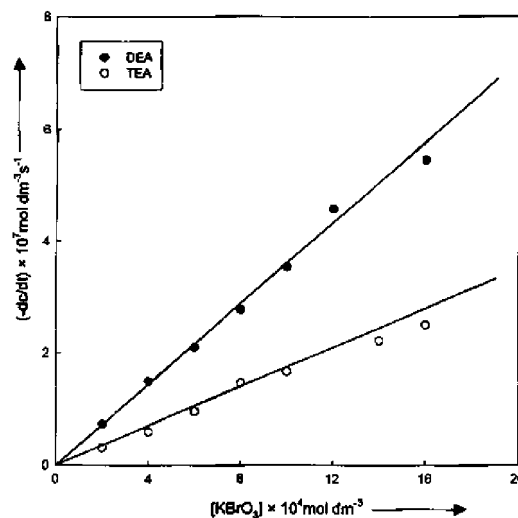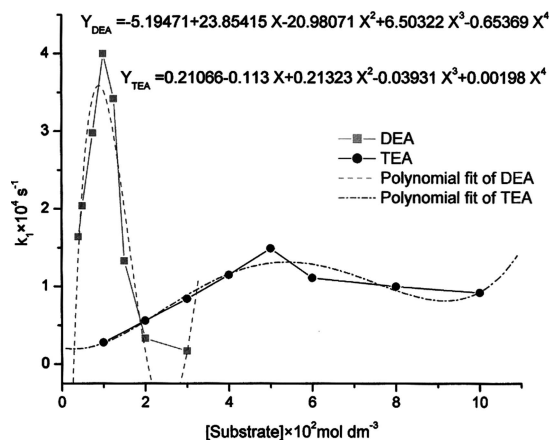**Table 2** Effect of variation of [substrate] on the rate constant at 35°C

$[DEA]^a \times 10^2$ mol dm⁻³	$k_1 \times 10^4$ s⁻¹		$[TEA]^b \times 10^2$ mol dm⁻³	$k_1 \times 10^4$ s⁻¹	
	Observed	Predicted		Observed	Predicted
0.40	1.64	1.56	1.00	0.28	0.28
0.50	2.04	1.95	2.00	0.56	0.56
0.75	2.98	2.90	3.00	0.84	0.84
1.00	4.00	3.85	4.00	1.15	1.11
1.25	3.42	–	5.00	1.49	1.39
1.50	1.33	–	6.00	1.11	–
2.00	0.33	–	8.00	1.00	–
3.00	0.17	–	10.00	0.92	–

Under the condition of [a][KBrO_3]= 10.0×10^{-4} mol dm⁻³, [H+] = 1.0×10^{-2} mol dm⁻³, [Ru(III)]= 4.58×10^{-5} mol dm⁻³, $[Hg(OAc)_2]$= 1.60×10^{-3} mol dm⁻³. [b][KBrO_3]= 10.0×10^{-4} mol dm⁻³, [H+]= 4.80×10^{-1} mol dm⁻³, [Ru(III)]=19.13×10^{-6} mol dm⁻³, $[Hg(OAc)_2]$= 4.96×10^{-3} mol dm⁻³.

Table 3 Effect of variation of [Ru(III)chloride] on the rate constant at 35°C

[DEA][a]			[TEA][b]		
[Ru(III)] × 10⁵ mol dm⁻³	$k_1 × 10^4$ s⁻¹		[Ru(III)] × 10⁵ mol dm⁻³	$k_1 × 10^4$ s⁻¹	
	Observed	Predicted		Observed	Predicted
1.53	0.63	0.62	0.38	0.28	0.27
2.28	0.92	0.94	0.77	0.56	0.55
3.06	1.19	1.27	1.15	0.87	0.83
3.82	1.62	1.61	1.53	0.99	1.11
4.58	2.03	1.94	2.30	1.81	1.68
6.10	2.41	2.60	3.83	2.88	2.82
9.15	4.00	4.00	4.59	3.44	3.40

Under the condition of [a][KBrO₃]= 10.0 × 10⁻⁴mol dm⁻³, [H⁺] = 1.0 × 10⁻² mol dm⁻³, [DEA]= 0.50 × 10⁻²mol dm⁻³, [Hg(OAc)₂]= 1.60 × 10⁻³mol dm⁻³. [b][KBrO₃]= 10.0 × 10⁻⁴mol dm⁻³, [H⁺]= 4.80 × 10⁻¹mol dm⁻³, [TEA]=5.0 × 10⁻² mol dm⁻³, [Hg(OAc)₂]= 4.96 × 10⁻³ mol dm⁻³.
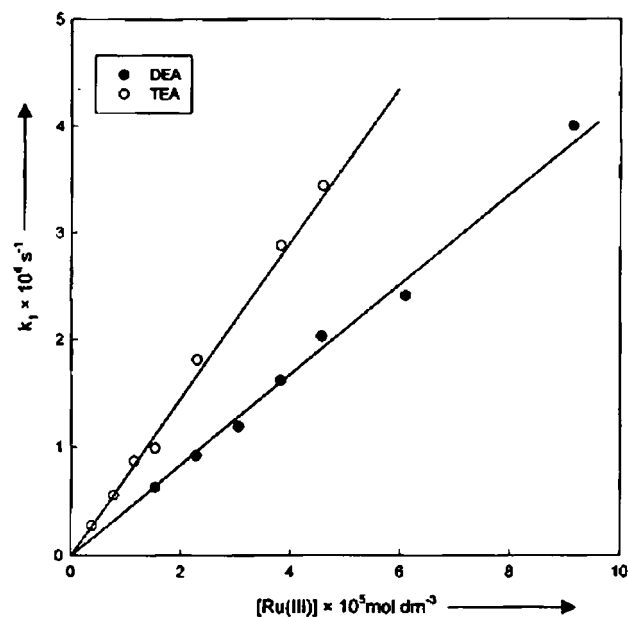
Fig. 3 Plot between k_1 and [Ru(III)] for both DEA and TEA under the conditions of Table 3.
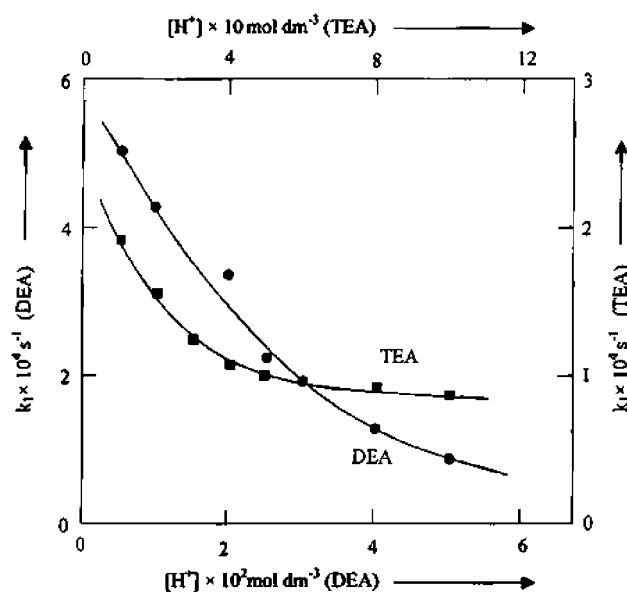
Fig. 4 Plot between k_1 and [H⁺] for both DEA and TEA under the conditions of Table 4.

Table 4 Effect of variation of [H⁺] on rate constant at 35°C

[DEA][a]			[TEA][b]		
[H⁺] × 10² mol dm⁻³	$k_1 × 10^4$ s⁻¹		[H⁺] × 10² mol dm⁻³	$k_1 × 10^4$ s⁻¹	
	Observed	Predicted		Observed	Predicted
0.50	4.95	6.40	1.00	1.92	1.91
1.00	4.18	3.80	2.00	1.58	1.50
2.00	3.33	2.30	3.00	1.23	1.30
2.50	2.13	1.95	4.00	1.10	1.18
3.00	1.89	1.71	5.00	0.99	1.09
4.00	1.22	1.38	8.00	0.92	0.86
5.00	0.89	1.17	10.00	0.88	0.76

Under the condition of [a][KBrO₃] = 10.0 × 10⁻⁴mol dm⁻³, [Ru(III)] = 4.58 × 10⁻⁵ mol dm⁻³, [DEA] = 1.0 × 10⁻²mol dm⁻³, [Hg(OAc)₂] = 1.60 × 10⁻³mol dm⁻³, μ = 0.053 mol dm⁻³, [b][KBrO₃] = 10.0 × 10⁻⁴mol dm⁻³, [Ru(III)] = 15.30 × 10⁻⁶ mol dm⁻³, [TEA] = 5.0 × 10⁻² mol dm⁻³, [Hg(OAc)₂] = 1.2 × 10⁻³ mol dm⁻³, μ = 1.20 mol dm⁻³.

Before the mechanism for Ru(III) catalysed oxidation of DEA and TEA by acidic solution of potassium bromate is proposed, it is worthwhile to ascertain the reactive species of potassium bromate and Ru(III) chloride in acidic medium. It is reported[7] that potassium bromate in presence of acid exists in the following equilibria:

$$BrO_3^- + H^+ \rightleftharpoons OBrO_2H \qquad (A)$$

$$OBrO_2H + H^+ \rightleftharpoons \overset{+}{OBrO_2H_2} \qquad (B)$$

$$\overset{+}{OBrO_2H_2} \rightleftharpoons \overset{+}{BrO_2} + H_2O \qquad (C)$$
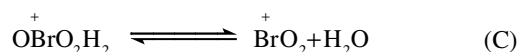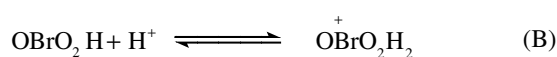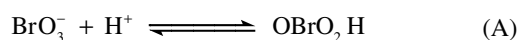
Table 5 Rate constant and activation parameters for Ru(III)chloride catalysed oxidation of DEA and TEA by KBrO₃ in the presence of perchloric acid at 35°C

| Parameters	Values	
	DEA	TEA
k_r (mol^{-2}dm^{-6}s^{-1})	29.06	114.13
$\log A$ (mol^{-2}dm^{6}s^{-1})	10.12	9.46
E_a(kcal mol^{-1})	12.20	10.42
$\Delta S^\#$(cal deg^{-1} mol^{-1})	−14.28	−17.32
$\Delta H^\#$(kcal mol^{-1})	11.59	9.82
$\Delta G^\#$(kcal mol^{-1})	15.99	10.35

From the above equilibria (A) and (B), it is evident that with positive effect of [H⁺] on the rate of reaction (either first order or second order with respect to [H⁺]), OBrO₂H or OBr⁺O₂H₂ can be taken as the reactive species of potassium bromate in the reaction. Further, if under the experimental conditions, the equilibrium(C) is assumed to be in existence, then with zero effect of [H⁺] on the rate of reaction only the species Br⁺O₂ can be taken as the reactive species of KBrO₃ in the reaction.

It is also reported[8] that the oxidation of Ru(III) to Ru(V) by bromate does not take place at lower acid strengths because of the low oxidising property of bromate, which is mainly present in the BrO₃⁻ form. Beck and co-workers[9] have suggested that both OBrO₂H and OBr⁺O₂H₂ are the existing form of bromate in moderately strong acid solution. This result is further verified by Sanjeeva Reddy and Sundaram.[10] In the present study of oxidation of DEA and TEA by potassium bromate in presence of perchloric acid, since throughout the study, a lower acid strength was maintained, hence, under our experimental conditions it can safely be assumed that potassium bromate in acidic medium remains in the form of BrO₃⁻ only. The species BrO₃⁻, being the lone species of KBrO₃ in the reaction, will be taken as reactive species of potassium bromate in present investigation. The conclusion that BrO₃⁻ is the reactive species of KBrO₃ also finds support from the observed negative effect of [H⁺] on the rate of reaction and thus HBrO₃ and H₂BrO₃⁺ are completely ruled out as reactive species of KBrO₃ in acidic medium.

Ru(III) chloride[11] has been used as homogeneous catalyst for the oxidation of organic substrates in acidic medium by several workers. They have reported the existence of the following equilibrium when Ru(III) chloride is dissolved in hydrochloric acid:

$$[RuCl_6]^{3-} + H_2O \rightleftharpoons [RuCl_5(H_2O)]^{2-} + Cl^- \quad (D)$$
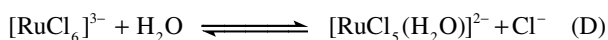
On the basis of order with respect to [Cl⁻], it is concluded that either [RuCl₆]³⁻ or [RuCl₅(H₂O)]²⁻ is the reactive species of Ru(III) chloride in the reaction. Recently Singh and co-workers,[12,13] while studying the Ru(III) chloride catalysed oxidation of reducing sugars by sodium metaperiodate in presence of sodium hydroxide, have observed that [RuCl₂(H₂O)₃OH] is the effective species of Ru(III) chloride. Taqui Khan et al.[14] have reported that at the instant of preparation, Ru(III) exists in solution in the pH range 0.4–2.0 as four major species [RuCl₄(H₂O)₂]⁻, [RuCl₃(H₂O)₃], [RuCl₂(H₂O)₄]⁺ and [RuCl(H₂O)₅]²⁺. Out of these four species, [RuCl₂(H₂O)₄]⁺ is stabilised in its hydrolysed form [RuCl₂(H₂O)₃OH] according to the following equilibrium

$$[RuCl_2(H_2O)_4]^+ + H_2O \rightleftharpoons [RuCl_2(H_2O)_3OH] + H_3O^+ \quad (E)$$
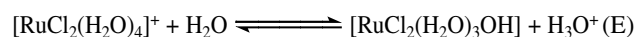
Since experiments were performed with Ru(III) chloride dissolved in 0.01 M HCl solution and throughout the study, the pH of the solution was maintained in between 0.4 and 2.0, hence it can easily be inferred that [RuCl₂(H₂O)₃OH] is the reactive species of Ru(III) chloride in the oxidation of DEA and TEA by potassium bromate in acidic medium. The existence of the sole species of Ru(III) chloride in acidic medium as [RuCl₂(H₂O)₃OH] is also confirmed by the spectrum of Ru(III) chloride solution (4.38×10^{-4}M) in presence of HCl (1.0×10^{-2}M) where a single peak at λ_{max} = 210 nm is observed.

In the oxidation of DEA and TEA, mercuric acetate has been used as Br⁻ scavenger[4,5] to eliminate the bromide ion, which could have produced Br₂ in the reaction as

$$BrO_3^- + 5Br^- + 6H^+ \rightleftharpoons 3Br_2 + 3H_2O \quad (F)$$
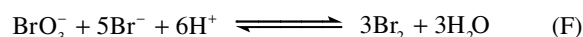
Bromine, thus produced sets parallel oxidation and creates complication in KBrO₃ oxidation. Addition of mercuric acetate obviates bromine oxidation and thus ensures oxidation purely through KBrO₃. It has been reported earlier that Hg(II) can also act as an oxidant as well as catalyst in the reaction. In order to ascertain the real role of Hg(OAc)₂ in addition to its function as Br⁻ scavenger, several experiments were performed with Hg(OAc)₂ in the absence of KBrO₃ under identical conditions. It has been observed that the reaction does not proceed, ruling out the possibility of Hg(II) acting as an oxidant under the present experimental conditions. Further, kinetic observations showed that the reaction velocity was almost constant with KBrO₃ as an oxidant in the presence of increasing concentration of Hg(OAc)₂, ruling out the catalytic role of Hg(OAc)₂. These experimentalobservations indicate that Hg(OAc)₂ acts as a Br⁻ ion scavenger only, in the oxidation of both aminoalcohols by KBrO₃ in the presence of acidic solution of Ru(III) chloride as homogeneous catalyst.

It is reported[15] that transition metal ions, like Pd(II), Os(VIII) and Ru(III), form a complex with amino alcohols. In order to verify the existence of [Ru(III)–aminoalcohol] complex, spectra for the solutions containing BrO₃⁻ alone, Ru(III) chloride and H⁺, Ru(III) chloride and H⁺ with two different concentrations of DEA and Ru(III) chloride, H⁺ and DEA with BrO₃⁻ solution have been collected at room temperature (Figure 5). Absorption spectra of Ru(III) and H⁺ with two different concentrations of DEA clearly indicate that the reactive species of Ru(III) i.e. [RuCl₂(H₂O)₃OH] forms a complex with the DEA molecule, showing an increase in the absorbance of Ru(III) chloride and H⁺ solution from 2.60(1) to 2.68(2) and 3.16(3). This increase in absorbance with the increase in DEA concentration can be considered as due to increase in the concentration of the complex, [RuCl₂(H₂O)₂(OH)₂.AA]⁻ according to the following equilibrium

$$[RuCl_2(H_2O)_3OH] + AA \rightleftharpoons$$
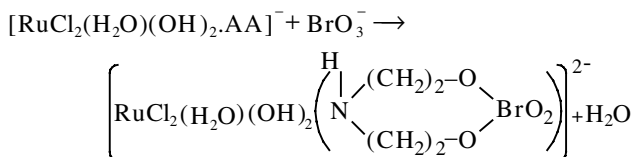$$[RuCl_2(H_2O)(OH)_2 AA]^- + H_3O^+ \quad (G)$$
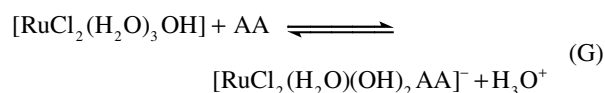
where AA stands for aminoalcohol.

With the increase in concentration of aminoalcohol, the above equilibrium shifts towards right side, with more and more formation of complex [RuCl₂(H₂O)₂(OH)₂. AA]⁻, which becomes the sole factor for the increase in absorbance.
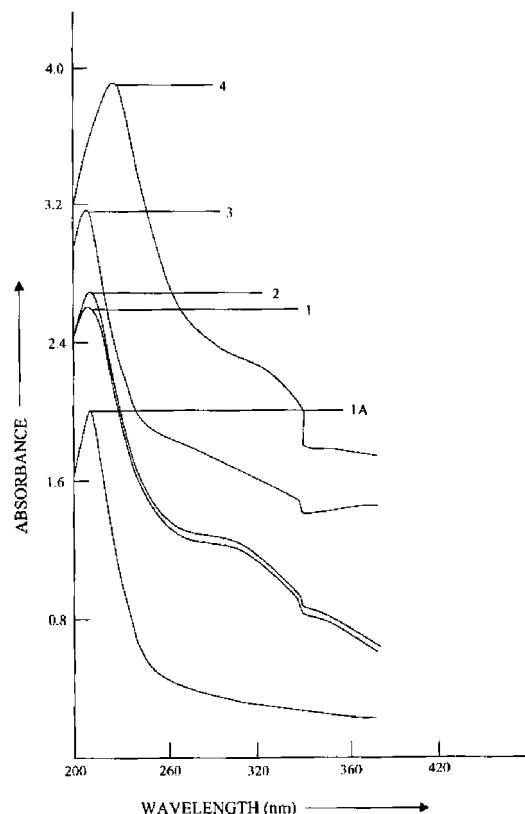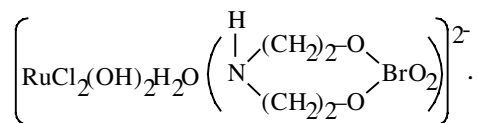
Fig. 5 Spectra of Ru(III) and DEA, Ru(III), DEA and KBrO$_3$ solutions.
(1)   [Ru(III)] = 4.58×10^{-4} mol dm^{-3}, [H$^+$] = 1.0×10^{-2} mol dm^{-3}.
(1A) [KBrO$_3$] = 2.0×10^{-3} mol dm^{-3}.
(2)   [Ru(III)] = 4.58×10^{-4} mol dm^{-3}, [H$^+$] = 1.0×10^{-2} mol dm^{-3}
        [DEA] = 4.0×10^{-3} mol dm^{-3}.
(3)   [Ru(III)] = 4.58×10^{-4} mol dm^{-3}, [H$^+$] = 1.0×10^{-2} mol dm^{-3}
        [DEA] = 10.0×10^{-3} mol dm^{-3}.
(4)   [Ru(III)] = 4.58×10^{-4} mol dm^{-3}, [H$^+$] = 1.0×10^{-2} mol dm^{-3},
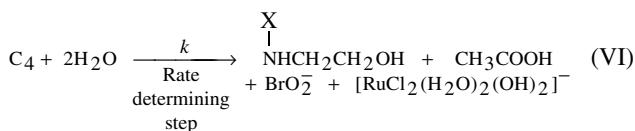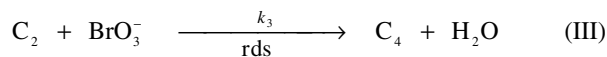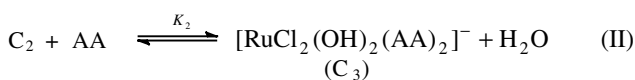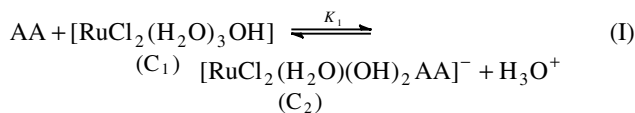   [DEA] = 4.0×10^{-3} mol dm^{-3}, [KBrO$_3$] = 2.0×10^{-3} mol dm^{-3}.

Further, when bromate solution has been added to the solution of Ru(III) chloride, H$^+$ and DEA, an increase in absorbance from 2.68(2) to 3.88(4) with shift in λ_{max} towards longer wavelength was observed. The increase in absorbance with the addition of BrO$_3^-$ solution is due to formation of a new complex according to the reaction

$$[RuCl_2(H_2O)(OH)_2.AA]^- + BrO_3^- \longrightarrow$$

$$\left[RuCl_2(H_2O)(OH)_2 \left(\begin{smallmatrix} H \\ | \\ N \end{smallmatrix} \diagup^{(CH_2)_2-O}_{(CH_2)_2-O} BrO_2 \right) \right]^{2-} + H_2O$$

This increase in absorbance with a shift in λ_{max} value towards longer wavelength can be considered as due to combination of a chromophore molecule (BrO$_3^-$) with an auxochrome (Cl$^-$), already present in the complex [RuCl$_2$(H$_2$O)(OH)$_2$.AA]$^-$, giving rise to a new chromophore,

$$\left[RuCl_2(OH)_2H_2O \left(\begin{smallmatrix} H \\ | \\ N \end{smallmatrix} \diagup^{(CH_2)_2-O}_{(CH_2)_2-O} BrO_2 \right) \right]^{2-} .$$
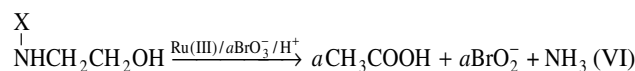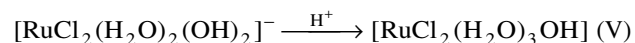
On the basis of above discussion and treating BrO$_3^-$ and [RuCl$_2$(H$_2$O)$_3$OH] as the reactive species of potassium bromate and Ru(III) chloride respectively, the reaction in Scheme 1 can be proposed for the oxidation of both amino alcohols.
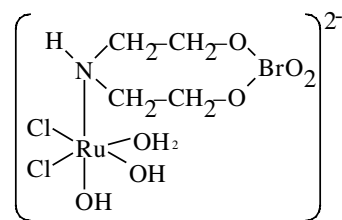
$$AA + [RuCl_2(H_2O)_3OH] \underset{}{\overset{K_1}{\rightleftharpoons}} \qquad (I)$$
$$(C_1) \quad [RuCl_2(H_2O)(OH)_2 AA]^- + H_3O^+$$
$$(C_2)$$

$$C_2 + AA \overset{K_2}{\rightleftharpoons} [RuCl_2(OH)_2(AA)_2]^- + H_2O \qquad (II)$$
$$(C_3)$$

$$C_2 + BrO_3^- \xrightarrow[rds]{k_3} C_4 + H_2O \qquad (III)$$

$$C_4 + 2H_2O \xrightarrow[\substack{Rate \\ determining \\ step}]{k} \overset{X}{\underset{}{N}}HCH_2CH_2OH + CH_3COOH \atop + BrO_2^- + [RuCl_2(H_2O)_2(OH)_2]^- \qquad (VI)$$

Scheme 1

Where X stands for H in DEA and for CH$_2$CH$_2$OH in TEA.

$$[RuCl_2(H_2O)_2(OH)_2]^- \xrightarrow{H^+} [RuCl_2(H_2O)_3OH] \quad (V)$$

$$\overset{X}{\underset{|}{N}}HCH_2CH_2OH \xrightarrow{Ru(III)/aBrO_3^-/H^+} aCH_3COOH + aBrO_2^- + NH_3 \quad (VI)$$

where a is 1 in the case of DEA and 2 in the case of TEA.
    The probable structure of C$_4$ in the case of DEA is

$$\left[\begin{smallmatrix} H \\ N \end{smallmatrix} \diagup^{CH_2-CH_2-O}_{CH_2-CH_2-O} \diagup BrO_2 \atop Cl \diagdown \underset{OH}{Ru} \diagup^{OH_2}_{OH} \right]^{2-}$$

and in the case of TEA is

$$\left[HO-H_2C-H_2C \diagdown \underset{N}{} \diagup^{CH_2-CH_2-O}_{CH_2-CH_2-O} \diagup BrO_2 \atop Cl \diagdown \underset{OH}{Ru} \diagup^{OH_2}_{OH} \right]^{2-}$$
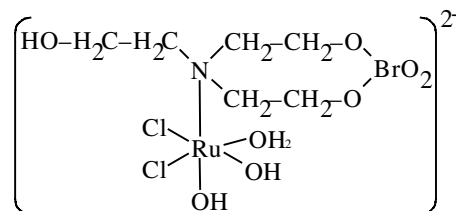
The observed decrease in first order rate constant at higher concentration of either DEA or TEA is ascribed to the formation of unreactive complex C$_3$ in step II of Scheme 1.
    On the basis of above mechanism, the rate in terms of disappearance of BrO$_3^-$ can be expressed as

$$-\frac{d[BrO_3^-]}{dt} = nk_3[BrO_3^-][C_2] \qquad (1)$$

where 'n' is 2 for DEA and 3 for TEA
    On applying the law of chemical equilibrium to steps (I) and (II)

$$[C_2] = \frac{K_1[C_1][AA]}{[H^+]} \qquad (2)$$

and

$$[C_3] = K_2[C_2][AA] \qquad (3)$$

By considering eqns (2) and (3), we have

$$[C_3] = \frac{K_1K_2[C_1][AA]^2}{[H^+]} \qquad (4)$$

Total concentration of ruthenium(III) chloride *i.e.* $[Ru(III)]_T$ at any moment of the reaction may be written as equation (5)

$$[Ru(III)]_T = [C_1] + [C_2] + [C_3] \quad (5)$$

By substituting the values of $[C_2]$ and $[C_3]$ from equations (2) and (4) respectively in equation (5), we have

$$[C_1] = \frac{[Ru(III)]_T [H^+]}{[H^+] + K_1 AA + K_1 K_2 [AA]^2} \quad (6)$$

From equations (1), (2) and (6), we obtain equation (7)

$$-\frac{d[BrO_3^-]}{dt} = \frac{nk_3 K_1 [BrO_3^-][AA][Ru(III)]_T}{[H^+] + K_1[AA]\{1 + K_2[AA]\}} \quad (7)$$

Equation (3) shows that

$$K_2[AA] = \frac{[C_3]}{[C_2]} \quad (8)$$

Since at low concentration of AA, the formation of C_3 is almost negligible, hence the inequality $K_2[AA] \ll 1$ can be assumed as valid one at low concentration of AA.

When $K_2[AA] \ll 1$, equation (7) will be reduced to equation (9)

$$-\frac{d[BrO_3^-]}{dt} = \frac{nk_3 K_1 [BrO_3^-][AA][Ru(III)]_T}{[H^+] + K_1[AA]} \quad (9)$$

Equation (9) is the final rate law valid for the oxidation of both aminoalcohols in their low concentration range.

Further, at very low concentration of AA, the inequality $K_1[AA] \ll [H^+]$ might be assumed as valid and equation (9) under this condition will take the shape of equation (10)

$$-\frac{d[BrO_3^-]}{dt} = \frac{nk_3 K_1 [BrO_3^-][AA][Ru(III)]_T}{[H^+]} \quad (10)$$

Observed first order kinetics with respect to both amino alcohols at their low concentration is very well explained by rate equation (10). At high concentrations of AA, step (II) will come into existence and as a result there will be more and more formation of unreactive complex C_3 with the increase in concentration of AA. Under this condition, since C_3 will be greater than C_2 hence the inequality $K_2[AA] \gg 1$ can be assumed as valid one. With this assumption, equation (7) will be reduced to equation (11).

$$-\frac{d[BrO_3^-]}{dt} = \frac{nk_3 K_1 [BrO_3^-][AA][Ru(III)]_T}{[H^+] + K_1 K_2 [AA]^2} \quad (11)$$

The presence of the term $K_1 K_2[AA]^2$ in the denominator of equation (11) clearly supports the decrease in first order rate constant with the increase in AA concentration.

On reversing equation (9), we have

$$\frac{1}{Rate} = \frac{[H^+]}{nk_3 K_1 [AA][Ru(III)]_T [BrO_3^-]} + \frac{1}{nk_3 [Ru(III)]_T [BrO_3^-]} \quad (12)$$

where rate $= -\dfrac{d[BrO_3^-]}{dt}$.

According to equation (12), when $\frac{1}{rate}$ values were plotted against $1/[AA]$, straight lines with positive intercepts were obtained (Figure 6). From the slopes and intercepts of the straight lines the values of k_3 and K_1 have been calculated and found as 18.19 $mol^{-1}dm^3\ s^{-1}$ and 0.29 respectively,

for the oxidation of DEA and 13.92 $mol^{-1}\ dm^3\ s^{-1}$ and 1.62 respectively for the oxidation of TEA.

On reversing equation (11), we have

$$\frac{1}{rate} = \frac{[H^+]}{nk_3 K_1 [AA][Ru(III)]_T [BrO_3^-]} + \frac{K_2[AA]}{nk_3 [Ru(III)]_T [BrO_3^-]} \quad (13)$$

When a plot between $\frac{1}{rate}$ and $[H^+]$ is made, a straight line having an intercept on *y*-axis was obtained (Figure 7). From the slopes and intercepts of the straight lines, the values of $k_3 K_1$ and $K_1 K_2$ were calculated and found as 12.57 $mol^{-1}\ dm^3$ and $15.08 \times 10^2\ mol^{-1}\ dm^3$ respectively for the oxidation of DEA and 28.98 $mol^{-1}\ dm^3$ and $1.22 \times 10^2\ mol^{-1}\ dm^3$ respectively for the oxidation of TEA.

It is well known[16] that solvation in general increases with the charge on the ion. In the case of reaction between two ions of opposite charge, their union will result in a lowering of the net charge and due to this some frozen solvent molecules
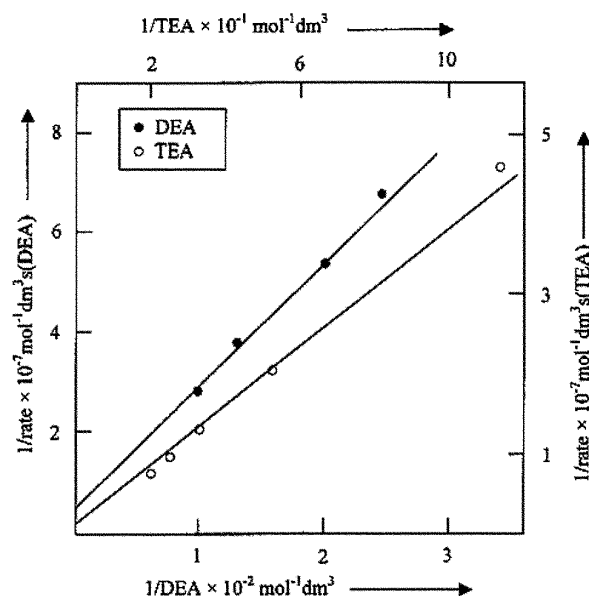

Fig. 6 Plot between 1/rate and 1/[substrate] for both DEA and TEA under the conditions of Table 2.

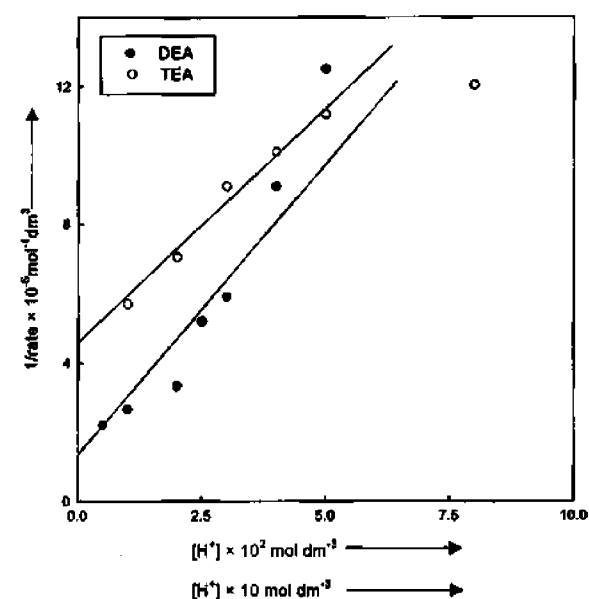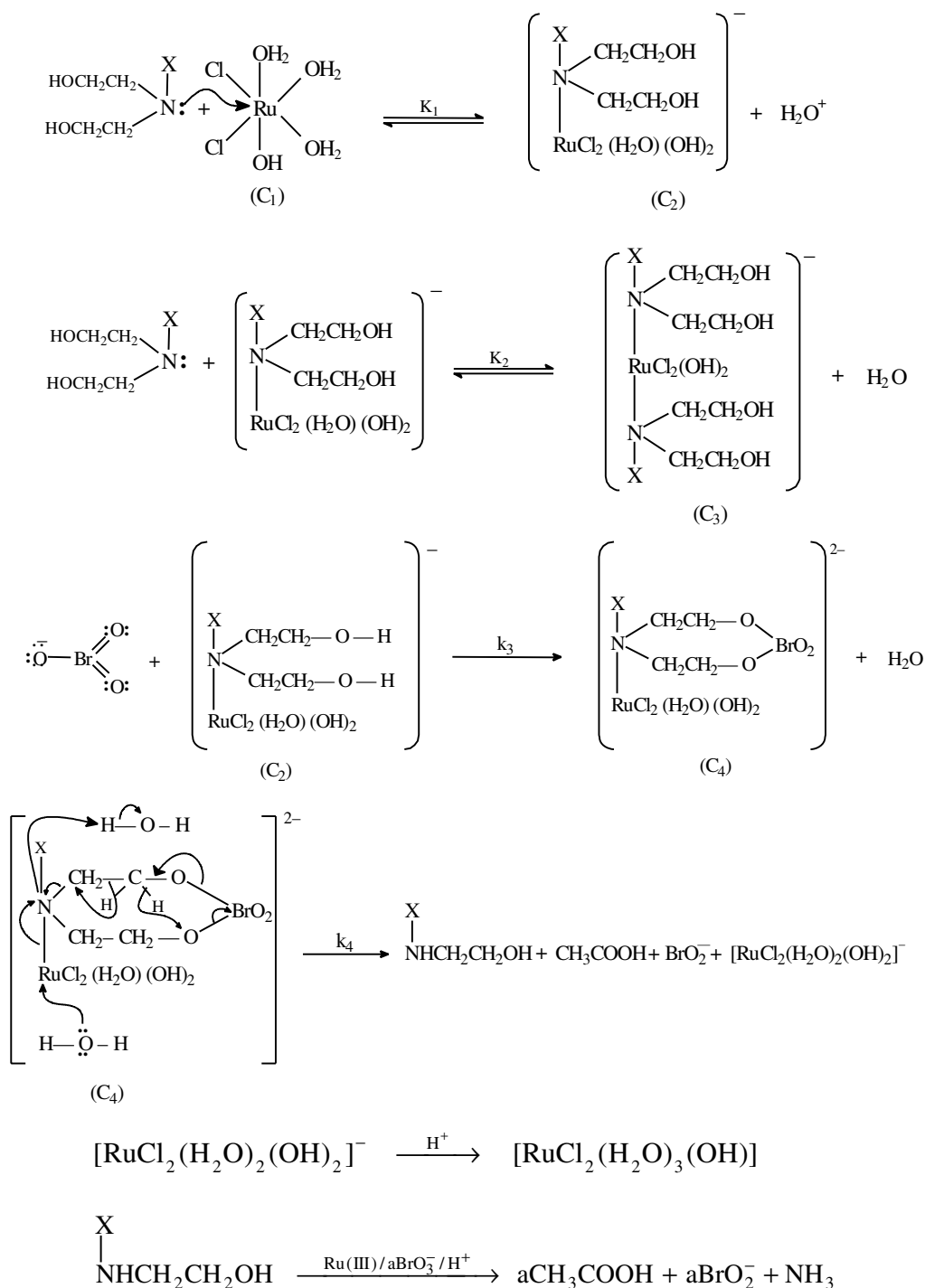**Fig. 7** Plot between 1/rate and [H+] for both DEA and TEA under the conditions of Table 4.

Scheme 2

will be released with an increase of entropy. But on the other hand when reaction takes place between two similarly charged ions, transition state will be more highly charged ion and due to this more solvent molecules will be required than for the separate ions. This would lead to a decrease in entropy. In the present study of oxidation of DEA and TEA by KBrO$_3$ in presence of Ru(III) as homogeneous catalyst, the observed negative entropy of activation can be considered as due to reaction between two similarly charged species, [RuCl$_2$(H$_2$O)$_2$(OH)$_2$AA]$^-$ and BrO$_3^-$ leading to a formation of a highly charged complex, which in the rate determining step decomposes into products via several fast steps.

For further verification of the proposed reaction Scheme 1, we have taken the help of multivariate regression analysis. For DEA the equation of the fitted model is

$$\log k_1 = 1.6065 + 0.9849 \log [AA] + 1.0437 \log [Ru(III)] + 0.7389 \log [H^+] \quad (14)$$

and for TEA, it is

$$\log k_1 = 2.1346 + 0.9955 \log [AA] + 1.0184 \log [Ru(III)] + 0.3465 \log [H^+] \quad (15)$$

Equations (14) and (15) are well in accordance with our observed order with respect to each reactant taking part in the

reaction and the predicted rates are in close resemblance with the observed rates for the variations of [AA], [Ru(III)] and [H$^+$], under the conditions of Tables 2, 3 and 4 respectively. The close agreement in the observed and predicted rates clearly confirms the rate law (9) and hence the proposed reaction Scheme 1. Multivariate regression analysis could not be used to calculate rates at high [AA] due to non-availability of sufficient kinetic data.

On the basis of our study for Ru(III) catalysed oxidation of DEA and TEA by potassium bromate in presence of HClO$_4$, the following four conclusions can very easily be drawn:

(i)   BrO$_3^-$ is the reactive species of KBrO$_3$

(ii)   [RuCl$_2$(H$_2$O)$_3$(OH)]$^-$ is the reactive species of RuCl$_3$.

(iii)   A complex, formed by the interaction of BrO$_3^-$ with [Ru(III)-amino alcohol] complex, ultimately changes into the reaction products.

(iv)   Kinetically inert complex [RuCl$_2$(OH)$_2$(AA)$_2$]$^{1-}$ is formed at very high concentration of amino alcohol.

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