Kinetics and mechanism of ruthenium(III) catalyzed oxidation of iso-propanol by cerium(IV) in sulfuric acid media

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ABSTRACT

The kinetics and mechanism of trace ruthenium(III) catalyzed oxidation of iso-propanol (IPA) by cerium(IV) in sulfuric acid media has been investigated by titrimetric technique of redox in the temperature range of 298-313K. It is found that the reaction is of first-order with respect to Ce(IV), first-order with respect to Ru(III), and zero-order with respect to IPA. It is found that the observed rate constant k_{obs} decreases with the increase of $[HSO_4^-]$ and $[H^+]$. Under the protection of nitrogen, the reaction system can not initiate polymerization of acrylonitrile, indicating no generation of free radicals. On the basis of the experimental results, a reasonable mechanism has been proposed and the rate equations derived from the mechanism can explain the experimental results.
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KEYWORDS

INTRODUCTION

Kinetic studies on oxidation of different types of organic compounds by cerium(IV) are well documented. Different metal ion catalysts like osmium (VIII)[1], silver(I)[2,3] copper(II)[4], chromium(III)[5], ruthenium(III)[6], iridium(III)[7], etc, have been used in the oxidation of substance by cerium(IV). Among the different metal ion catalysts, ruthenium(III) and iridium(III) are highly efficient even at trace concentration. In case of ruthenium(III), different catalytic cycles such as Ru(III)/Ru(IV)[8] and Ru(III)/Ru(VIII)[9] have been proposed in different cases.

Our preliminary observations indicate that oxidation of iso-propanol by Ce(IV) in aqueous sulfuric acid is kinetically sluggish, but the addition of traces of ruthenium(III) enhances the rate significantly. To explore the mechanistic role of ruthenium(III) in oxidation of iso-propanol (IPA) by Ce(IV) in aqueous sulfuric acid, the present investigation was undertaken.

MATERIALS AND REAGENTS

Ceric sulfate $(Ce(SO_4)_2)$, ferrous ammonium sulfate $(Fe(NH_4)_2(SO_4)_2)$, IPA and Ruthenium trichloride $(RuCl_3)$ were of A.R. grade. Doubly distilled water was employed throughout the experiment. Ceric sulfate solution was prepared by dissolving $Ce(SO_4)_2$ in 0.5mol·L^{-1} sulfuric acid and standardized with ferrous ammonium sulfate using ferroin as an indicator. IPA was purified by distillation and its concentration was obtained from its density measurement. Stock solution of $RuCl_3$ was prepared by dissolving $RuCl_3$ in 1.0 mol·L^{-1} HCl solution. The concentration of Ru (III) in the stock so-

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lution was determined by spectrophotometry. The ionic strength (μ) was maintained by adding $NaClO_4$ solution.

Procedure and kinetic measurements

At fixed temperature, 25mL of solution containing definite [Ce(IV)], [Ru(III)], [H_2SO_4], [$NaHSO_4$], [$HClO_4$] and [$NaClO_4$], and 25mL of IPA solution with appropriate concentration were transferred separately to the upper and lower branch tubes of λ type two-cell reactor. After it was thermally equilibrated in a thermostat (about five minutes), the solutions were thoroughly mixed. The progress of the reaction was monitored by withdrawing aliquot of the reaction mixture at regular time intervals, adding it into excess standard $Fe(NH_4)_2(SO_4)_2$ solution in sulfuric acid to quench the reaction, then back-titrating the unreacted iron(II) by standard cerium(IV) solution using ferroin as indicator. The pseudo first-order rate constants k_{obs} were evaluated from the slope of the plots of $\ln[Ce(IV)]_t$ versus time (t) i.e. $\ln (V\infty-V_t)$ versus t(Figure 1), where $V\infty$ and V_t denote the volume of standard cerium (IV) solution needed in back titration for the unconsumed iron(II) solution at infinity and time(t) respectively. To evaluate k_{obs}, generally 9-10 values at least up to 75% completion of the reaction were used. Average values of at least two independent determinations of k_{obs} were taken for analysis. The observed rate constants were reproducible within the experimental error$\pm$5%.
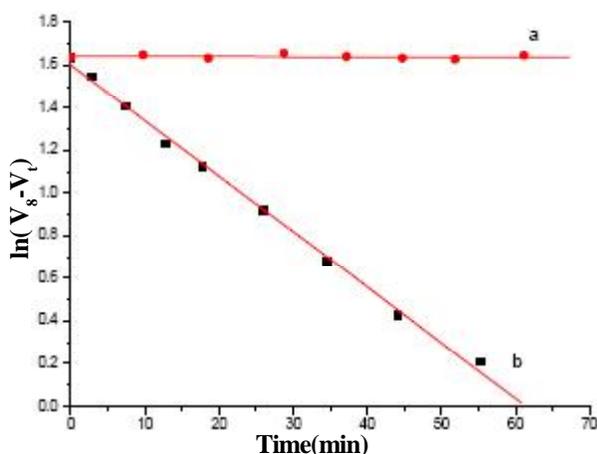
Figure 1 : Plots of ln ($V_\infty-V_t$) vs. t at 298K; [Ce(IV)]=2.5× 10^{-3} mol·L⁻¹, [IPA]=0.5 mol·L⁻¹, μ=1.0 mol·L⁻¹, [H_2SO_4]=1.0 mol·L⁻¹, (a) [Ru(III)]=0.0 mol·L⁻¹; (b) [Ru(III)]=2×10^{-7} mol·L⁻¹

RESULTS AND DISCUSSIONS

Dependence of rate constant on [Ru(III)]

The fact that under the experimental conditions in the absence of Ru(III) ions the reaction practically does not take place is supported by an independent experiment (Figure 1 curve a). Addition of trace Ru(III) enhances the rate significantly (Figure 1 curve b), which indicates that Ru(III) has efficient catalysis to the reaction.

At fixed [Ce(IV)], [IPA], [H_2SO_4] and ionic strength (μ), k_{obs} increases with the increase of [Ru(III)]. Observed reaction order (n_{ap}) of Ru(III) can be obtained from the liner regression of $\ln k_{obs}$ vs. $\ln[Ru(III)]$, n_{ap} =1.0 at 298K. This indicates that the reaction is of first-order with respect to [Ru(III)]. k_{obs} vs. [Ru(III)] yielded good linear plot (r=0.998) nearly through the origin(Figure 2).

Dependence of rate constant on [IPA]

At fixed [Ce(IV)], [Ru(III)], [H_2SO_4] and μ under different temperature (T), [IPA] has almost no effect on the k_{obs}. This indicates that the reaction is of zero-order with respect to [IPA]. k_{obs} vs. [IPA] yielded good linear plot(Figure 3).

Dependence of rate constant on [H⁺]

[H⁺] was varied over the range of 0.2 mol·L⁻¹~1.0 mol·L⁻¹ at fixed [HSO_4^-] ([HSO_4^-] = 1.0 mol·L⁻¹= [H_2SO_4]+[$NaHSO_4$]), [Ce(IV)], [IPA], [Ru(III)] and μ. [H⁺] was calculated ignoring the dissociation of [HSO_4^-] and assuming [H⁺]≈[H_2SO_4]. Here k_{obs} decreases with the increase of [H⁺], n_{ap} [H⁺] is -0.24 obtained from the liner regression of $\ln k_{obs}$ vs. $\ln[H⁺]$. And the plot of k_{obs} against 1/[H⁺] at 298K is found to be linear (regression coefficient r=0.9963) with positive intercept and slope (Figure 4).

Dependence of rate constant on [HSO_4^-]

[HSO_4^-] was varied in the range of 0.2 mol·L⁻¹~1.0 mol·L⁻¹ at fixed [H⁺] ([H⁺]=1.0 mol·L⁻¹≈ [H_2SO_4]+ [$HClO_4$]), [Ce(IV)], [IPA], [Ru(III)], μ and T. Here [HSO_4^-] ≈ [H_2SO_4] ignoring the dissociation of [HSO_4^-] in the strongly acidic solution. From figure 5, it can be seen that k_{obs} decreases with the increase of [HSO_4^-]. Therefore HSO_4^- shows a rate retarding effect (n_{ap} = -

TABLE 1: Effect of ionic strength μ on k_{obs}

$\mu/mol\cdot L^{-1}$	0.5	0.8	1.1	1.4	1.8
k_{obs}/min^{-1}	0.1531	0.1300	0.1107	0.09655	0.08258

0.26). The plot of $1/k_{obs}$ against $[HSO_4^-]$ was found to be linear (regression coefficient r=0.9932) with positive intercept and positive slope. Thus the hydrogen sulfate dependence can be represented as follows:

$$k_{obs} = \frac{a}{b + c[HSO_4^-]} \qquad (1)$$

Where a, b and c are constants under the experiment conditions.

Dependence of rate constant on ionic strength (μ)

At fixed [Ce(IV)], [Ru(III)], $[H_2SO_4]$, [IPA] and T, the ionic strength (μ) was adjusted by controlling the dosage of $NaClO_4$. From TABLE 1, it can be seen that k_{obs} decreases with the increase of μ, showing weak negative salt effect.

Analysis of product and test of free radicals

The completion of the reaction was marked by the complete fading of Ce(IV) color (yellow). One of the reaction products as Ce(III) was detected by spot test[10]. The product of oxidation of IPA was detected and estimated by following method. After the completion of the reaction, adding 2,4-dinitrophenylhydrazine into the solution, the solution appear red deposition and if adding Fehling's reagent into the solution, the solution do not appear red deposition, which indicats that the product has ketonic group.

Acrylonitrile solution(40%, volume fraction) was added to the reaction mixture under the protection of nitrogen gas, no white deposition could be found, indicating the reaction system can not initiate polymerization of acrylonitrile and proving no generation of free radicals in the reaction.

According to the experiments, the overall reaction is following,

$$2Ce(IV) + CH_3CHOHCH_3 \rightarrow 2Ce(III) + CH_3COCH_3 + 2H^+$$
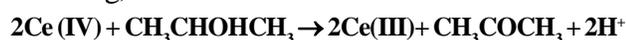
Mechanism of the reaction

Considering hydrolysis of the catalyst, and free radicals can not be generated in the reaction, the following reactions (2-8) are proposed incorporating the various possible species of IPA both in the bulk solvent and in coordination sphere of the catalyst[8]:

$$Ru(III) + H_2O \xrightarrow{K_h} Ru(III)\cdot OH + H^+ \qquad (2)$$

$$Ru(III) + IPA \xrightarrow{K_1} Ru(III)\cdot IPA \text{ (adduct(I))} \qquad (3)$$

$$Ru(III)\cdot OH + IPA \xrightarrow{K_2}$$
$$Ru(III)\cdot CH_3CHO^-CH_3(adduct(II)) + H_2O \qquad (4)$$

$$Adduct(I) + Ce(IV)^* \xrightarrow[\text{Slow}]{k_1} Ru(IV)\cdot IPA + Ce(III) \qquad (5)$$

$$Adduct(II) + Ce(IV)^* \xrightarrow[\text{Slow}]{k_2} \cdot$$
$$Ru(IV)\ CH_3CHO^-CH_3 + Ce(III) \qquad (6)$$

$$Ru(IV)\cdot IPA + Ce(IV) \xrightarrow{fast} Ru(III) +$$
$$CH_3COCH_3 + Ce(III) + 2H^+ \qquad (7)$$

$$Ru(IV)\cdot CH_3CHO^-CH_3 + Ce(IV) \xrightarrow{fast}$$
$$Ru(III) + CH_3COCH_3 + Ce(III) + H^+ \qquad (8)$$
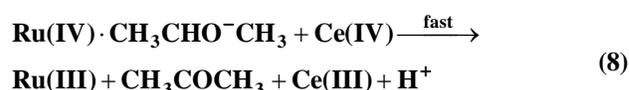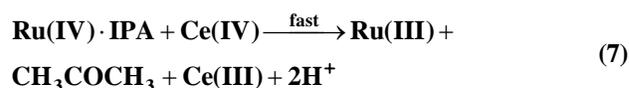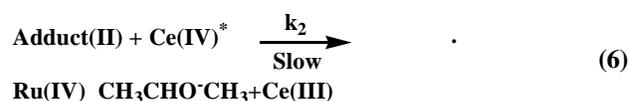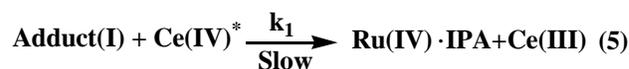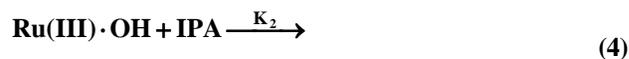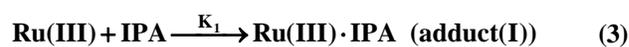
Here, $Ce(IV)^*$ presents active specie of Ce(IV). Step (5) and Step (6) are the rate-determining steps. According to the above mechanism, the conclusion can be made from the rate-determining steps,

$$-d[Ce(IV)]_T/dt = \{k_1[adduct(I)] + k_2[adduct(II)][Ce(IV)^*]$$
$$= f[Ce(IV)]_T\{k_1[adduct(I)] + k_2[adduct(II)]\} \qquad (9)$$

Subscripts T and e stand for total and equilibrium concentration respectively. f denotes the fraction of kinetically active species to the total cerium(IV).

From the mass balance relationship, we have:

$$[Ru(III)]_T = [Ru(III)]_e + [Ru(III)\cdot OH]_e + [adduct(I)]_e + [adduct(II)]_e$$

According to Eq.(2) ~Eq.(9), we have

$$[adduct(I)]_e = \frac{[Ru(III)]_T K_1[IPA]}{1 + K_h[H^+]^{-1} + K_1[IPA] + K_2K_h[IPA][H^+]^{-1}} \qquad (10)$$

$$[adduct(II)]_e = \frac{K_2K_h[Ru(III)]_T[IPA][H^+]^{-1}}{1 + K_h[H^+]^{-1} + K_1[IPA] + K_2K_h[IPA][H^+]^{-1}} \qquad (11)$$

Substituting Eq.(10) and Eq. (11) into Eq.(9), we get :

$$\frac{-d[Ce(IV)]_T}{dt} = \frac{f[Ru(III)]_T[IPA](k_1K_1 + k_2K_2K_h[H^+]^{-1})}{1 + K_h[H^+]^{-1} + K_1[IPA] + K_2K_h[IPA][H^+]^{-1}}[Ce(IV)]_T$$

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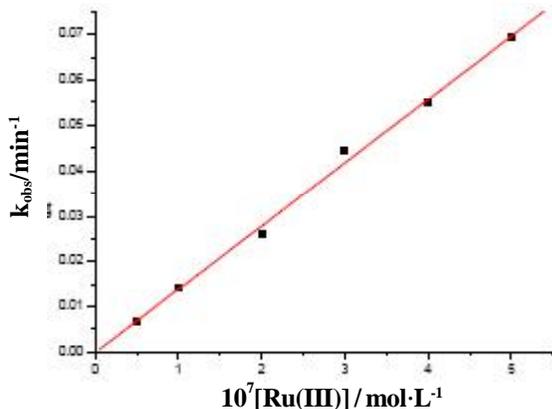
Figure 2 : Plot of k_{obs} vs. [Ru(III)] at 298k; [Ce(IV)]=2.5× 10^{-3} mol·L^{-1}, [IPA]=0.5mol·L^{-1}, [H$_2$SO$_4$]=1.0 mol·L^{-1}, μ=1.0 mol·L^{-1}
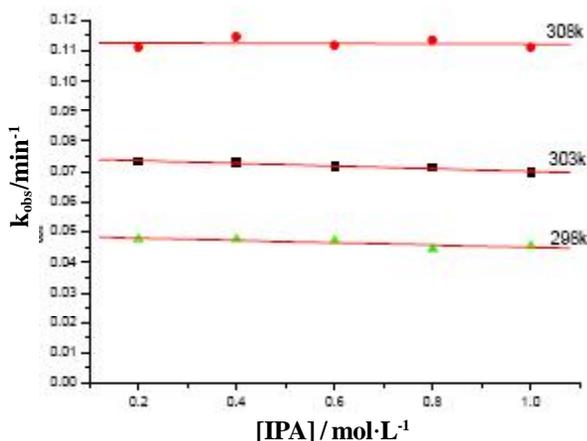
Figure 3 : Plots of k_{obs} vs. [IPA] at different temperatures; [Ce(IV)]= 2.5×10^{-3} mol·L^{-1}, [Ru(III)]= 5×10^{-7} mol·L^{-1}, [H$_2$SO$_4$]=1.0 mol·L^{-1}, μ=1.0 mol·L^{-1}
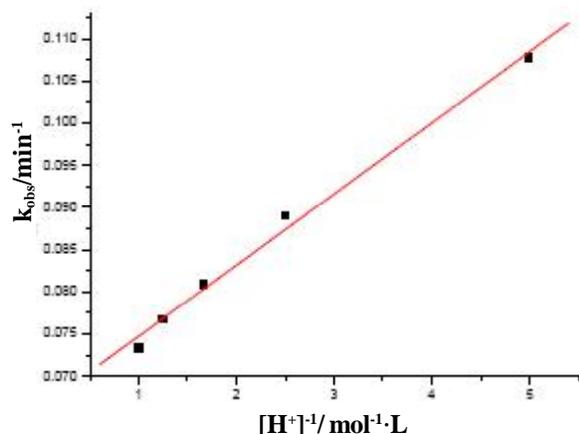
Figure 4 : Plot of k_{obs} vs. [H$^+$]$^{-1}$ at 298k; [Ce(IV)]=2.5× 10^{-3} mol·L^{-1}, [IPA]=0.5 mol·L^{-1}, [Ru(III)] = 5×10^{-7} mol·L^{-1}, μ=1.0mol·L^{-1}
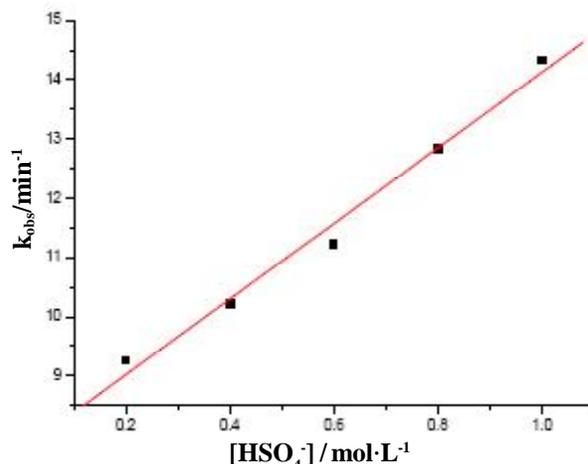
Figure 5 : Plot of k_{obs} $^{-1}$ vs. [HSO$_4^-$] at 298k; [Ce(IV)] =2.5×10^{-3} mol·L^{-1}, [IPA]=0.5mol·L^{-1}, [Ru(III)]=5×10^{-7} mol·L^{-1}, [H$^+$]= 1.0mol·L^{-1}, μ=1.0mol·L^{-1}

$$= k_{obs}[Ce(IV)]_T \tag{12}$$

$$k_{obs} = \frac{f[Ru(III)]_T[IPA](k_1K_1 + k_2K_2K_h[H^+]^{-1})}{1 + K_h[H^+]^{-1} + K_1[IPA] + K_2K_h[IPA][H^+]^{-1})} \tag{13}$$

In the experiments, [H$^+$]=1.0mol·L^{-1}, K_h=1.26× 10^{-3} [8] at 298k, so $K_h[H^+]^{-1}$<<1, then Eq.(13) is simplified to:

$$k_{obs} = \frac{f[Ru(III)]_T[IPA](k_1K_1 + k_2K_2K_h[H^+]^{-1})}{1 + [IPA](K_1 + K_2K_h[H^+]^{-1})} \tag{14}$$

Eq.(12) indicats that the reaction is first-order with respect to [Ce(IV)]. Eq.(14) suggests that k_{obs} vs. [Ru(III)] at constant [IPA] and [H$^+$] should yield good linear plot through origin(confirmed by figure 2)

If [IPA](K_1+ $K_2K_h[H^+]^{-1}$) >>1, then Eq.(14) leads to:

$$k_{obs} \approx \frac{f[Ru(III)]_T (k_1K_1 + k_2K_2K_h)[H^+]^{-1}}{K_1 + K_2K_h[H^+]^{-1}} \tag{15}$$

Eq.(15) explains the zero-order dependence on IPA(confirmed by figure 3).

If $K_2K_h[H^+]^{-1} << K$, then Eq.(15) is reduced to:

$$k_{obs} \approx f[Ru(III)]_T k_1 + \frac{fk_2K_2K_h[Ru(III)]_T [H^+]^{-1}}{K_1} \tag{16}$$

Eq.(16) suggests that k_{obs} vs. [H$^+$]$^{-1}$ should yield good linear plot with positive intercept and slope , which is confirmed by figure 4.

Determination of kinetically active Ce(IV) species

Under the experimental conditions in aqueous sul-

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furic acid medium, the important cerium(IV)-sulfato complexes are $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$ and $HCe(SO_4)_3^-$ and the relevant equilibrium[11] are as follows:

$$Ce^{4+} + HSO_4^- \rightarrow Ce(SO_4)^{2+} + H^+ \quad \beta_1 = 3500 \qquad (17)$$

$$Ce(SO_4)^{2+} + HSO_4^- \rightarrow Ce(SO_4)_2 + H^+ \quad \beta_2 = 200 \qquad (18)$$

$$Ce(SO_4)_2 + HSO_4^- \rightarrow HCe(SO_4)_3^- \quad \beta_3 = 3.4 \qquad (19)$$
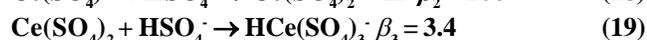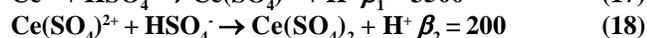
From the relationship between hydrogensulfate and k_{obs}, $Ce(SO_4)_2$ has been found as the kinetically active species in the present study. According to the mass balance, the following Eq. can be obtained:

$$[Ce(IV)]_T = [Ce^{4+}] + [Ce(SO_4)^{2+}] + [Ce(SO_4)_2] + [HCe(SO_4)_3^-] \qquad (20)$$

From the relevant Eqs.(17)~(19), and considering the relative magnitudes of the successive formation equilibrium constants which are in the order $\beta_1 \gg \beta_2 \gg \beta_3$, we get Eq.(21) from Eq. (20)[12]

$$[Ce(IV)]_T \approx [Ce(SO_4)_2](1 + \beta_3[HSO_4^-]) \qquad (21)$$

So, $$Ce(SO_4)_2 = \frac{[Ce(IV)]_T}{1 + \beta_3[HSO_4^-]} = f[Ce(IV)]_T$$

$$f = \frac{1}{1 + \beta_3[HSO_4^-]} \qquad (22)$$

Substituting Eq.(22) into Eq.(16), we get:

$$k_{obs} = \frac{[Ru(III)]_T k_1}{1 + \beta_3[HSO_4^-]} + \frac{k_2 K_2 K_h [Ru(III)]_T [H^+]^{-1}}{K_1(1 + \beta_3[HSO_4^-])} \qquad (23)$$

Assuming,

$$m = [Ru(III)]_T k_1 + \frac{k_2 K_2 K_h [Ru(III)]_T [H^+]^{-1}}{K_1} \qquad (24)$$

Eq.(23) is turned into:

$$k_{obs} = \frac{m}{1 + \beta_3[HSO_4^-]} \qquad (25)$$

or $$\frac{1}{k_{obs}} = \frac{1}{m} + \frac{\beta_3}{m}[HSO_4^-] \qquad (26)$$

Eq.(25) is the same as Eq.(1), which can explain well negative number order ($n_{ap} = -0.24$) dependence on $[HSO_4^-]$. Eq.(26) suggests that $1/k_{obs}$ vs. $[HSO_4^-]$ should be linear, which was evidenced by figure 5. From the slope(β_3/m) and intercept ($1/m$) obtained by the liner regression of $1/k_{obs}$ vs. $[HSO_4^-]$, we get $\beta_3 = 1.2$, which is in good agreement with the previously reported value[13].

Derivation of thermodynamic parameters

Substituting $\beta_3 = 1.2$ into Eq. (22), we get f=0.46.

According to the linear plot of k_{obs} against $1/[H^+]$ (Figure 4), the slope is 0.00842, and the intercept is 0.0663. Associating Eq. (16), it can be obtained,

$$fk_2 K_2 K_h [Ru(III)]_T/K_1 = 0.00842 \qquad (27)$$

$$f[Ru(III)]_T k_1 = 0.0663 \qquad (28)$$

Substitutzing f =0.46 and $[Ru(III)]_T = 5 \times 10^{-7} mol \cdot L^{-1}$ into Eq.(28), we get $k_1 = 2.88 \times 10^5$. According to Eq. (16), the slope B of the linear plot of k_{obs} against $[Ru(III)]$ is following,

$$B = fk_1 + fk_2 K_2 K_h [H^+]^{-1}/K_1 \qquad (29)$$

From Eq.(27), $[Ru(III)]_T = 5 \times 10^{-7} mol \cdot L^{-1}$, $[H^+] = 1 mol \cdot L^{-1}$, f =0.46 and $k_1 = 2.88 \times 10^5$, we get the slope $B = 1.49 \times 10^5$. From figure 2, we get the slope $B = 1.40 \times 10^5$. Two values of the slope are proximity. This result shows that the proposed hypothesis ($[IPA](K_1 + K_2 K_h [H^+]^{-1})] \gg 1$, $K_2 K_h [H^+]^{-1} \ll K_1$) in mechanism is reasonable.

REFERENCES

[1] Y.A.El-Tantawy, A.I.Abu-Shady, I.Ezzat Inas; J.Inorg.Nucl.Chem., **40**, 1683 (**1978).**

[2] P.K.Sai Prakash, B.Sethuram; Indian J.Chem., **11(3)**, 246 (**1973**).

[3] G.Singh, S.Bansal, D.Gupta, et al.; Indian J.Chem., **40A**, 714 (**2001**).

[4] R.Gupta, R.Chaturvedi, K.K.Mishra; Indian J.Chem., **45A**, 2431 (**2006**).

[5] W.Y.Song, Q.M.Jiang, Y.D.Liu; J.Hebei Univ., **24(6)**, 594 (**2004**).

[6] Y.Q.Zhai, H.M.Liu, B.S.Liu, et al.; Tran.Metal Chem., **32(5)**, 570 (**2007**).

[7] Y.Q.Zhai, H.M.Liu, G.Z.Yang, et al.; J.Rare Earths, **24**, 124 (**2006**).

[8] A.K.Das, M.Das; Int.J.Chem.Kinet, **27(1)**, 7 (**1995**).

[9] B.Singh, M.Singh, D.Kesarwani; Indian J.Chem, **41A(3)**, 547 (**2002**).

[10] Department of Chemistry, Hangzhou University; 'Handbook of Analytical Chemistry', Chemical Industry Press; Beijing, (**1982**).

[11] S.K.Mishra, Y.K.Gupta; J.Chem.Soc.(A) , 2918 (**1970**).

[12] Y.Q.Zhai, H.M.Liu, L.Yang; Chem.Res.Chinese U., **23(3)**, 333 (**2007**).

[13] S.K.Mondal, D.Kar, M.Das, et al.; Indian J.Chem., **37A**, 765 (**1998**).