Indian Journal of Chemistry
Vol. 63, March 2024, pp. 245-252
DOI: 10.56042/ijc.v63i3.2562

Ru(III) catalysed oxidation of EDTA by N-bromophthaliamide in aqueous alkaline medium: A kinetic and mechanistic study

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Received 11 June 2023; accepted (revised) 22 December 2023

The present study discusses the NBP oxidation in alkaline medium. Different workers have acknowledged unexpected products with unusual oxidants for EDTA oxidation. The role of the homogeneous catalyst ruthenium(III) has been investigated in alkaline media. It forms various intermediate complexes, oxidation states and free radicals. Herein, we have given an account of the Ru(III) catalyzed oxidation of EDTA by NBP to elucidate the possible mechanism and immediate species of oxidant, reductant and catalyst.

Keywords: NBP, EDTA, Oxidation, Kinetics, Alkaline medium

The studies involving the NBP oxidations are extensive in acid medium, while those in alkaline medium are relatively less studied. The mechanistic study of these reactions have been reported[1-4]. Bromamine-B is a mild oxidizing agent and is found to be a better oxidizing agent than the chloro compounds. The disodium salt of ethylenediaminetetraacetic acid Na_2H_2Y or EDTA is known as oxidizing as well as chelating and used for the detection of metal ions in the acid and alkaline media. Kinetic study of oxidation of glycine and L-alanine by NBP using SDS has been reported in earlier works[5-8]. Different workers have acknowledged unexpected products with unusual oxidants for EDTA oxidation. In the recent years, a homogeneous catalyst ruthenium(III) has played a very important role in acidic and alkaline media[9,10]. It forms various intermediate complexes, oxidation states and free radicals[12]. The mechanism of catalysis depends on the nature of the substrate, oxidant and other experimental conditions followed by different paths like formation of a complex with reactants[11,13-17]. Herein, we have given an account of the Ru(III) catalyzed oxidation of EDTA by NBP to elucidate the possible mechanism and immediate species of oxidant, reductant and catalyst.

Experimental Section

Analar grade chemicals and doubly distilled water was used during the course of the reaction. The NBS (Sisco) and EDTA (BDH) solution were prepared by dissolving a known mass in water. Their concentration was determined by known procedure[18-20]. A known quantity of $RuCl_3$ (S. D. Fine) was dissolved in water to prepare Ru(III) catalyst and standardized by known procedure[6]. Some kinetic runs were carried out in the absence of chloride, so the presence of chloride ion in the ruthenium (III) stock solution was precipitated with $AgNO_3$ and removed completely by repeated centrifugation. The resulting clear solution of ruthenium(III) catalyst contained less than 1.0×10^{-6} mol/dm^3 of Cl^- and Ag^+ and required chloride concentration was maintained with NaCl. The required alkalinity and ionic strength was maintained by the use of NaOH and $NaClO_4$ respectively[21,22]. During each kinetic run a fresh solutions were used.

Kinetic measurements

Pseudo-first order conditions were used to run kinetic measurements, where concentration of EDTA was more than NBP concentration at constant temperature 25°C[23-27]. The appropriate amount of the reactants solutions such as [EDTA], [NaOH], Ru(III) and [$NaClO_4$] were thermostatted to attain the equilibrium. A known volume of NBP solution was also thermostatted at the same temperature. The progress of the reaction was followed by measuring the unconsumed NBP iodometrically[28,29]. From the plots of log[NBP] *vs.* time the pseudo-first order rate constants were determined. Such plots were linear upto75% c of the reaction, after that they deviate from the linearity due to retarding effect of the product phthalimide.

Results and Discussion

The different sets of reaction mixtures containing certain quantity of NBP, EDTA and Ru(III)] catalyst were used to carry stoichiometric study at constant concentration of alkali and ionic strength. The reaction mixture was kept for about 24 hours at 25 ± 1°C in an inert atmosphere to react. When [EDTA] > [NBP], the remaining NBP was determined and main oxidation products were identified (Scheme 1, Table 1).

The reaction orders were determined from the slopes of log k_c *versus* log (concentration) plots with the variation of oxidant, reductant and alkali concentrations while keeping the others at constant[30-34]. The NBP concentration was varied from 3.0×10^{-3} to 3.0×10^{-2} mol dm^{-3} (Table 2) at constant concentration of EDTA, catalyst, alkali and the ionic strength. The plots of log [NBP] *versus* time were linear indicated as reaction order in [NBP] as unity. The EDTA concentration was varied from 5.0×10^{-3} to 5.0×10^{-2} mol dm^{-3} at 25°C, keeping all other reactant concentrations at constant condition (Table 2). It was found that with increase of EDTA concentration the reaction rate also increases and hence order with respect to [EDTA] was less than unity. The influence of alkali on the reaction was studied by varying [OH$^-$] from 3.0×10^{-3} to 3.0×10^{-2} mol dm^{-3} at constant concentrations of NBS, EDTA and Ru(III), while other conditions kept constant. The rate constants increases with raise in [OH$^-$] and indicates less than unit order dependence on [OH$^-$] (Fig. 1, Fig. 2 and Fig. 3).

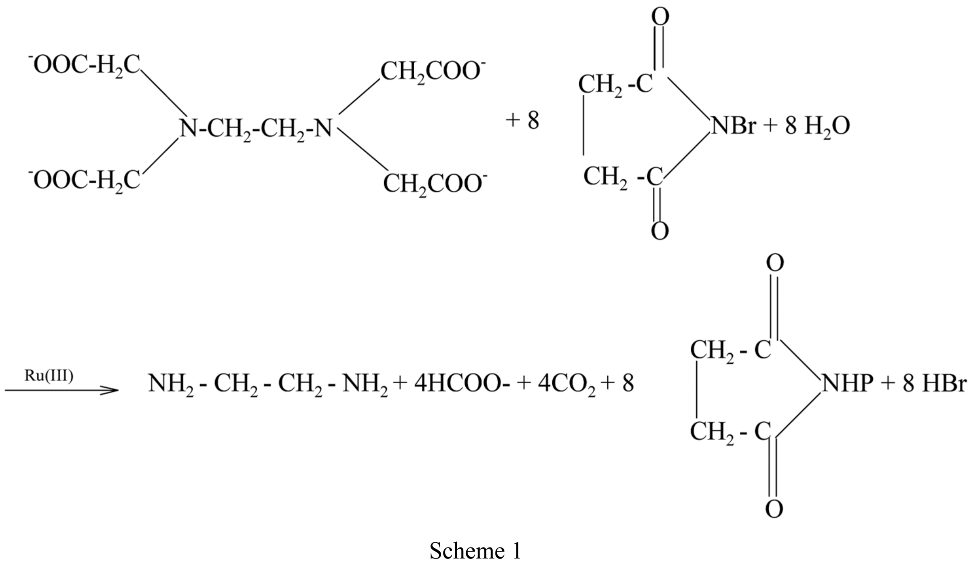
Table 1 — Stoichiometry of NBP on Ru(III) catalyzed oxidation of EDTA in aq. alkaline medium at 25°C [SDS] = 1.0×10^{-3}, I = 0.05 mol/dm^3

[NBP] = × 10^3 Taken	[EDTA] × 10^3 Taken	[NBP] = × 10^3 Taken	[EDTA] × 10^3 Taken
4.0	1.0	0.01	0.48
8.0	2.0	0.02	1.03
10.0	1.0	1.98	0.01
10.0	0.5	6.03	0.02

Error ± 0.5%

*All concentrations are in mol/dm^3

The influence of ionic strength (I) was studied by the salt sodium perchlorate concentration variation in the reaction medium from 0.1-1.0 at 25°C at constant concentrations of NBP, EDTA, Ru(III) and OH$^-$[33-36]. The relative permittivity (ƐT) effect was studied by varying the t-butanol-water percentage in the series of 0-30%. Both ionic strength and dielectric constant have negligible effect on the rate of reaction. A known volume of CH_2=CHCN scavenger had been added to the reaction mixture, was kept in an inert atmosphere to react for about 4 hours, on diluting with methanol, no appearance of precipitate in the reaction mixture, indicating the absence free radical in the reaction. The initially added products, formic acid, ethylene diamine and Br$^-$ did not have any important effect on the rate of reaction. The influence of catalyst was studied in the range of $0.5\times10^{-5} – 5.0\times10^{-5}$ mol dm^{-3} at 25°C and at constant concentration of NBP, EDTA, OH$^-$, Ru(III) and $NaClO_4$. The rate of the reaction increased with an raise in the concentration of catalyst. The reaction order with respect to catalyst concentration was found



Scheme 1

Table 2 — Influence of [NBP] and [EDTA] on Ru(III) catalyzed oxidation of EDTA in aqueous .alkaline medium at 25°C. $[OH^-] = 1.0\times10^{-3}$, $[Ru(III)] = 3.0\times10^{-5}$, I = 0.05 mol dm^{-3}

$EDTA\times10^{-3}$ mol dm^{-3}	$NBP10^{-4}$ mol dm^{-3}	$SDS\times10^{-3}$ mol dm^{-3}	$k\times10^{-4}s^{-1}$	
			Experimental	Calculated
0.5	2.0	5.0	0.50	0.45
2.0	2.0	5.0	1.50	1.8
3.0	2.0	5.0	2.70	2.7
4.0	2.0	5.0	3.30	3.62
5.0	2.0	5.0	3.60	4.3
10.0	0.5	5.0	1.90	1.90
10.0	2.0	5.0	2.00	1.83
10.0	3.0	5.0	2.10	2.7
10.0	4.0	5.0	2.00	3.6
10.0	5.0	5.0	2.20	4.5
10.0	2.0	1.0	1.50	0.52
10.0	2.0	3.0	2.00	1.56
10.0	2.0.	5.0	2.60	2.6
10.0	2.0\	7.0	3.40	3.64
10.0	2.0	9.0	4.10	4.68

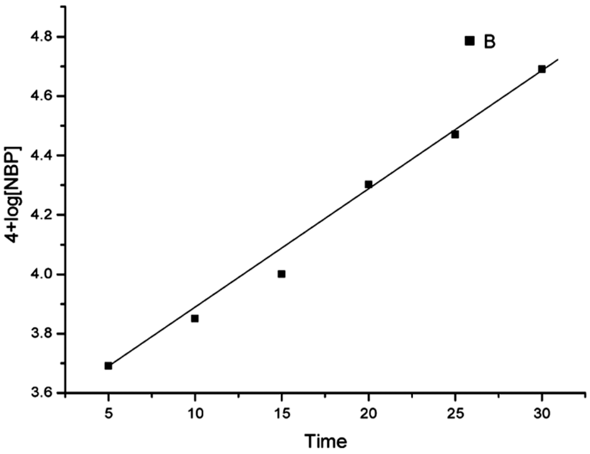


Fig. 1 — First order in [NBP] on Ru(III) catalyzed oxidation of EDTA in aqueous alkaline medium at 25°C.

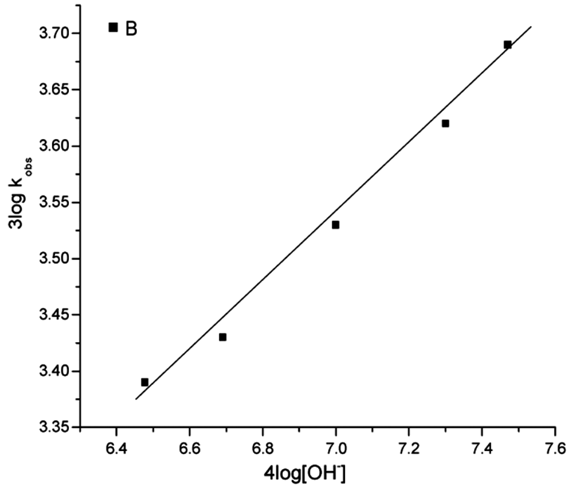


Fig. 2 — Order in [EDTA] on Ru(III) catalyzed oxidation of EDTA in aqueous alkaline medium at 25°C.

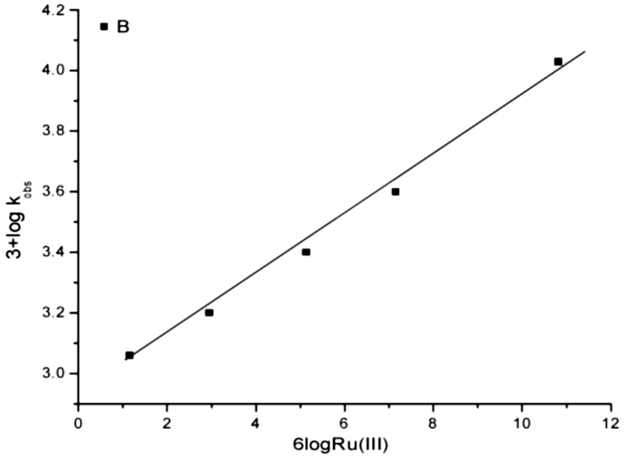


Fig. 3 — Order in $[OH^-]$ on Ru(III) catalyzed oxidation of EDTA in aqueous alkaline medium at 25°C

to be unity from the plot of $\log k_{obs}$ *vs.* log [Ru(III)] (Fig. 4, Fig. 5, Table 2).

Influence of temperature

Kinetic reaction was considered at four dissimilar temperatures 298, 303, 308 and 313 K, under varying concentrations of ethylenediaminetetraacetic acid and alkali, other experimental conditions being constant[37,38]. The reaction rate increased with raise in temperature. The rate constants (k) of slow step of Scheme were calculated from the intercepts and slopes $[Ru(III)]/ k_c$ *vs.* 1/ [EDTA], $[Ru(III)]/ k_c$ *vs.* $1/ [OH^-]$. The energy of activation corresponding to these rate constants was evaluated from the plot of log k *versus* 1/T (Fig. 6). The other activation parameters were calculated[39] (Table 3, Table 4, Table 5 and Table 6).

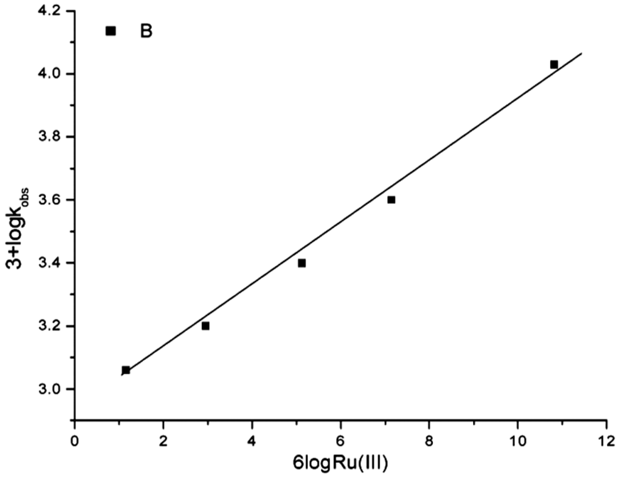


Fig. 4 — 6 log (Ru(III)] *vs* 3 + log K_{obs} on Ru(III) catalyzed oxidation of EDTA in aqueous alkaline medium at 25°C

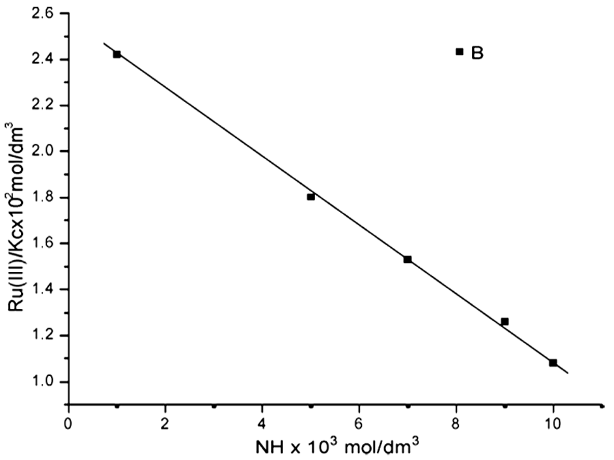


Fig. 5 — Effect of added products on Ru(III) catalyzed oxidation of EDTA in aqueous alkaline medium at 25°C

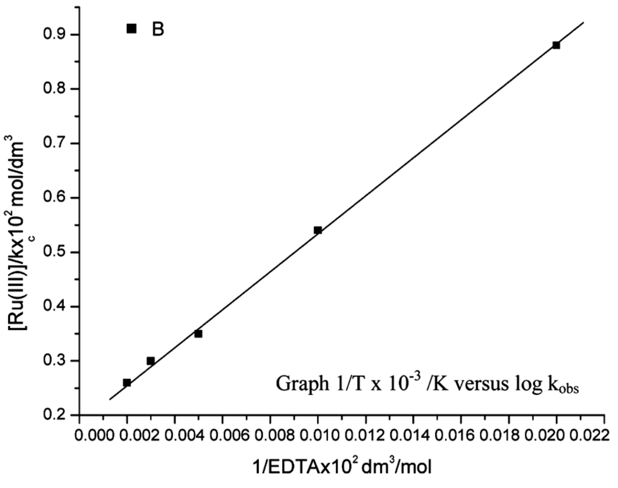
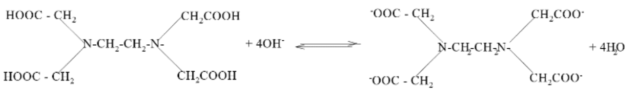


Fig. 6 — Influence of temperature on Ru(III) catalyzed oxidation of EDTA in aq. alkaline medium at 25°C

Mechanism

EDTA is known to exist as zwitter ion or neutral molecule in aqueous acidic medium[10]. However, in alkaline medium exists as anionic form as given below.



The oxidant, NBP is a two equivalent oxidant which oxidizes many substrates through HOBr and NBP itself. The reaction between NBP and EDTA in presence of Ru(III) catalyst in alkaline medium has a stoichiometry of 1:8 with fractional order dependence each in [EDTA] and [OH^-] and unit order in [NBP] and [Ru(III)][40-42]. It is interesting to note that, the rate of reaction is dependent of substrate concentration. The initial addition of one of the product, Phthaliamide retards the rate of reaction, which may beattributed to the change in concentration of free OH^- as shown below.

This reaction is possible because succinimide is a weak acid with pK_a 9.6 enlarge in rate with boost in [OH^-] may be explained by the following equilibrium.

Table 3 — Influence of ionic strength (I) and relative permittivity on Ru(III) catalyzed oxidation of EDTA in aqueous alkaline medium at 25°C
[NBP] = 1.0×10^{-3} , [EDTA] = 2.0×10^{-2}
[OH^-] = 1.0×10^{-3} , I = 0.05 mol/dm^3

$I\times10^{-2}$ mol/dm^3	$K_c\times10^4(S^{-1})$	% of D t-butanol–water (v/v)		$K_c\times10^3$
1.0	2.16	5	75.18	2.92
3.0	2.52	10	71.94	3.76
5.0	2.73	15	68.49	4.15
7.0	3.25	20	65.35	5.37
10.0	4.12	30	58.47	6.63

Table 4 — Influence of initial addition of phthalimide on Ru(III) catalyzed oxidation of EDTA in aqueous alkaline medium at 25°C
[NBP] = 1.0×10^{-3} , [EDTA] = 2.0×10^{-2} , [SDS] = 1.0×10^{-3} , I = 0.05 mol/dm^3

$[NH]\times10^3$ (mol/dm^3)	$k_C\times10^3$ (s^{-1})	
	Experimental	Calculated
1.0	2.48	2.45
5.0	1.69	1.67
7.0	1.45	1.42
9.0	1.26	1.28
10.0	1.20	1.22

NH - Phathaliamide

Table 5 — Influence of temperature on Ru(III) catalyzed oxidation of EDTA in aqueous alkaline medium at 25°C.

[NBP] = 1.0×10^{-3} , [OH^{-}] = 1.0×10^{-5}
[EDTA] = 2.0×10^{-2} , I = 0.05 mol/dm^3

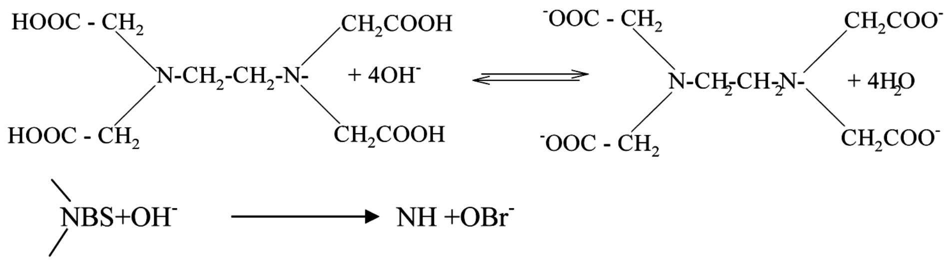
T* (k)	K×10^2 (dm^3 mol^{-1} s^{-1}	1/T×10^3 (K^{-1})	Log k
298	2.06	3.35	0.313
303	2.35	3.30	0.371
308	2.78	3.25	0.445
313	3.16	3.19	0.499

* Temperature

Table 6 — Thermodynamic parameters on Ru(III) catalyzed oxidation of EDTA in aqueous alkaline medium at 25°C

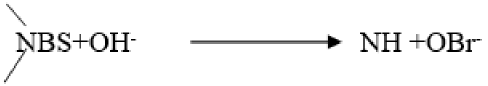
[NBP] = 1.0×10^{-3} , [Ru (III)] = 3.0×10^{-5} [EDTA] = 2.0×10^{-2} , I = 0.05/mol/dm^3

Activation Parameters	Catalysed Reaction	Uncatalysed Reaction
Ea (kJ mol^{-1})	42 ±1	48 ± 2 kJ
Δ$H^{\#}$ (kJ mol^{-1})	38 ± 3	52.0 ± 2.5
Δ$S^{\#}$(J K^{-1}mol^{-1})	–145 ± 5	–151.5± 6
Δ$G^{\#}$ (kJ mol^{-1})	86 ± 3	91 ± 4



Where, NH denotes the product succinimide.

Scheme 2



Where, NH denotes the product succinimide

$$\mathrm{NBP + H_2O \underset{}{\overset{k_1}{\rightleftharpoons}} HOBr{+}NHP} \quad \dots (1)$$

$$\mathrm{[RuCl_2(H_2O)(OH)_3] + Cl\text{-} \overset{k_2}{\rightleftharpoons} [RuCl_3(H_2O)\,(OH)_2]^- + HO^-} \quad \dots (2)$$

$$\mathrm{[RuCl_3(H_2O)(OH)_2]^- + HOBr \overset{k_3}{\rightleftharpoons} [RuCl_3(OBr)_2(H_2O)OH]^{2-}} \quad \dots (3)$$

$$\mathrm{[RuCl_3(OBr)_2{+}(H_2O)\,OH]^{2-} \underset{slow}{\overset{k}{\rightleftharpoons}} [RuCl_2(OBr)_2(H_2O)OH]^- + Cl\text{-}} \quad \dots (4)$$

The result suggest that active species of Ru(III) catalyst reacts with EDTA to form a and NBP in alkaline medium has the stoichiometry 2:1 (NBP:EDTA)[41]. The active species of NBP, reacts with anionic form of substrate in the second step to form a complex, then decomposes in slow step to form free radical intermediate, Br^{-} and Ru(III). This free radical reacts in fast steps with seven more molecules of active species of oxidant to form the products (Scheme 2). Such type of complex formation has been reported in other studies[14]. The stoichiometric observation satisfies the derived mechanism.

In the presence of catalyst the reaction is assumed to take place in parallel paths with support from the catalyzed and un catalyzed path.

Thus the above mechanism leads to rate law (5) $\mathrm{Rate_{cat} = rate_{Total} - rate_{uncat}}$

$$= \frac{\mathrm{kK_1K_2\,[NBP]_T[EDTA]_T\,[Ru(III)]_T\,(\,[OH^-\,] - [NHP])}}{\mathrm{[NHP] + K_2\,[NHP]\,[EDTA] + K_1(\,[OH\ ^-] - [NHP]) + K_1\,K_2\,[EDTA]\,([OH^-]_T\text{-}[NHP])}}$$

$$\mathrm{Rate_{cat}/[NBP] = k_c = k_T - k_u} \quad \dots (5)$$

It can be derived as follows

From Scheme 2 the rate law in the slow step is given by,

$$\mathrm{Rate{=}k[HOBr^-][C]} \quad \dots (6)$$

$$\mathrm{C = k_2[EDTA][Ru(III)]}$$

$$[HOBr^-] = \frac{K_1[NBP][OH^-]}{[NHP]} \quad \ldots (7)$$

Putting the values of $HOBr^-$ and C in the above rate equation (7), we get,

$$Rate = \frac{kK_1K_2[NBP][OH^-][Ru(III)][EDTA]}{[NHP]} \quad \ldots (8)$$

The total [NBP] may be expressed as,

$$[NBP]_T = [NBP]_f + [HOBr^-]$$

$$[NBP]_T = [NBP]_f + \frac{K1[NBP][OH^-]}{[NHP]}$$

$$[NBP]_T = \left[[NBP]_f \quad 1 + \frac{K_1[OH^-]}{[NHP]} \right]$$

$$[NBP]_f = \frac{[NBP]_T[NHP]}{[NHP]\ K_1[OH^-]} \quad \ldots (9)$$

Here f and T refers to free and total respectively

Similarly, total catalyst concentration $[Ru(III)]T$, may be obtained as

$[Ru(III)\ ]_T = [Ru(III)]_f + K_2\ [Ru(III)_f\ [EDTA]$

$= [Ru(III)]_f\{1 + K_2[EDTA]\}$

Therefore,

$$[Ru(III)]_f = \frac{[Ru(III)]_T}{1 + K_2[EDTA]} \quad \ldots (10)$$

The total concentration of EDTA is given by $[EDTA]_T = [EDTA]_f + [C]$

$= [EDTA]_f + K_2[Ru(III)])[EDTA]$

$= [EDTA]_f\ (1 + K_2[Ru(III)])$

$$[EDTA]_f = \frac{[EDTA]_T}{(1 + K_2[Ru(III)])}$$

Denominator approximately becomes unity due to low concentration of EDTA. Hence the above equation becomes,

$$[EDTA]_f = [EDTA]_T \quad \ldots (11)$$

The $[OH^-]_T$ is given by $[OH^- = [OH^-] + [NHP]$

Substituting the values of equation (8), (9), (10) and (11) in equation (8), we get

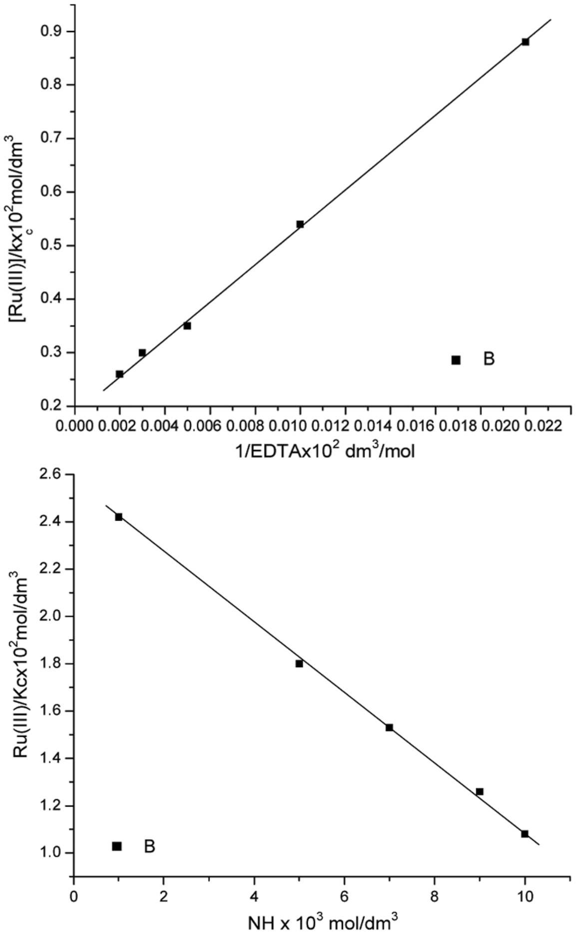


Fig. 7 — Verification of rate law (12) in the form of (13) (Conditions in Table 2)

$$Rate_{cat}/\ [NBP] = k_c = k_T - k_u$$

$$= \frac{kK_1K_2\ [NBP]_T[EDTA]_T\ [Os(VIII)]_T\ (\ [OH^-\ ] - [NHP])}{[NHP] + K_2\ [NHP]\ [EDTA] + K_1(\ [OH^-\ ] - [NHP]) + K_1\ K_2\ [EDTA]\ (\ [OH^-]_T - [NHP])} \quad \ldots (12)$$

Where k, K_1 and K_2 are the rate constant of slow step and equilibrium constants of steps 1 and 2 of Scheme 2 respectively.

Suitable rate law for verification can be obtained by the rearrangement of equation (6),

$$[Ru(III)]/\ k_c = \frac{[NHP]}{k\,K \cdot K_2\ [EDTA]\ (\ [OH^-]_T - [NHP])} + \frac{[NHP]}{k\,K_1\ (\ [OH^-]_T - [NHP])} + \frac{1}{k\,K_1\ [EDTA]} + \frac{1}{k} \quad \ldots (13)$$

According to Equation 13, plots of $[Ru(III)]\ /\ k_c$ *vs.* [NHP] and [Ru(III)]/ kc *vs.* 1/ [EDTA] should be linear (Fig. 7) at different temperatures. The slopes and intercepts of plots leads to the values of k, K_1 and K_2 were $(1.8 + 0.1)\times10^2$ dm^3 mol^{-1} s^{-1},

$1.8 + 0.1)\times 10^2$ dm^3 mol^{-1} and $58 + 2$ dm^3 mol^{-1} respectively. The obtained kinetic values are in good with earlier report [16]. Using these values, the rate constants over different conditions have been calculated and agree with the experimental rate constants. The value of Ea and ΔS^* by least square method was found to be $30 \pm 1 kJmol^{-1}$ and -135 ± 5 J $K^{-1}mol^{-1}$ respectively compared to un catalyzed reaction [15].

Importance of Work

It is motivating to note that the oxidizing property of NBP varies very much and decrease from acidic to basic medium[43-46]. The Ru(III) catalyst is identified to catalyzes a variety of reactions. The dynamic species of the catalyst was $[RuCl_2(H_2O)_3OH]^-$. The reaction constants in the mechanism were evaluated[47]. The activation parameters for the slow step and equilibrium constants were calculated and discussed. The overall mechanistic study described here is consistent with product.

Oxidation of EDTA with N-Bromophthalimide in the presence of catalyst has been studied in aqueous alkaline medium at 30°C. In the absence of catalyst reaction proceeds with a measurable rate, where as in the presence of catalyst the reaction occurs in a parallel path with contributions from the un-catalyzed and the catalyzed paths. Thus, the total rate constant (k_T) is equal to the sum of rate constants of catalyzed (k_c) and un-catalyzed (k_u) reactions. First- order kinetics was observed for Ru(III) at low concentration and has zero-order at higher concentrations. A positive effect for alkali concentration whereas negative effect for acid and phthalimide concentration was observed. The rate constant of slow step of Scheme 2 was obtained from the intercept of Ru(III)/ k_c *vs*. [NHS] plot. The catalytic effect on the reaction was understood by the difference in the activation parameters of the catalyzed and the un-catalyzed reactions.

References

1 a) DeMattos R T, Lachter E R, Elizabeth R, Neto A C, *Quim Nova*, 1 (1985) 17 ; b) Sharma J P, Singh R N P, Singh A K & Singh B, *Tetrahedron*, 42 (1986) 2739.

2 a) Kamble D L, Hugar G H & Nandibewoor S T, *Indian J Chem*, 35A (1996) 144 ; b) Kamble D L, Chougale R B & Nandibewoor S T, *Indian J Chem*, 35A (1996) 865; b) Saroja P, Kishore K B, Kandlikar S, *Indian J Chem*, 28A (1989) 501; c) Chougale R B, Kamble D L, Nandibewoor S T, *Polish J Chem*, 71 (1997) 986.

3 a) Hanna S B, Al-Hashimi S, Webb W H & Carroll W R, *Z Anal Chem*, 246 (1969) 231; b) Rao G N, *Indian J Chem*, 8 (1970) 328.

4 Sanehi E, Mehrotra R M & Mushran S P, *Z Naturforsch*, 28B (1973) 483.

5 Motekaitis R J, Martell A E & Hays D, *Can J Chem*, 58 (1980) 199.

6 Ito S, Matsuda T & Nagai T, *Talanta*, 27 (1980) 25.

7 Joshi G K, Katre Y R & Singh A K, J vol. 50, p. 367–376.(2009)

8 Taciolu S, *Tetrahedron*, 52 (1996) 11113.

9 Fendler J H & Fendler E J, *Catalysis in micellar and Macro molecular system*, (Academic Press, New York) 1975, p.308.

10 Fendler J H, *Membrane-Mimetic Chemistry*, (Wiley, NewYork), 1982.

11 Martinek K, Yatsimirsky A K, Levashov A V & Berezin I V, *Micellization, SolubilizationandMicro-emulsions, Mittal K L*, Vol 2, (Plenum, NewYork) 1977.

12 Bunton C A & Savelli G, *Adv Phys Org Chem*, 22 (1986) 213.

13 Bunton, C A, Nome F, Quina F H & Romsted L S, *Acc Chem Res*, 24 (1991) 357.

14 Bunton C A, *J Mol Liq*, 72 (1997) 231.

15 Romsted L S, Bunton C A & Yao J, *Curr Opin Colloid Interface Sci*, 2 (1997) 622.

16 Yunes S J, Gillitt N D & Bunton C A, *J Colloid Interface Sci*, 281 (2005) 482.

17 Bunton C A, *J Phys Org Chem*, 18 (2005) 115.

18 Whiddon C R, Bunton C A & Soderman O, *J Col-loid Interface Sci*, 278 (2004) 461.

19 Beber R C, Bunton C A, Savelli G & Nome F, Colloid Polym Sci, 128 (2004) 249.

20 Marco Chiarini, Nicholas D. Gillitt, Clifford A. Bunton, Langmuir, vol 18,(2002) p. 3836–3842.

21 Profio L P D, Germani R, Giacomini V, Savelli G & Bunton C A, *Langmuir*, 16 (2000) 222.

22 Germani R, Ponti P P, Savelli G, Spreti N, Capi-ciani A, Cerichelli G & Bunton C A, *J Phy Org Chem,* 2 (1989) 553.

23 KhatoryA, Kern F, Appel F, Morie G, Ott A & Urbach W, *Langmuir*, 9 (1993) 993.

24 Kumar S, Aswal V K, Singh H N, Goyal P S & Kabir-ud-Din, *Langmuir*, 10 (1994) 4069.

25 Hoiland H, Ljoslad E & Backlund S, *J Colloid Interface Sci*, 101 (1984) 467.

26 Feigl F & Anger V, *Spot testsinorganicAnalysis*, (Elsevier, New York) 1975, p. 256.

27 Imae T & Ikeda S, *Colloid Poly Sci*, 265 (1987) 1090.

28 Jabbar S F A & Rao V S, *Indian J Chem A*, 33 (1994) 69.

29 Krishnakumar V, Balachandran V & Chithambar-athanu T, *Spectrochim Acta Part A*, 62 (2005) 918.

30 Khazaei A & Manesh A A, J Braz Chem Soc, 16 (2005) 874.

31 Anjum A & Srinivas P, *Asian J Chem*, 17 (2005) 553.

32 Kirsch A & Luning U, *J Prakt Chem*, 340 (1998) 129.

33 Kirsch A, Luning U & Kruger U, *J Prakt Chem*, 341 (1999) 649.

34 Zachariah A, *Asian J Chem*, 15 (2003) 1567.

35 Day J C, Govindaraj N, McBain D S, Skell P S & Tanko J M, *J Org Chem*, 51 (1986) 4959.

36 Thiagarajan V & Ramakrishnan S, *Indian J Chem B*, 37 (1998) 443.

37 Ramachandrappa R, Puttaswamy S M M & Gowda N M M, *Int J Chem Kinet*, 30 (1998) 407.

38 Nair T D R & Zachariah A, *Asian J Chem*, 9 (1997) 297.
39 Filler R, *Chem Rev*, 63 (1963) 21.
40 Das C M & Indrasenan P, *Indian J Chem A,* 25 (1986) 605.
41 Das C M & Indrasenan P, *Indian J Chem A*, 26 (1987) 717.
42 Das C M & Indrasenan P, *Indian J Chem A*, 23 (1984) 869.
43 Berezin I V, Martinek K & Yatsimirskii A K, *Russ Chem Rev*, 42 (1973) 787.
44 Steigmam J & Shane N, *J Phys Chem*, 69 (1965) 968.
45 Menger F M & Jerkunica J M, *J Am Chem Soc*, 101 (1979) 1896.
46 Gillespie B E, Smith M J & Wyatt P A H, *J Chem Soc*, 89 (1969) 4698.
47 Bunton C A, Minch M, Hidalgo J & Sepulveda L, *J Am Chem Soc*, 95 (1973) 3262.