

## Kinetics and Mechanism of $[\text{Fe}(\text{bipy})_3]^{2+}$ and $[\text{BrO}_3^-]$ System in Aqueous Acidic Medium

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**Summary:** The kinetics of the oxidation of tris (2,2'-bipyridine)iron(II) ( $[\text{Fe}(\text{bipy})_3]^{2+}$ ) by bromate ion ( $\text{BrO}_3^-$ ) in aqueous medium have been investigated. The reaction was probed spectrophotometrically in the pH range 3.5-5.0, and from 0.01 to 0.1 mol/dm<sup>3</sup> ionic strength. The kinetic runs were pursued to more than two half lives of the reaction. The pseudo first order rate constant was found independent of the concentration of tris (2, 2'-bipyridine) iron (II), and increases with increasing concentration of bromate ion in the reaction mixture. Protonation of  $\text{BrO}_3^-$  in the acidic medium yields monoprotonated ( $\text{HBrO}_3$ ) and diprotonated ( $\text{H}_2\text{BrO}_3^+$ ) species. The rising figure of the rate constant upon lowering the pH refers to the involvement of protonated species in the rate-determining step. A rise in the value of the rate constant with increasing ionic strength implies, however, the diprotonated species,  $\text{H}_2\text{BrO}_3^+$ , as the reactive species among the two competing. Involvement of the other Br(V) species results in a complex reaction pathway, consequently. The rate law is suggested as follows:

$$\text{Rate} = k_1 [\text{Fe}((2,2'\text{-bipy})_3)^{2+}] [\text{HBrO}_3] + \frac{k_2 K_{ip} [\text{Fe}((2,2'\text{-bipy})_3)^{2+}] [\text{H}_2\text{BrO}_3^+]}{(1 + K_{ip} [\text{H}_2\text{BrO}_3^+])}$$

Key Words: Electron transfer reaction, Bromate, tris (2, 2'-bipyridine)iron(II), Ion-pair formation

### Introduction

Bromate ( $\text{BrO}_3^-$ ) is an inorganic ion which naturally exists in water reservoirs due to reaction of bromide ion with ozone [1]. Potassium salts of bromate have wide applications in different textile and food industries [2, 3]. Investigation declares reduction of bromate in water to yield bromide by the reaction with reduced forms of iron i.e. Fe (II), and, or, Fe (0)[4, 5].

Bromate with redox potential of 1.44 V [6] is a valuable chemical reagent, widely used as a powerful oxidizing agent. Kinetics of its reactions in acidic media is complex. In acidic medium Bromate has been widely used in the oxidations of various organic and inorganic compounds [7-14]. Oxidation of aquoiron (II) by bromate has been reported [15]. Simple and mixed second order kinetics with complex hydrogen ion dependence was suggested for this redox reaction. Oxidation of various metal ions by bromate ion has also been studied [16-20], these investigations include  $\text{Ce}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Np}^{5+}$ ,  $\text{VO}^{2+}$ ,  $\text{V}^{3+}$ ,  $\text{V}^{2+}$ ,  $\text{Hg}^0$ , and  $\text{U}^{4+}$  as the reducing agents.

The kinetics of the oxidation of transition metal complexes specifically the substitution inert complexes by bromate ion remained in focus of different researchers. These studies involved the high acidity regions of limited concentrations, where autocatalytic behavior is obvious, which was attributed to the bromine formation in the reactions. Kinetics and mechanism of oxidation of hexachloroiridate (III) [21] by bromate ion has been studied at high acidity (0.05-0.5 mol dm<sup>-3</sup>), 0.5 M ionic strength and at 25°C. No partial or totally autocatalytic behavior was observed. A few reports appeared that probe the oxidation of iron(II) complexes such as  $[\text{Fe}(\text{phen})_3]^{2+}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{bipy})(\text{CN})_4]^{2-}$ , and  $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$  by bromate in a

low pH range, from 0.2 to 2.5[22-25]. The kinetics of the oxidation of diaquotetrakis (2, 2'-bipy)- $\mu$ -oxodiruthenium (III) ion by bromate in aqueous perchloric medium has been investigated [26]. The reaction was proposed to occur by parallel acid-independent and acid dependent pathways suggesting  $\text{H}_2\text{BrO}_3^+$  and  $\text{BrO}_3^-$  as the reactive bromate species. Both pathways follow outer-sphere mechanism. The suggested rate law is:

$$-\frac{d[\text{RuORu}]^{4+}}{dt} = 5 [k + k_H [\text{H}^+]] [\text{BrO}_3^-]_T [\text{RuORu}^{4+}]$$

Birk and Kozub [25] pursued the kinetics of the redox reaction between  $[\text{Fe}(\text{bipy})_3]^{2+}$  and  $\text{BrO}_3^-$  under the condition of an excess concentration of bromate as well as protons (0.05-0.494 M). The reaction was concluded to be autocatalytic that proceeds by an outer - sphere mechanism. Suggestions and proposals were given on the basis of a few uncertain assumptions by considering the other Fe (II) complexes.

According to the surveyed literature, no further studies at high pH range are available for this reaction system. We, therefore, focus upon the kinetics of the redox reaction between  $[\text{Fe}(\text{bipy})_3]^{2+}$  and bromate in the moderate acidic medium within the pH range 3.5 – 5.0. This study brings to surface the issues and reasons behind them, which were not elucidated in previous studies.

### Experimental

#### Materials & Methods

All the chemicals used that include 2, 2' -bipyridine (CMS, UK), ferrous ammonium sulfate hexahydrate (Merck), sodium sulfate (Merck), sodium

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acetate (Merck), acetic acid (Merck) and Potassium bromate (Merck), were of analytical reagent grade (AR) and of the highest purity available. Distilled and deionized water was used for preparation of solutions.

All of the spectroscopic measurements were carried out with Shimadzu UV-1800, UV-Visible spectrophotometer using quartz cells equipped with a thermostated cell holder. pH measurements were done on digital HANNA pH meter (HI-8314 model) using combined glass electrodes, HI-1332 and digital pH – meter (1990 Orion research Inc Boston, MA02129 USA). Thermostat bath (HAAKE KT33) was used for maintaining the temperature of reagents before mixing.

#### Synthesis and Characterization of tris (2, 2'-bipyridine) iron (II) sulphate

Tris (2, 2'-bipyridine) iron (II) sulphate complex was synthesized by the method [27]. The complex was characterized on the basis of UV/visible spectrum by monitoring absorption spectrum and the absorption maximum by employing Shimadzu UV1800, UV-Visible recording spectrophotometer. The absorption maximum ( $\lambda_{\max}$ ) of complex was found to be 522 nm. While, the molar extinction coefficient ( $\epsilon$ ) of complex was calculated through plotting a working curve of absorbance as a function of concentration at  $\lambda_{\max}$  522 nm by considering Beer-Lambert's law ( $A = \epsilon b c$ ), where, A=absorbance of absorbing species,  $\epsilon$  = molar extinction coefficient, b=cell path length and c=concentration of absorbing species. The curve yields as  $8600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . This value is in close agreement with the one mentioned in literature [28].

#### Procedure

The reaction between  $[\text{Fe} (2, 2\text{-bipy})_3]^{2+}$  and  $\text{BrO}_3^-$  was performed under pseudo-first order condition. The concentration of  $\text{BrO}_3^-$  was always in excess over  $[\text{Fe} (2, 2\text{-bipy})_3]^{2+}$ . The pH of the solution was acquired to the desired value by sodium acetate-acetic acid buffer that helped to maintain acidic medium within the range from 3.5 to 5.0. Sodium sulphate was used to maintain the ionic strength in the reaction mixture, and to provide a range from 0.01 to 0.1  $\text{mol dm}^{-3}$ . The reactants such as  $[\text{Fe} (2, 2\text{-bipy})_3]^{2+}$ ,  $\text{BrO}_3^-$ ,  $\text{Na}_2\text{SO}_4$  and buffer were mixed in the quartz cell (1 cm) to a total volume of 3-ml to retain different ratios. The temperature of the reaction was maintained at 300 K.

The kinetic measurements were performed spectrophotometrically. A change in the optical density of complex at 522 nm was recorded as a function of time (with a difference of 1 second) for each set of reaction. The value, 522 nm, is the wavelength of maximum absorption of  $[\text{Fe} (2, 2\text{-bipy})_3]^{2+}$ . The rate constants were evaluated by following integrated rate equation. A plot of  $\ln A_t$  versus time yields a slope

equivalent to pseudo-first order rate constant ( $k_{\text{obs}}$ ). All the plots were linear to a more than 50% completion of the reaction with an intercept.

### Results and Discussion

#### Effect of Variation in the Concentration of tris (2, 2'-bipyridine) iron (II) on $k_{\text{obs}}$

Different sets of experiment were performed to study the influence of variation in the concentration of the complex on the rate of reaction. The kinetic runs were carried out by varying the concentration of  $[\text{Fe} (2, 2\text{-bipy})_3]^{2+}$  from  $1.0 \times 10^{-5}$  to  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$  keeping all other experimental conditions constant such as  $[\text{BrO}_3^-]$  ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ), pH (3.8) and  $\mu$  (0.01  $\text{mol dm}^{-3}$ ). The observed pseudo-first order rate constant ( $k_{\text{obs}}$ ) was found to be independent of  $[\text{Fe} (2, 2\text{-bipy})_3]^{2+}$  (Table-1, Fig 1). This pattern confirms the first order with respect to  $[\text{Fe} (2, 2\text{-bipy})_3]^{2+}$ .

Table-1: Dependence of pseudo first order rate constant ( $k_{\text{obs}}$ ) on  $[\text{Fe} (2, 2\text{-bipy})_3]^{2+}$ .

S. No.	$[\text{Fe}(2,2'\text{-bipy})_3]^{2+} / 10^{-4} \text{ mol dm}^{-3}$	$k_{\text{obs}} / 10^{-2} \text{ s}^{-1}$
1	0.1	2.50
2	0.2	2.52
3	0.4	2.60
4	0.6	2.50
5	0.8	2.52
6	1.0	2.50
7	3.0	2.53
8	4.0	2.50
9	5.0	2.50

$[\text{BrO}_3^-] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ , pH = 3.8,  $\mu = 0.01 \text{ mol dm}^{-3}$ , T = 300 K,  $\lambda_{\max} = 522 \text{ nm}$

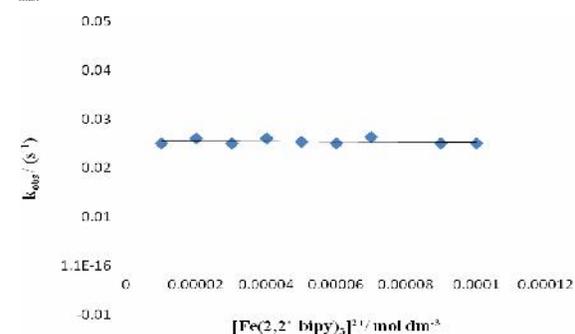


Fig. 1: A Plot of pseudo-first order rate constant ( $k_{\text{obs}}$ ) versus  $[\text{Fe} (2, 2\text{-bipy})_3]^{2+}$  for redox reaction between  $[\text{Fe} (2, 2\text{-bipy})_3]^{2+}$  and  $[\text{BrO}_3^-]$  at pH 3.8, 0.01  $\text{mol dm}^{-3}$  ionic strength and at 300 K temperature.

#### Effect of Variation in Concentration of Bromate on $k_{\text{obs}}$

To study the sway of variation in concentration of bromate ( $1 \times 10^{-2}$  to  $8 \times 10^{-4} \text{ mol dm}^{-3}$ ) over the rate of reaction, all the experimental conditions were kept constant. The concentration of  $[\text{Fe} (2, 2\text{-bipy})_3]^{2+}$  ( $1 \times 10^{-4} \text{ mol dm}^{-3}$ ), pH (3.8), and  $\mu$  (0.025  $\text{mol dm}^{-3}$ ) were fixed. Sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) was used to maintain the ionic strength of the reaction system.

Different sets of experiments were performed. The observed absorbance-time data was plotted as  $\ln A_t$  versus time. The values of pseudo first order rate constant  $k_{obs}$  were evaluated from the gradient of these plots (Table-2). Results show that the value of the rate constant increases with increasing concentration of bromate up to a saturation point at higher concentrations. When the values of  $k_{obs}$  for different sets of experiments were plotted as a function of  $[\text{BrO}_3^-]$  (Fig 2), a nonlinear curve is obtained. This reflects involvement of more than a single species of bromate ion in the reaction. Bromate is very well known to be protonated in acidic medium, and yields mono/di-protonated species [29]. According to the revealed studies [30]  $\text{HBrO}_3$  and  $\text{H}_2\text{BrO}_3^+$  are the existing species of Br (V) in moderately strong acid medium. The saturation point at higher concentrations of bromate ion helps to recognize the leading character of the protonated species, as a fixed pH provides a limiting factor to protonation. Whereas, a plot of  $1/k_{obs}$  versus  $1/[\text{BrO}_3^-]$  is linear with a positive and non-zero intercept (Fig 3) which is indicative of ion pair formation between charged species.

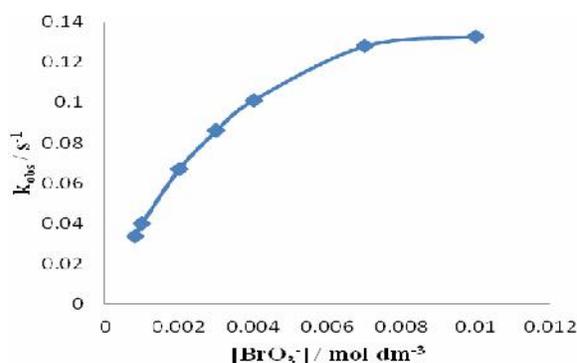


Fig. 2: A Plot of pseudo-first order rate constant ( $k_{obs}$ ) versus  $[\text{BrO}_3^-]$  for redox reaction between  $[\text{Fe}(2, 2\text{'-bipy})_3]^{2+}$  and  $[\text{BrO}_3^-]$  at pH 3.8, 0.025 mol  $\text{dm}^{-3}$  ionic strength and at 300 K temperature

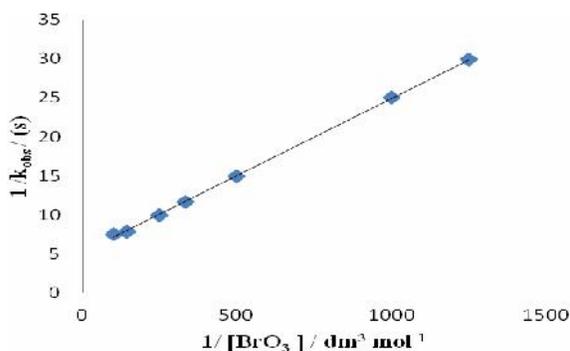


Fig. 3: A Plot of  $1/k_{obs}$  versus  $1/[\text{BrO}_3^-]$  for electron transfer reaction between  $[\text{Fe}(2, 2\text{'-bipy})_3]^{2+}$  and  $[\text{BrO}_3^-]$ .

Table-2: Dependence of pseudo first order rate constant ( $k_{obs}$ ) on  $[\text{BrO}_3^-]$ .

S. No.	$[\text{BrO}_3^-] / 10^{-3} \text{mol dm}^{-3}$	$k_{obs} / 10^{-2} (\text{s}^{-1})$
1	0.8	3.34
2	1.0	4.01
3	2.0	6.7
4	3.0	8.6
5	4.0	10.1
6	7.0	12.8
7	10.0	13.3

$[\text{Fe}(2, 2\text{'-bipy})_3]^{2+} = 1 \times 10^{-4} \text{mol dm}^{-3}$ , pH = 3.8,  $\mu = 0.025 \text{mol dm}^{-3}$ , T = 300 K,  $\lambda_{max} = 522 \text{nm}$

#### Effect of the Concentration of Protons on $k_{obs}$

To investigate the dependence of the rate of reduction of bromate on  $[\text{H}^+]$ , various sets of experiments were performed by varying pH from 3.5 – 5.0. The pH was maintained by sodium acetate - acetic acid buffer under fixed experimental conditions ( $[\text{Fe}(2, 2\text{'-bipy})_3]^{2+} = 1 \times 10^{-4} \text{mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = 4 \times 10^{-3} \text{mol dm}^{-3}$ ,  $\mu = 0.025 \text{mol dm}^{-3}$ ). Values of pseudo first order rate constant were obtained from gradient of the plots of  $\ln A_t$  versus time (Table-3). A plot of  $k_{obs}$  versus  $[\text{H}^+]$  was non-linear (Fig. 4), while a plot of  $1/k_{obs}$  versus  $1/[\text{H}^+]$  is linear with a non-zero intercept (Fig. 5). The linearity of the curve is an indication of the leading role of protonated bromate species in the rate-determining step. The intercept, however represents the involvement of deprotonated bromate ion ( $\text{BrO}_3^-$ ). Stooping of the linear pattern at higher concentrations of protons is justifiable considering the fixed concentration of bromate ions in the reaction mixture, which acts as the limiting reactant.

Table 3: Dependence of pseudo first order rate constant ( $k_{obs}$ ) on  $[\text{H}^+]$

S. No.	$[\text{H}^+] / 10^{-4} \text{mol dm}^{-3}$	$k_{obs} / 10^{-2} (\text{s}^{-1})$
1	3.16	10.56
2	2.51	10.43
3	1.995	10.30
4	1.58	10.10
5	1.00	9.52
6	0.631	8.71
7	0.398	7.71
8	0.251	6.53
9	0.158	5.26
10	0.100	6.70

$[\text{Fe}(2, 2\text{'-bipy})_3]^{2+} = 1 \times 10^{-4} \text{mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = 4 \times 10^{-3} \text{mol dm}^{-3}$ ,  $\mu = 0.025 \text{mol dm}^{-3}$ , T = 300 K,  $\lambda_{max} = 522 \text{nm}$

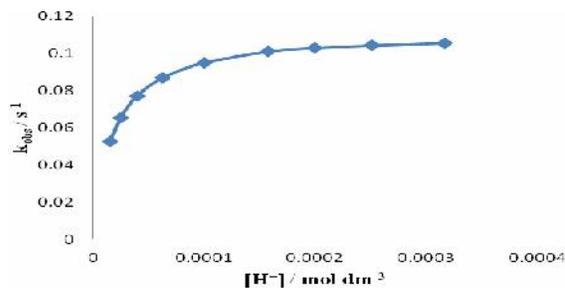


Fig. 4: A Plot of pseudo-first order rate constant ( $k_{obs}$ ) versus  $[\text{H}^+]$  for redox reaction between  $[\text{Fe}(2, 2\text{'-bipy})_3]^{2+}$  and  $[\text{BrO}_3^-]$  at 0.025 mol  $\text{dm}^{-3}$  ionic strength and at 300 K temperature.

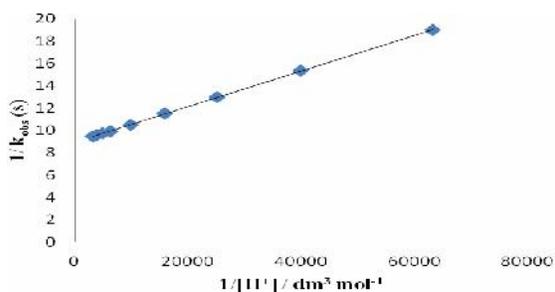


Fig. 5: A Plot of  $1/k_{obs}$  versus  $1/[H^+]$  for electron transfer reaction between  $[Fe(2,2'-bipy)_3]^{2+}$  and  $[BrO_3^-]$ .

#### Influence of Ionic Strength on $k_{obs}$

Primary kinetic salt effect on the rate of reaction was investigated by adding inert salt  $Na_2SO_4$  to the reaction mixture to maintain the ionic strength within the range,  $0.01-0.1 \text{ mol dm}^{-3}$ . The influence of ionic strength over the observed rate constant was monitored at fixed conditions i.e.,  $[Fe(2,2'-bipy)_3]^{2+} = 1 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[BrO_3^-] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $pH = 3.8$ . An increasing value of the rate constant upon scaling ionic strength (Table-4) confirms the involvement of the positively charged ions in the rate-determining step. This observation verifies  $[Fe(2,2'-bipy)_3]^{2+}$  and  $H_2BrO_3^+$  as the active species to control the rate of reaction. When a graph is plotted between  $\log k_{obs}$  and  $\mu$ , a straight line with a positive slope is obtained (Fig. 6). The gradient of the line yields  $Z_A Z_B$  as  $+1.60$ , which is very close to the expected value  $+2$ .

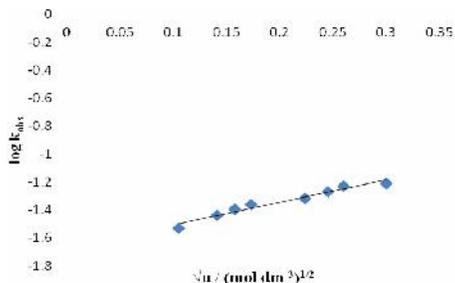


Fig. 6: Plot of  $\log k_{obs}$  versus  $\mu$ , in order to determine the influence of ionic strength on pseudo-first order rate constant ( $k_{obs}$ ) for the electron transfer reaction between  $[Fe(2,2'-bipy)_3]^{2+}$  and  $[BrO_3^-]$  at  $pH 3.8$  and  $300 \text{ K}$  temperature.

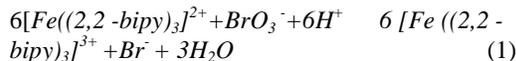
Table-4: Dependence of pseudo first order rate constant ( $k_{obs}$ ) on Ionic Strength of Medium.

S. No.	$\mu / 10^2 \text{ mol dm}^{-3}$	$k_{obs} / 10^{-2} \text{ s}^{-1}$	$(\mu)^{1/2}$	$\log k_{obs}$
1	1.0	2.50	0.105	-1.60
2	2.0	3.63	0.141	-1.44
3	2.5	4.01	0.158	-1.40
4	3.0	4.40	0.173	-1.36
5	5.0	4.80	0.224	-1.32
6	6.0	5.40	0.245	-1.27
7	7.0	5.90	0.265	-1.23
8	9.0	6.20	0.300	-1.21

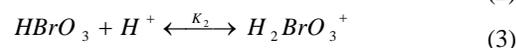
$[BrO_3^-] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[Fe(2,2'-bipy)_3]^{2+} = 1 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $pH = 3.8$ ,  $T = 300 \text{ K}$ ,  $\lambda_{max} = 522 \text{ nm}$

#### Proposed Reaction Mechanism

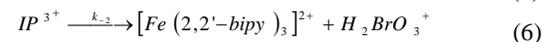
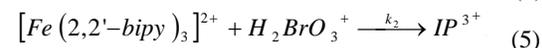
The stoichiometry of the oxidation reaction of  $[Fe(bipy)_3]^{2+}$  by  $BrO_3^-$ , when  $BrO_3^- \gg [Fe(bipy)_3]^{2+}$ , established earlier in the preliminary part of experiment by following the procedure [24]. Stoichiometry was found to be 6:1 as shown in equation(1):



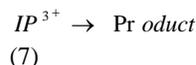
According to the obtained data and concluded results, we propose an initial protonation of the bromate ions to yield a neutral monoprotonated and diprotonated bromate species<sup>[29]</sup>, as follows:



On the basis of evidences gathered from our data and in view of literature, we therefore propose the following reaction scheme. Where, equations 4 and 5 are suggested to be the rate-determining steps.



where,  $IP^{3+}$  (Ion Pair) =  $([Fe(2,2'-bipy)_3] \cdot [H_2BrO_3^+])^{3+}$  and  $k_2/k_3 = K_{ip}$  (Ion pair formation constant)



Considering the kinetic data we propose the following rate equation:

$$\text{Rate} = k_1 [Fe(2,2'-bipy)_3]^{2+} [HBrO_3] + \frac{k_2 K_{ip} [Fe(2,2'-bipy)_3]^{2+} [H_2BrO_3^+]}{(1 + K_{ip} [H_2BrO_3^+])} \quad (8)$$

where,  $K_{ip}$  = ion pair formation constant.

The equilibrium between monoprotonated bromate compound and diprotonated bromate ion is considered;

$$K_2 = \frac{[H_2BrO_3^+]}{[HBrO_3][H^+]} \quad (9)$$

where,  $[HBrO_3]$  is the molar concentration of monoprotonated bromate species in the reaction mixture.

By rearranging equation(9), we get equation(10) as follows:

$$[HBrO_3] = \frac{[H_2BrO_3^+]}{K_2 [H^+]} \quad (10)$$

Inserting the value of  $[HBrO_3]$  from equation (10) in equation (8) we get equation (11)

$$\text{Rate} = k_1 [\text{Fe}((2,2\text{'-bipy})_3)^{2+}] \frac{[\text{H}_2\text{BrO}_3^+]}{K_2[\text{H}^+]} + \frac{k_2 K_{ip} [\text{Fe}((2,2\text{'-bipy})_3)^{2+}] [\text{H}_2\text{BrO}_3^+]}{(1 + K_{ip}[\text{H}_2\text{BrO}_3^+])} \quad (11)$$

Since, the concentration of bromate ions in the reaction mixture is sufficiently high to yield considerable amounts of monoprotonated and diprotonated species corresponding to the constant concentration of bromate ion, then  $[\text{BrO}_3^-]_{\text{T}}$  may suppose to become equalized to  $[\text{HBrO}_3]$  and  $[\text{H}_2\text{BrO}_3^+]$ . Therefore;

$$[\text{BrO}_3^-]_{\text{T}} = [\text{HBrO}_3] + [\text{H}_2\text{BrO}_3^+] \quad (12)$$

and, by inserting the value of  $[\text{HBrO}_3]$  from equation (10) in equation (12) and further solving leads towards equation(13);

$$[\text{H}_2\text{BrO}_3^+] = \frac{K_2[\text{H}^+][\text{BrO}_3^-]_{\text{T}}}{(1 + K_2[\text{H}^+])} \quad (13)$$

Substituting the value of  $[\text{H}_2\text{BrO}_3^+]$  from equation (13) into equation (11), and considering the pseudo- first order reaction condition i.e.,  $[\text{Fe}(\text{bipy})_3]^{2+} \ll [\text{BrO}_3^-]_{\text{T}}$ , we get equation(14);

$$k_{\text{obs}} = \frac{k_2 K_2 K_{ip} [\text{H}^+] [\text{BrO}_3^-]_{\text{T}}}{(1 + k_2 K_2 K_{ip} [\text{H}^+] [\text{BrO}_3^-]_{\text{T}})} \quad (14)$$

Reported value of  $\text{p}K_a$  of  $\text{H}_2\text{BrO}_3^+/\text{HBrO}_3$  couple is 0.68 that gives  $K_a$  as 0.21 [30] where,  $K_a$  is the dissociation constant of  $\text{H}_2\text{BrO}_3^+$ . From  $K_a$  the value of  $K_2$  was calculated to be 4.762.

Therefore, either at constant pH or at constant  $[\text{BrO}_3^-]$  of reaction mixture equation (14) provides equation (15);

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_2 K_{ip} K_2 [\text{H}^+] [\text{BrO}_3^-]_{\text{T}}} + \frac{1}{k_2} \quad (15)$$

According to equation (15), at fixed  $[\text{H}^+]$  concentration  $1.58 \times 10^{-4} \text{ mol dm}^{-3}$  corresponding to the  $\text{pH}=3.8$ , a plot of  $1/k_{\text{obs}}$  versus  $1/[\text{BrO}_3^-]_{\text{T}}$  and at fixed concentration of bromate ( $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ), a plot of  $1/k_{\text{obs}}$  versus  $1/[\text{H}^+]$  should be linear with intercept. This is verified from Fig. 3 and 5, from intercept the value of  $k_2$  is calculated to be 0.195 and  $0.112 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  respectively from the two plots. While, from slope the value of  $K_{ip}$  is calculated to be  $3.44 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$  and  $2.34 \times 10^5$  respectively. This verifies the proposed mechanism.

## Conclusions

The kinetics of electron transfer reaction between  $[\text{Fe}((2,2\text{'-bipy})_3)^{2+}]$  and  $[\text{BrO}_3^-]$  ions under the conditions with  $[\text{BrO}_3^-]$   $[\text{Fe}((2,2\text{'-bipy})_3)^{2+}]$  and within the employed pH range (3.5-4.8) indicates  $\text{H}_2\text{BrO}_3^+$  as active Br(V) species. The reaction between  $[\text{Fe}((2,2\text{'-bipy})_3)^{2+}]$  and  $[\text{BrO}_3^-]$  is proposed to follow an outer-sphere mechanism. In addition, no formation of  $\text{Br}_2$  and no autocatalysis was observed during the course of experiment.

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## References

1. W. R. Haag and J. Hoig e, Ozonation of Bromide-Containing Waters: Kinetics of Formation of Hypobromous Acid and Bromate, *Env. Sci. Tech.*, **17**, 261(1983).
2. R. B. Mack, Round Up the Usual Suspects. Potassium Bromate Poisoning, *North Carolina Medical Journal*, **49**, 243 (1988).
3. US FDA, Code of Federal Regulations, Vol.21, *Food and Drugs*, Part 136-137 and 172-730 (1994).
4. L. Xie, C. Shang, The Effects of Operational Parameters and Common Anions on the Reactivity of Zero-Valent Iron in Bromate Reduction, *Chemosphere.*, **66**, 1652 (2007).
5. M. Siddiqui, G. Amy, K. Ozekin, W. Y. Zhai and P. Westerhoff, Removal of Bromate after Ozonation during Drinking Water Treatment *J. Am. Water Works. Ass.*, **86**, 81(1994).
6. J. U. Lurie, "Hand book of Analytical Chemistry", Mir Publishers, Moscow, p. 301 (1975).
7. H. Taube, "Electron Transfer Reactions of Complex Ions in Solution", Academic, New York, (1970).
8. A. Anderson and N. A. Bonner, The Exchange Reaction Between Chromous and Chromic Ions in Perchloric Acid Solution, *J. Am. Chem. Soc.*, **76**, 3826 (1954).
9. H. Taube and H. Mayers, Evidence for a Bridged Activated Complex for Electron Transfer Reactions, *J. Am. Chem. Soc.*, **76**, 2103 (1954).
10. H. Taube and E. L. King, The Bridged Activated Complex for the Electron Exchange of Chromium(II) and Monochlorochromium(III) Ion, *J. Am. Chem. Soc.*, **76**, 4053 (1954).
11. H. Taube, H. Mayers, and R. L. Rich, "The Mechanism of Electron Transfer in Solution", *J. Am. Chem. Soc.*, **75**, 4118 (1953).
12. K. W. Hicks, D. L. Toppen, R. G. Linck, Inner-Sphere Electron-Transfer Reactions of vanadium(II) with Azidoamine Complexes of Cobalt(III), *Inorg. Chem*, **11**, 310 (1972).
13. H. Taube, Anions as Bridging and Non-bridging Ligands in Reactions of Co(III) Compounds with  $\text{Cr}^{++}$ , *J. Am. Chem. Soc.*, **77**, 4481 (1955).
14. H. Taube and E. L. King, The Bridged Activated Complex for the Electron Exchange of Chromium(II) and Monochlorochromium(III) Ion, *J. Am. Chem. Soc.*, **76**, 4053 (1954).
15. J. P. Birk, Mechanism of the Bromate in Oxidation of Aquoiron (II), *Inorg. Chem.*, **12**, 2468 (1973).
16. R. M. Noyes, R. J. Field and R. C. Thompson, Mechanism of Reaction of Bromine(V) with Weak

- One-Electron Reducing Agents, *J. Am. Chem. Soc.*, **93**, 7315 (1971).
17. G. C. Knight and R. C. Thompson, Kinetic Study of the Reduction of Bromate Ion by Neptunium (V) in perchlorate solution, *Inorg. Chem.*, **12**, 63 (1973).
  18. R. C. Thompson, Kinetic Study of the Reduction of Bromate Ion by Oxovanadium (IV) in Perchlorate Solution, *Inorg. Chem.*, **10**, 1892 (1971).
  19. A. Bakac, A. J. Thornton and A. G. Sykes, Mechanistic Studies on the Vanadium (II) and Vanadium (III) Reductions of Iodate and Bromate, *Inorg. Chem.*, **15**, 274 (1976).
  20. R. Davies, B. Kipling and A. G. Sykes, Mechanistic Studies of One- and Two-Equivalent Oxidations of the Mercury(I) Dimer, *J. Am. Chem. Soc.*, **95**, 7250 (1973).
  21. J. P. Birk, Kinetics and Mechanism of the Reduction of Bromate Ion by Hexachloroiridate (III), *Inorg. Chem.*, **17**, 504 (1978).
  22. M. Ali, Kinetic Studies on the Bromate Ion Oxidation of 12-tungstocobaltate(II) in Aqueous Acid, *Trans. Met. Chem.*, **28**, 345 (2003).
  23. J. P. Birk and S. G. Kozub, Mechanism of the Reduction of Bromate Ion by hexacyanoferrate (II) and by Bromide Ion in Acidic Aqueous Solution, *Inorg. Chem.*, **12**, 2460 (1973).
  24. G. Rabai and I. R. Epstein, Kinetics And Mechanism Of The Oxidation Of Hexacyanoferrate (II) By Bromate, *Inorg. Chem.*, **28**, 732 (1989).
  25. J. P. Birk and S. G. Kozub, Mechanism of the Reduction of Bromate ion by cyano(bipyridyl)iron(II) Complexes, *Inorg. Chem.*, **17**, 1186 (1978).
  26. J. F. Iyun, G. A. Ayoko, Y. N. Lohdip, The Kinetics and Mechanism of the Oxidation of diaquotetrakis(2,2-bipyridine)- $\mu$ -oxodiruthenium(III) Ion by Bromate in Aqueous Perchloric Acid, *Polyhedron.*, **11**, 2389 (1992).
  27. R. C. Taylor, J. S. Schilt, Infra-Red Spectra of 1:10-Phenanthroline Metal Complexes in the Rock Salt Region below 2000  $\text{cm}^{-1}$ , *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).
  28. P. Krumholtz, Ferrous Mono- , -dipyridyl, *J. Am. Chem. Soc.*, **71**, 3654 (1949).
  29. J. O. Edward, Rate Laws and Mechanisms of Oxyanion Reactions with Bases, *Chem. Rev.*, **50**, 455 (1952).
  30. M. T. Beck, G. Rabai and G. Bazsa, Kinetic Investigation of the Bromate-Ascorbic Acid-Malonic Acid System, *Int. J. Chem. Kinet.*, **13**, 1277 (1981).