



Mechanism of the Redox Reaction of Hydroxylamine and Bromate Ions in Aqueous Hydrochloric Acid Medium

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ABSTRACT

Redox kinetics of the reaction of hydroxylamine hydrochloride ($H_2NOH.HCl$) and BrO_3^- was carried out in aqueous acidic medium, at temperature of $29.5 \pm 0.5^\circ C$; ionic strength $\mu = 1.0 \text{ mol dm}^{-3}$ ($NaCl$), $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ (HCl). The reaction showed a stoichiometry of 1:1.3, first order kinetics in both $[NH_3OH^+]$ and $[BrO_3^-]$, dependence on acid concentrations, positive salt effect, catalysis due to anions and absence of evidence of intermediate complex formation. Rate equation for the reaction has been proposed as: $-d[NH_3OH^+]/dt = (a[H^+])[NH_3OH^+][BrO_3^-]$. The second order rate constant for the $NH_3OH^+ - BrO_3^-$ reaction was found to be $0.233 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Based on the results obtained experimentally, the outer - sphere mechanism is suggested for the reaction.

Keywords: redox, kinetics, mechanism, catalysis, salt effect.

INTRODUCTION

Hydroxylammonium chloride is the hydrochloric acid salt of hydroxylamine, which is a biological intermediate in the nitrification (biological oxidation of ammonia with oxygen into nitrite) and in the anammox (biological oxidation of nitrite and ammonium into dinitrogen gas) which are important in the nitrogen cycle in soil and in waste water treatment [1]. It is used in organic synthesis for preparation of oximes and hydroxamic acids from carboxylic acids. During the acetyl bromide method of extracting lignin from lignocellulosic biomass, it has been used to remove bromine and polybromide from the solution [2]. In surface treatments, it is used in the preparation of anti - skinning agents, corrosion inhibitors and cleaner additives. It is also a starting material for pharmaceuticals and agrochemicals manufacturing. In the rubber and plastic industries, it is an antioxidant, vulcanization accelerator and radical scavenger. It is also used as a fixative for textile dyes, auxiliary in some dyeing processes, as a metal extraction and flotation aid, as an antioxidant in fatty acids and soaps and as a colour stabilizer and emulsion additive in colour films. It is oxidized by nitrous and nitric acids [3], monochloramine [4], and 12-tungstocobaltate (III) [5].

Literature has shown that despite its numerous applications, kinetics of its redox reaction is scanty.

Bromate, an oxyanion, is a versatile oxidizing agent [6-10]. It oxidizes and is itself reduced to bromide. Bromate ion reaction with real and synthetic gastric juices has been documented [10]. This work is carried out to obtain relevant kinetic data for the hydroxylammonium chloride and bromate redox reactions and the plausible mechanism involved in the reaction. This would aid understanding of reactions involved in their applications.

MATERIALS AND METHODS

Preparation of reagents

All chemicals and reagents used in the work were analar grade and were used without further purification. HCl was used to furnish H^+ to the reaction, $KBrO_3$ was used as the oxidant and NaCl was used to maintain a constant ionic strength for each run. Hydroxylammonium chloride, the oxidant and the other solutions were prepared with distilled water.

The rate of reactions of the oxidant (BrO_3^-) and the reductant (NH_3OH^+) were studied by monitoring increase in absorbance of the product solution 400 nm using Corning Colorimeter 252. All kinetic measurements were carried out under pseudo-first order conditions with [oxidant] concentrations in excess of the [reductant] at temperature of 29.5 ± 0.5 °C, ionic strength of 1.0 mol dm^{-3} and $[H^+] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$. The pseudo-first order plots of $\log (A_t - A_\infty)$ against time were made and the slope of the plots gave the pseudo- first order rate constant, k_1 . The second – order rate constants, k_2 , were determined from k_1 as $k_1/[BrO_3^-]$.

RESULTS AND DISCUSSION

Stoichiometry

Stoichiometric studies show that one mole of NH_3OH^+ are consumed by one mole of BrO_3^- , which conforms to the equation (1).



Order of reaction

Plots of $\log (A_t - A_\infty)$ versus time obtained under pseudo-first order conditions were linear for almost 100% of the reactions. (A_t and A_∞ are the absorbances of the complex at time 't' and at the end of the reaction respectively), suggesting that the reaction is first order with respect to $[NH_3OH^+]$. Pseudo-first order rate constants, k_1 , for the plots were obtained from the slope of the plots of $\log (A_t - A_\infty)$ versus time. Order of reaction was obtained from the slope of the plots of $\log k_{obs}$ versus $\log [BrO_3^-]$, which was 0.96 ± 0.03 (Fig. 1), suggesting that the reaction is first order in $[BrO_3^-]$. This means that the reaction is second order overall and the second order rate constant determined from $k_1/[BrO_3^-]$ are reported in Table 1. The rate law can therefore be represented by equation (2).

$$-d[NH_3OH^+]/ dt = k_2 [NH_3OH^+][BrO_3^-] \quad \dots\dots\dots(2)$$

The second order rate constants, k_2 , calculated from $k_1/[BrO_3^-]$ were fairly constant, and the average was found to be $(0.233 \pm 0.002) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Effect of acid on the reaction rate

In the acid range used ($5.00 \times 10^{-3} \leq [\text{H}^+] \leq 3.00 \times 10^{-2} \text{ mol dm}^{-3}$), rate of reaction increased with increase in $[\text{H}^+]$. (Table 1). Plot of $\log k_1$ versus $\log [\text{H}^+]$ gave a slope of 1.07, suggesting a first order acid dependence (Figure 2). Plot of acid dependent second order rate constant, k_{H^+} versus $[\text{H}^+]$ is linear without an intercept with a slope of $25.78 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ (Figure 3). The H^+ dependent second order rate constant can thus be presented by equation (3).

$$k_2 = a[\text{H}^+] \dots\dots\dots(3)$$

Acid dependence of this nature indicates that equilibrium between protonated and deprotonated forms of a reactant prior to the rate determining step is rapid, that the equilibrium constant for protonation is small and is not complete at high acidities, only the protonated species is reactive [11].

Literature review on the redox reactions of bromated ions shows some interesting features [12]. Cases of parallel inner- and outersphere mechanism for the acid dependent and acid independent pathways respectively have been observed [13-14]. In some cases, rate comparison and Marcus theory [15] have been used to diagnose parallel outersphere bromate reductions [13]

In the range of $[\text{H}^+]$ used, the overall rate equation is represented by equation (4).

$$-d[\text{NH}_3\text{OH}^+]/dt = a[\text{H}^+][\text{NH}_3\text{OH}^+][\text{BrO}_3^-] \dots\dots\dots(4)$$

Effect of ionic strength and medium dielectric constant on reaction rate

The rate of reaction was found to increase with increase in ionic strength. The results are presented in Table 1. Plot of $\log k_2$ versus $\sqrt{\mu}$ (Figure 4) shows a positive Bronsted – Debye salt effect with a gradient of 1.35. This observation suggests that reactant ions of like charges are involved in the slow step and that each of these ions have univalent charge.

However, this result is at variance with the observation made on varying the dielectric constant, D from 73.2 to 81 as described in our earlier report [16]. Increase in D caused diminution in the rate of the reaction. This is indicative of reaction occurring between oppositely charged ions. The values obtained from the variation of ionic strength of reaction medium on the reaction rate and its variance with that obtained when D was varied probably suggest that more than one route for the reaction [11, 17]

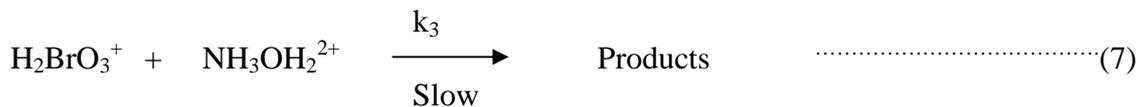
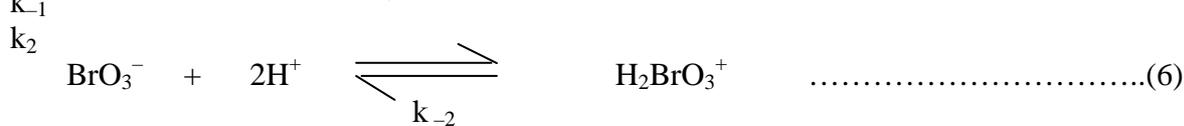
Effect of added ions on reaction rate

Added SO_4^{2-} and NO_3^- in the range $1 \times 10^{-3} \leq [\text{M}^{n+}] \leq 1 \times 10^{-1} \text{ mol dm}^{-3}$ decreased the rate of reaction (Table 4). This effect is reminiscent of occurring via outersphere mechanistic pathway.

Test for intermediate complex

Michaelis – Menten plot of $1/k_1$ versus $1/[\text{BrO}_3^-]$ gave a straight line without an intercept (Figure 5), suggesting that participation possible reaction intermediates is unlikely. Also, spectrophotometric test did not show any shift any λ_{max} as the reaction progressed thereby ruling out the formation of stable intermediates.

Based on the observed stoichiometry, order of reaction, acid dependence and effects of changes in the ionic strength and dielectric constant of the reaction medium, the following mechanism which accommodates all the experimental findings is proposed.



Equation (7) is the rate determining step.

$$\text{Rate} = k_3[\text{H}_2\text{BrO}_3^+][\text{NH}_3\text{OH}_2^{2+}] \dots\dots\dots(9)$$

If the $[\text{H}^+]$ in equation (6) is in excess, we have equation (10)

$$k_2[\text{BrO}_3^-] = k_{-2}[\text{H}_2\text{BrO}_3^+] \dots\dots\dots(10)$$

$$\begin{aligned} \text{Therefore, } [\text{H}_2\text{BrO}_3^+] &= k_2/k_{-2}[\text{BrO}_3^-] \\ &= K_2[\text{BrO}_3^-] \dots\dots\dots(11) \end{aligned}$$

Substituting equation (11) into equation (9), we have equation (12),

$$\text{Rate} = K_2k_3[\text{BrO}_3^-][\text{NH}_3\text{OH}_2^{2+}] \dots\dots\dots(12)$$

But from equation (5)

$$k_1[\text{NH}_3\text{OH}^+][\text{H}^+] = k_{-1}[\text{NH}_3\text{OH}_2^{2+}] \dots\dots\dots(13)$$

$$\begin{aligned} [\text{NH}_3\text{OH}_2^{2+}] &= k_1/k_{-1}[\text{NH}_3\text{OH}^+][\text{H}^+] \\ &= K_1[\text{NH}_3\text{OH}^+][\text{H}^+] \dots\dots\dots(14) \end{aligned}$$

Putting equation (14) into equation (12), we get equation (15) below:

$$\text{Rate} = K_1K_2k_3[\text{NH}_3\text{OH}^+][\text{BrO}_3^-][\text{H}^+] \dots\dots\dots(15)$$

Equation (15) conforms to the observed rate law in equation (4), where ‘a’ =

$$K_1K_2k_3 = 25.78 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1} .$$

The positive salt effect observed for the reaction showed the interaction of like charges in the activated complex [Wilkins, 1974]. This agrees with equation (7) in the reaction scheme.

Table 1: Pseudo – first order and second order rate constants for the reaction of NH_3OH^+ and BrO_3^- . $[\text{NH}_3\text{OH}^+] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\lambda = 400 \text{ nm}$; Temp. $29.5 \pm .5 \text{ }^\circ\text{C}$

$10^2 [\text{BrO}_3^-]$ mol dm^{-3}	$10^2 [\text{H}^+]$ mol dm^{-3}	μ mol dm^{-3}	$10^2 k_1, \text{min}^{-1}$	$k_2, \text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$
6.0	1.0	1.0	1.40	0.233
9.0	1.0	1.0	2.05	0.232
12.0	1.0	1.0	2.91	0.226
15.0	1.0	1.0	3.45	0.230
18.0	1.0	1.0	4.20	0.233
21.0	1.0	1.0	5.10	0.243
15.0	0.5	1.0	1.73	0.115
15.0	1.0	1.0	3.24	0.220
15.0	1.5	1.0	5.18	0.350
15.0	2.0	1.0	7.62	0.510
15.0	2.5	1.0	9.20	0.610
15.0	3.0	1.0	11.50	0.740

Table 2: Effect of changes in ionic strength on the rate of the reaction of NH_3OH^+ and BrO_3^- $[\text{NH}_3\text{OH}^+] = 6.0 \times 10^{-3} \text{ mole dm}^{-3}$; $[\text{BrO}_3^-] = 15.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; $\mu = 1.0 \text{ mol dm}^{-3}$; $\lambda = 400 \text{ nm}$; T = $29.5 \pm 0.5 \text{ }^\circ\text{C}$

$\mu, \text{mol dm}^{-3}$	$10^2 k_1, \text{min}^{-1}$	$k_2, \text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$
0.4	1.00	0.067
0.5	1.15	0.077
0.6	1.70	0.113
0.7	1.90	0.127
0.8	2.35	0.157
0.9	2.99	0.199
1.0	3.41	0.228
1.1	3.43	0.229

Table 3: Rate data for the effect of added anions (SO_4^{2-} and NO_3^-) on the rate of reaction of NH_3OH^+ and BrO_3^- $[\text{NH}_3\text{OH}^+] = 6.0 \times 10^{-3} \text{ mole dm}^{-3}$; $[\text{BrO}_3^-] = 15.0 \times 10^{-2} \text{ mole dm}^{-3}$; $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mole dm}^{-3}$; $\mu = 1.0 \text{ mole dm}^{-3}$; $\lambda = 400 \text{ nm}$; T = $29.5 \pm .5 \text{ }^\circ\text{C}$

Ion	$10^3 [\text{Ion}]$, mol dm^{-3}	$10^2 k_1 \text{min}^{-1}$	$k_2, \text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$
SO_4^{2-}	1.00	3.18	0.212
	10.00	2.56	0.171
	20.00	2.03	0.135
	40.00	1.55	0.103
	50.00	1.33	0.089
	70.00	0.86	0.058
	90.00	0.57	0.038
	100.00	0.53	0.035
NO_3^-	1.00	3.20	0.213
	10.00	2.90	0.193

20.00	2.84	0.189
40.00	2.73	0.182
50.00	2.60	0.174
70.00	2.49	0.166
100.00	2.30	0.153

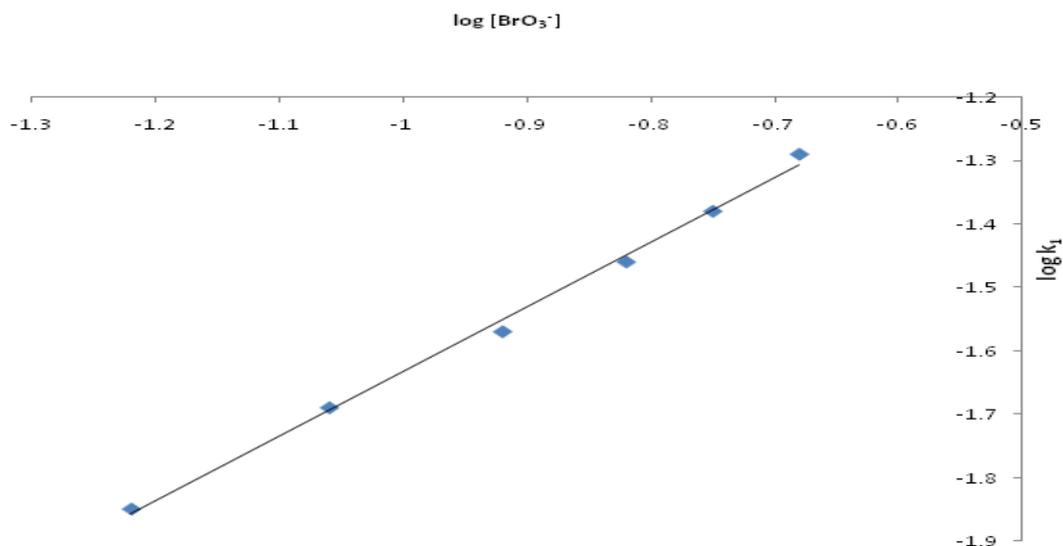


Figure 1 : Plot of $\log k_1$ versus $\log [\text{BrO}_3^-]$ for the reaction of hydroxylammonium chloride and bromate ions

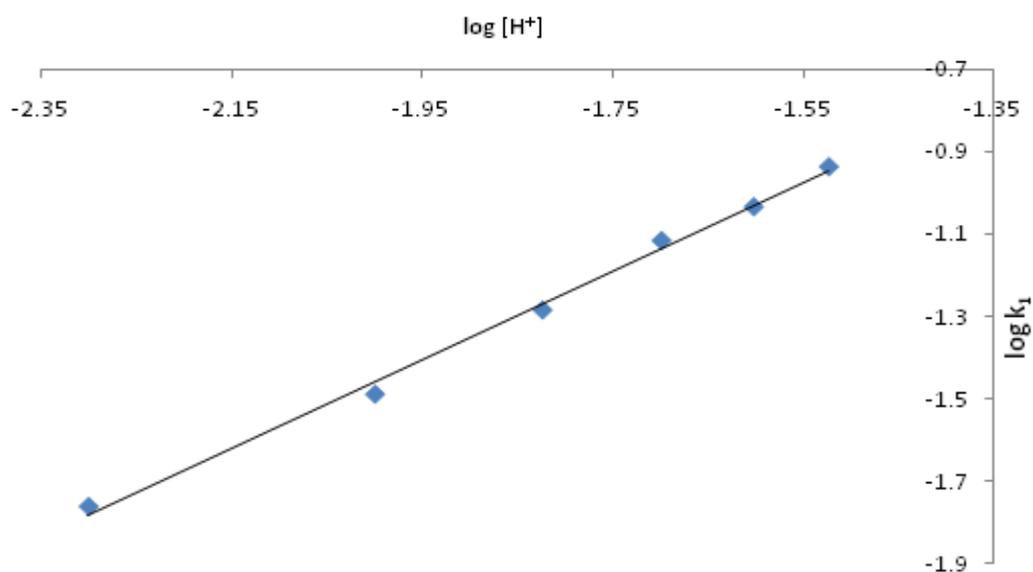


Figure 2 : Plot of $\log k_1$ versus $\log [\text{H}^+]$ for the reaction of hydroxylammonium chloride and bromate ions.

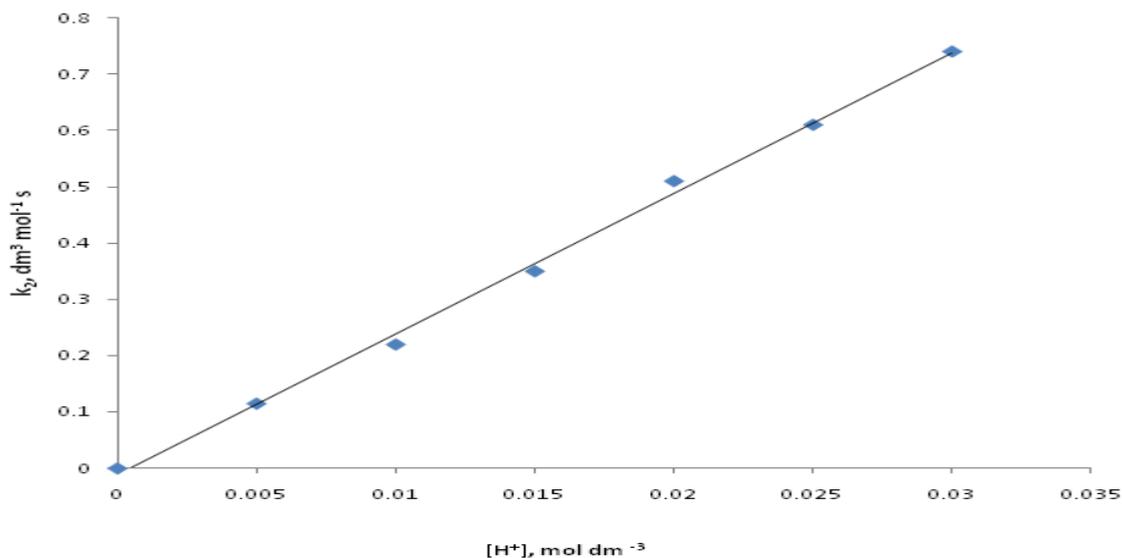


Figure 3 : Plot of k_2 versus $[\text{H}^+]$ for the reaction of hydroxylammonium chloride and bromate ions

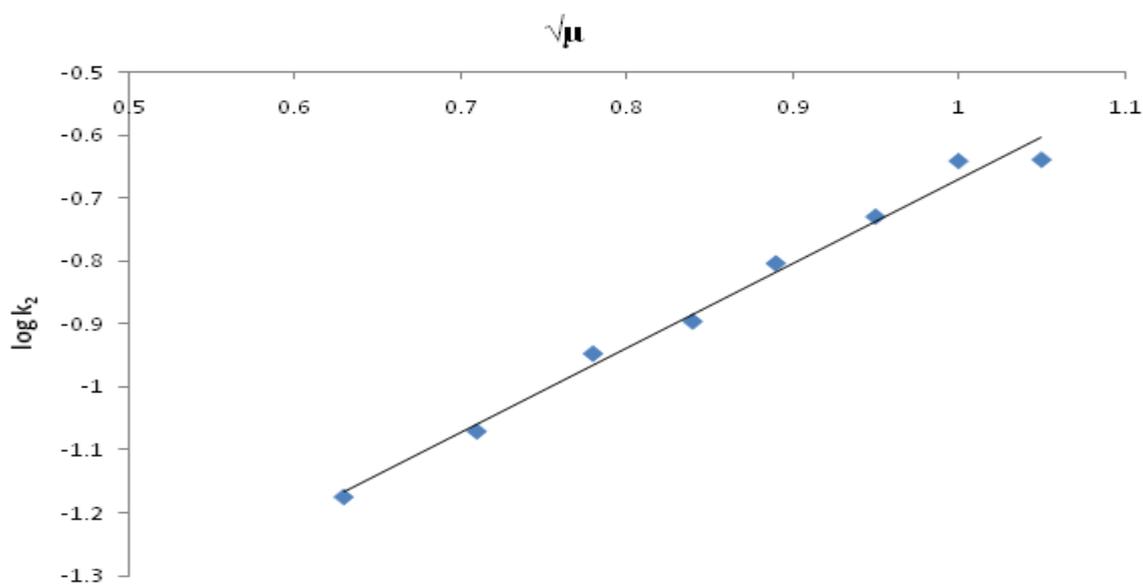


Figure 4: Plot of $\log k_2$ versus $\sqrt{\mu}$ for the reaction of hydroxylammonium Chloride and bromate ions

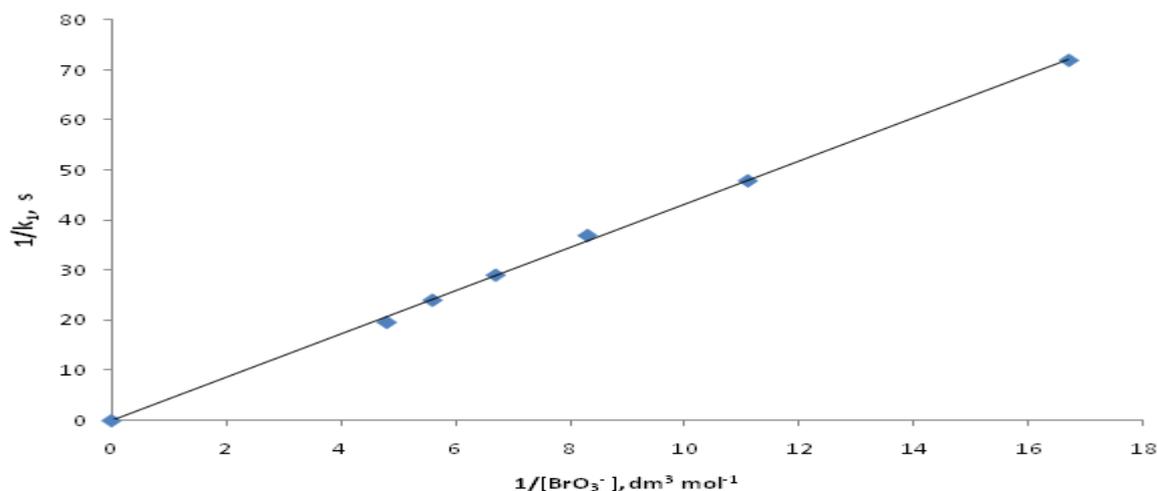


Figure 5: Michaelis Menten plot for the reaction of hydroxylammonium chloride and bromate ions

CONCLUSION

Based on the results obtained, it is evident that stoichiometric ratio for the $NH_3OH^+ - BrO_3^-$ reaction is 1:1, The reaction is first order in both $[NH_3OH^+]$ and $[BrO_3^-]$. The rates of redox reaction show positive dependence on changes in $[H^+]$. The positive salt effect displayed in the reaction suggests that species of like charges are reacting in the rate determining step. Lack of evidence of intermediate complex formation (from Michaelis- Menten plot analysis) and catalysis due to added ions strongly suggest that the reaction proceeded through the outersphere pathway.

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