KINETIC APPROACH TO THE MECHANISM OF OXIDATION OF HEXAMETHYLPARAROSANILINE CHLORIDE BY BROMATE ION IN ACIDIC MEDIUM

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Abstract: The kinetics of the oxidation of hexamethylpararosaniline chloride (hereafter referred to as HPR^+) by bromate ion have been studied in acidic medium under pseudo-first order conditions of excess $[BrO_3^-]$ at 30 ± 1°C, $[H^+] = 2.00 \times 10^{-2}$ mol dm^{-3}, ionic strength, I = 0.5 mol dm^{-3} (NaCl). The stoichiometry of the reaction was found to be 2:3 mole ratio of HPR to BrO_3 ions. The redox reactions at constant hydrogen concentration follows first order with respect to the reductant concentration $[HPR^+]$ and the oxidant concentration $[BrO_3^-]$ respectively and second order overall. The rate of reaction increased with increase in hydrogen ion concentration. The overall reaction conforms to the rate law $\frac{-d[HPR^+]}{dt} = (a + b[H^+]^2)[HPR^+][BrO_3^-]$; a = 9.22 dm^6 mol^{-2} s$^{-1,}$ b = 1.16 dm^9 mol^{-3} s^{-1}. Added anions and cations (X= $HCOO^-$, CH_3COO^-, Ca^{2+}, Mg^{2+}) to the reaction mixture significantly inhibited the rate of the reaction. Spectroscopic test and Michaelis-Menten analysis showed no evidence of intermediate complex of significant stability. Free radical polymerization test showed no free radicals. Based on the results obtained experimentally, outersphere mechanism is proposed for the hexamethylpararosaniline -BrO_3^- reaction.

Keywords: Hexamethylpararosaniline chloride, bromate ion, redox reaction, outersphere, polymerisation

Introduction

Hexamethylpararosaniline chloride (Crystal violent, Gentian violet) with a molecular formula $C_{25}H_{30}N_3Cl$ is a triphenyl methane dye, which is antimicrobial (Hall and Hamilton, 1982). It is readily soluble in water and highly stable, with the absorption maximum (λ_{max}) of approximately 590 nm. It is very important in biological stains for the study of bacteria and related microorganisms. The dye is also used as a constituent of culture media, as indicator and for laboratory diagnosis of disease (Docampo and Moreno, 1990). Kinetics and mechanisms of the dye with oxyanions (ClO_3^-, HSO_5^- and $Cr_2O_7^{2-}$) have been studied (Mohammed *et al.*, 2011; Kranti, 2011; Mohammed and Komolafe, 2010).

Bromate is a strong oxidizing agent. Its redox reaction with both organic and inorganic substances has been studied (Birk, 1978; Jonnalagadda *et al.*, 1995, Lohdip *et al.*, 1996). The rate of redox reactions of bromate have been shown to depend strongly on acid concentration (Birk and Kozub, 1973; Ayoko *et al.*, 1991). Kinetics and mechanisms of the oxidation of bromate ion has been studied by various researchers (Birk, 1978, Ayoko *et al.*, 1991, Iyun and Asala, 1994; Adetoro *et al.*, 2010). In this paper, we present our findings on the oxidation of hexamethylpararosaniline chloride by bromate ion with the aim of providing insight into the mechanistic pathways for the reaction.

Materials and Methods

Materials

All the reagents used were Analar grade. Hexamethylpararosaniline chloride and bromate ion were used without further purifications. Sodium chloride (M&B) was used to maintain the ionic strength of the reaction medium. Hydrochloric acid was standardized titrimetrically using sodium bicarbonate. All other reagents were used as supplied.

Methods

Stoichiometry: The stoichiometry of the reaction was determined using spectrophometric titration, by the mole ratio method (Iyun *et al.*, 1995). Reaction mixtures containing fixed amount of $[HPR^+]$ and varied amount of $[BrO_3^-]$ were allowed to stand for 24 h after which the excess $[HPR^+]$ was determined by measuring the absorbance of the solutions at 585 nm on a Jenway uv/vis spectrophotometer until a steady value was attained, the stoichiometry was evaluated from the plot of absorbance against mole ratio of HPR^+/BrO_3^-. A point of inflexion on the plot indicates the stoichiometry of the reaction (Adetoro *et al.*, 2010).

Kinetic studies: The progress of the reaction was monitored under pseudo-first order condition with the $[BrO_3^-]$ in at least 100 fold excess of $[HPR^+]$, by following the decrease in the concentration of HPR^+ at 585 nm, $[H^+] = 2.00 \times 10^{-2}$mol dm^{-3}, I = 0.5 mol dm^{-3} and T= 30±1°C.

The pseudo-first order plots of log (A_t-A_∞) versus time were made (where A_t and A_∞ are the absorbance at time t and at the end of the reaction respectively) and from the slope of the plots, the pseudo-first order rate constants (k_1) were determined. The second order constants (k_2) were obtained from the relation:

$$k_2 = k_1/BrO_3^-] \qquad (1)$$

Effect of changes in $[H^+]$ on the reaction rate

The effect of changes in $[H^+]$ on the rate of reaction was studied in the range $0.6 \leq [H^+] \geq 2.4$ mol dm^{-3} while concentration of HPR^+ and BrO_3^- ions were kept constant at 1.0×10^{-5} and 2.00×10^{-3} mol dm^{-3}, respectively at 30 ± 1°C and I =0.50 mol dm^{-3}.

Effect of changes in ionic strength

The effect of changes in ionic strength on the rate of the reaction was investigated in the range 0.2-1.0 mol dm^{-3}

(NaCl), while the concentrations of other reactant were kept constant at T = 30±1°C.

Effect of added cation and anion

The effect of added cation and anion were investigated for [X] = 1.0 x 10^{-3}-1.0 x 10^{-2} mol dm^{-3} (X= $HCOO^-$, CH_3COO^-, Ca^{2+}, Mg^{2+}) and the concentration of all other reactants were kept constant at T = 30±1°C and the ionic strength was maintained constant at I = 0.50 mol dm^{-3}.

Test for free radicals

Acrylamide solution was added to the partially oxidized reaction mixture of HPR and BrO_3 ions in a large excess of methanol to initiate free radical polymerization.

Test for intermediate complex

The electronic spectra of the reaction mixture were obtained after two minutes of the commencement of the reaction, over the wavelength range of 500- 700 nm. This was compared with the spectra of the dye alone within the same range.

Results and Discussion

Stoichiometry study

From the stoichiometry studies, the mole ratio of the reaction was found to be 2:3 (Fig. 1), this indicates that for every two moles of HPR^+, three moles of BrO_3^- is being oxidized. This is according to the equation:

$$2HPR^+ + 3BrO_3^- \rightarrow \text{Products} + Br_2 \qquad (1)$$

A stoichiometry of 1:5 has been reported by (Iyun and Asala, 1994) in the oxidation of methylene blue by bromate ion.

Kinetics

The pseudo first order plot of log (A_t-A_∞) versus time, t, for these reactions were linear to about 90% extent of the reaction (Fig. 2), this indicates that the reaction is first-order with respect to [HPR^+] at constant [H^+]. The slope was calculated and k_1 was determined by multiplying the slope by 2.303. Plot of log $k_1$versus log [BrO_3^-] gave a slope of 0.98 (Fig. 3), suggesting that the reaction is first order in [BrO_3^-]. The second order rate constant k_2 was obtained from k_2= k_1/[BrO_3^-] (Table 1). The constancy of the second order rate constant further confirmed the first order dependence of reaction on [BrO_3^-]. Therefore the rate equation order for the reaction is:

$$\frac{-d[HPR^+]}{dt} = k_1 [HPR^+][BrO_3^-] \qquad (2)$$

Similar second order kinetics was observed in the reaction of bromate by tetrahedral cobalt (II) (Birk and Kozub, 1973) and methylene blue (Ayoko *et al.*, 1991).

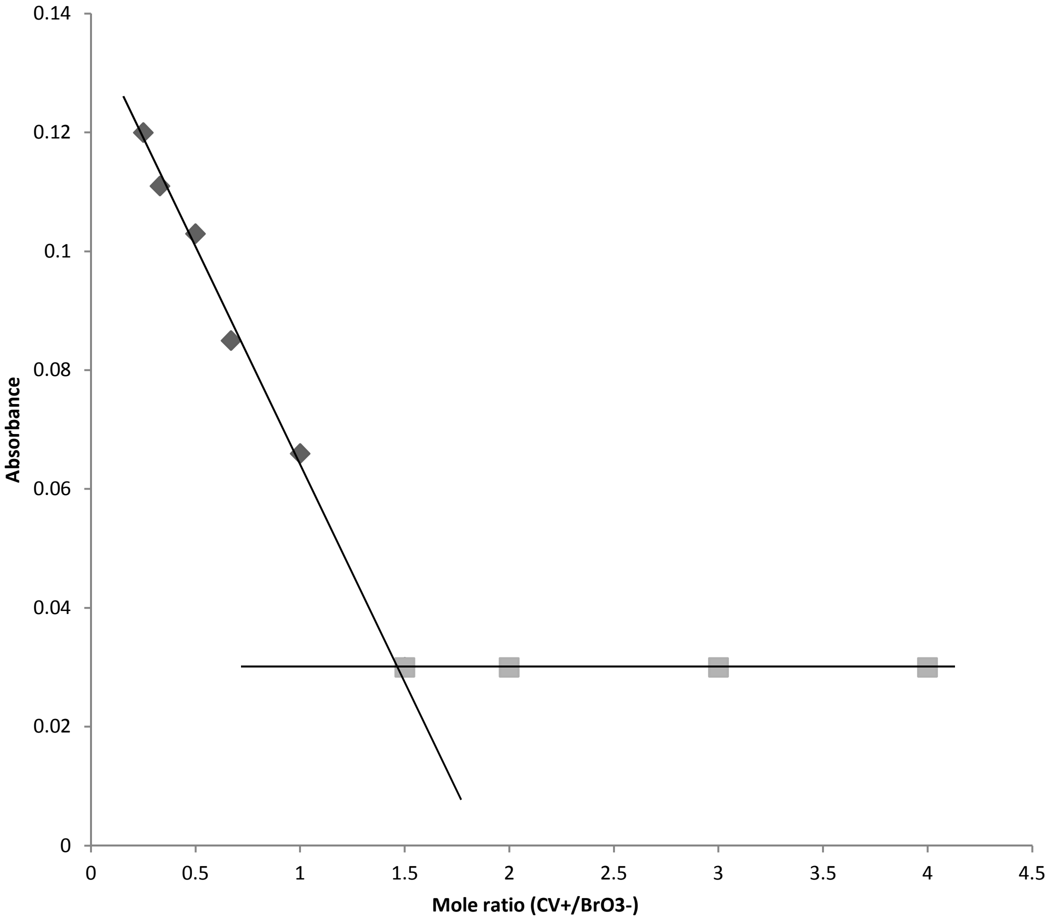

Fig. 1: Plot of absorbance versus mole ratio for the redox reaction of crystal violet with bromate ion at [CV^+] = 1.0 x 10^{-5} mol dm^{-3}, [H^+] = 2.0 x 10^{-2} mol dm^{-3}, I = 0.50 mol dm^{-3} and T= 30 ± 1 ºC

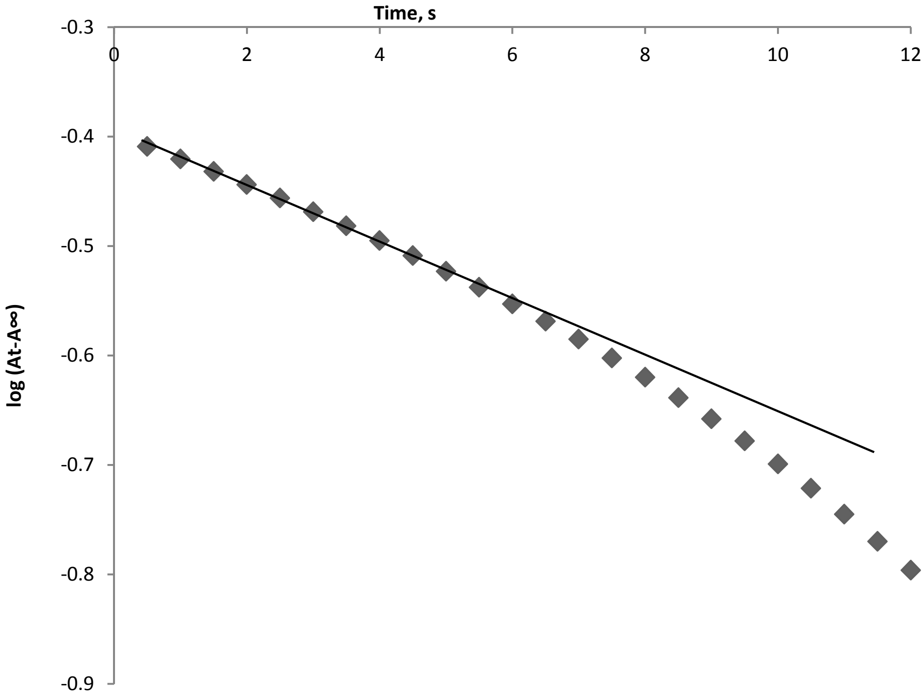

Fig. 2: Typical pseudo-first order plot for the redox reaction of crystal violet with bromate ions at $[CV^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-2}$ mol dm^{-3}, I = 0.50 mol dm^{-3} and T = 30 ± 1 ºC

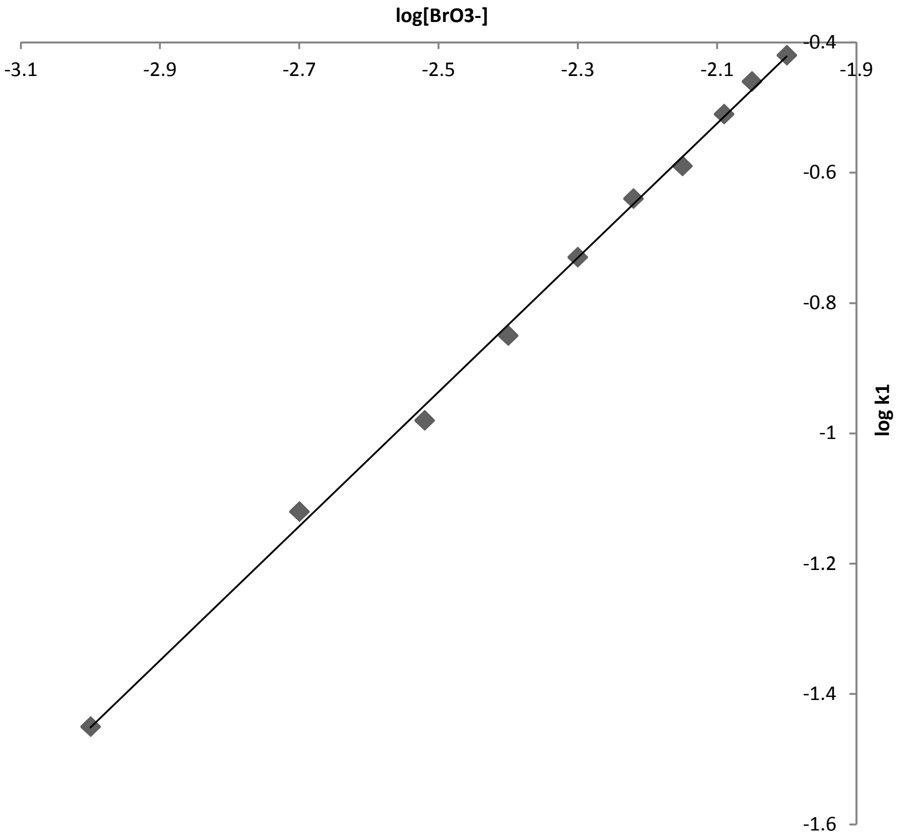

Fig. 3: Pseudo-first plot of log k_1 versus log $[BrO_3^-]$ for the redox reaction of hexamethylpararosaniline chloride and bromate ion at $[HPR^+] = 1.0\times10^{-5}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, λ_{max} = 585 nm and T = 30 ± 1℃

Table 1: Pseudo-first order and second order rate constants for the redox reaction of hexamethylpararosaniline chloride and bromate ions in aqueous HCl medium at $[HPR^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 30± 1°C, and λ_{max} = 585 nm

$10^3[BrO_3^-]$, mol dm^{-3}	$10^1 k_1$, s^{-1}	K_2, dm^3 mol^{-1} s^{-1}
1.00	0.39	38.50
2.00	0.77	38.35
3.00	1.16	38.53
4.00	1.54	38.40
5.00	1.94	38.84
6.00	2.33	38.84
7.00	2.66	38.01

Table 2: Pseudo-first order and second order rate constants for the effect of changes in changes in $[H^+]$ for the redox reaction of hexamethylpararosaniline chloride and bromate ions in aqueous HCl medium at $[HPR^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-] = 8.0 \times 10^{-3}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 30 ± 1°C, and λ_{max}= 585 nm

$10^2[H^+]$,mol dm^{-3}	$10^1 k_1$, s^{-1}	K_2, dm^3 mol^{-1} s^{-1}
0.60	0.34	4.26
0.80	0.39	4.85
1.00	0.77	9.59
1.20	1.12	14.03
1.40	1.55	19.36
1.60	2.24	27.99
1.80	2.82	35.23
2.00	3.07	38.38

Effect of changes in $[H^+]$ on the reaction rate

The effect of $[H^+]$ was investigated within the range $[H^+] = (0.6\text{-}2.4) \times 10^{-2}$ mol dm^{-3} (Table 2), the rate of the reaction was found to increased with increase in concentration of hydrogen ions. Plot of log k_1 versus log $[H^+]$ gave a slope of 2.03; this shows second order $[H^+]$ dependence (Fig. 4). The second order $[H^+]$ dependence was rationalized in term of the pre-equilibrium, protonation of BrO_3^- to give $H_2BrO_3^+$ (Birk and Kozub, 1973; Ayoko*et al.*,1991; Iyun and Asala, 1994; Adetoro *et al.,* 2010). Also plot of second order acid dependence rate constant k_2 versus $[H^+]^2$ was also linear with positive intercept (Fig. 5), this indicates two reaction pathways: an acid independent pathway and a parallel acid dependent way. It shows that parallel reactions of protonated and unprotonated species of BrO_3^- occurs as in most other reactions of BrO_3^- and that a protonated equilibrium preceeds the electron transfer step (Birk, 1973, Birk and Kozub, 1973, Lohdip and Iyun, 1993). Therefore the acid dependent rate constant k_H is given by:

$$k_H = a + b[H^+]^2 \qquad (3)$$

Substituting equation 3 in equation 2, the rate equation for the reaction can now be written as:

$$\frac{-d[HPR^+]}{dt} = (a + b[H^+]^2)[HPR^+][BrO_3^-] \qquad (4)$$

Effect of ionic strength

The rate of the reaction was found to increase with increase in ionic strength (Table 3). Plot of log k_2 versus √I gave a slope of 1.04 (Fig. 6). This positive salt effect suggests that the product of the charges on the reactants in the transition state is +1 (Mohammed and Komolafe, 2010; Idris *et al.,* 2010). This strongly suggests that the principal reactant species in this reaction are most likely HPR^+ and $H_2BrO_3^+$. This further suggests the existence of $H_2BrO_3^+$ as one of the reactive species in the medium (Benson, 1969; Birk, 1978).

Table 3: Pseudo-first order and second order rate constants for the effect of changes in ionic strength (I) on the redox reaction of hexamethylpararosaniline chloride and bromate ions in aqueous HCl medium at $[HPR^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-] = 8.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 2 \times 10^{-2}$ mol dm^{-3} T = 30 ± 1°C, and λ_{max}= 585 nm

I, mol dm^{-3}	$10^1 k_1$,s^{-1}	K_2, dm^3 mol^{-1} s^{-1}
0.3	2.153	26.91
0.4	2.530	31.63
0.5	3.070	38.38
0.6	3.573	44.66
0.7	4.396	54.95
0.8	5.048	63.10
0.9	5.334	66.68

Effect of added ions

Added anions and cations significantly inhibited the rate of the reaction (Tables 4 & 5). Inhibitive effect of added cations could be explained in terms of columbic forces of attraction, as the activated complex in this reaction is made up of positively charged species, bringing in another positive charged species would lead to overall repulsion, thereby decreasing the rate of reaction (Benson, 1969; Babatunde *et al.,* 2013). The observed inhibitive effect of added anions could only be explained in terms of ion pairing. The anions might undergo extensive ion pairing with one of the reactant, thereby hindering the chances of the two reactants coming into contact. The inhibitive effects of these ions suggest that outersphere mechanism might be operating (Babatunde *et al.,* 2013).

Table 4: Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of hexamethylpararosaniline chloride and bromate ion at $[HPR^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-] = 8.0 \times 10^{-3}$ mol dm^{-3}, I = 0.50 mol dm^{-3} and T= 30 ± 1 °C

X	$10^3[X]$, mol dm^{-3}	k_1, s^{-1}	k_2, mol^{-1}dm^{-3}
Ca^{2+}	0	0.31	38.38
	10	0.30	37.09
	20	0.29	36.26
	40	0.28	35.56
	80	0.28	34.65
	100	0.27	33.75
Mg^{2+}	0	0.31	38.38
	10	0.29	35.85
	20	0.26	32.00
	40	0.24	30.40
	80	0.23	28.95
	100	0.22	27.66

Table 5: Pseudo-first order and second order rate constants for the effect of added anions on the redox reaction of hexamethylpararosaniline chloride and bromate ion at $[HPR^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-] = 8.0 \times 10^{-3}$ mol dm^{-3}, I = 0.50 mol dm^{-3}and T= 30 ± 1 °C

X	10^3[X], mol dm^{-3}	k_1, s^{-1}	k_2,dm^{3}mol^{-1}s^{-1}
$HCOO^-$	0	0.31	38.38
	10	0.28	35.14
	20	0.27	33.40
	40	0.25	31.26
	60	0.24	29.40
	80	0.21	26.41
	100	0.19	23.78
CH_3COO^-	0	0.31	38.38
	10	0.31	38.38
	20	0.29	36.30
	40	0.28	35.55
	60	0.28	34.66
	80	0.26	32.10
	100	0.24	30.44

Polymerization Test

The result of free radical polymerization was negative suggesting that free radicals are not involved in the reaction.

Test for intermediate complex formation

There is no shift in the λ_{max} of 585 nm, when reactants were mixed together and the electronic spectra were recorded after two minutes of mixing. This suggests the probable absence of intermediate complex formation indicating outersphere mechanism operating. Plot of $1/k_1$ versus $1/[BrO_3^-]$ was linear with zero intercept (Fig. 7), confirming the absence of pre-electron transfer intermediate complex formation. This also implicates the reaction as occurring most likely through outersphere mechanism.

Product analysis

Product analysis was carried out by reacting equimolar amount of the dye and the bromate at $[H^+] = 2.00 \times 10^{-2}$ mol dm^{-3} and I= 0.5 mol dm^{-3} (NaCl) after the completion of the reaction, a colorless solution was obtained and UV visible spectra of the product showed no absorption peak at λ_{max} 585 nm. This indicates the destruction of the quinoid structure that gives the dye color. Qualitative test for bromide ion and bromine was carried out. Bromine was confirmed to be present by formation of reddish brown vapour with irritating smell and acidic to litmus paper when MnO_2 and KBr were added in the present of sulphuric acid.

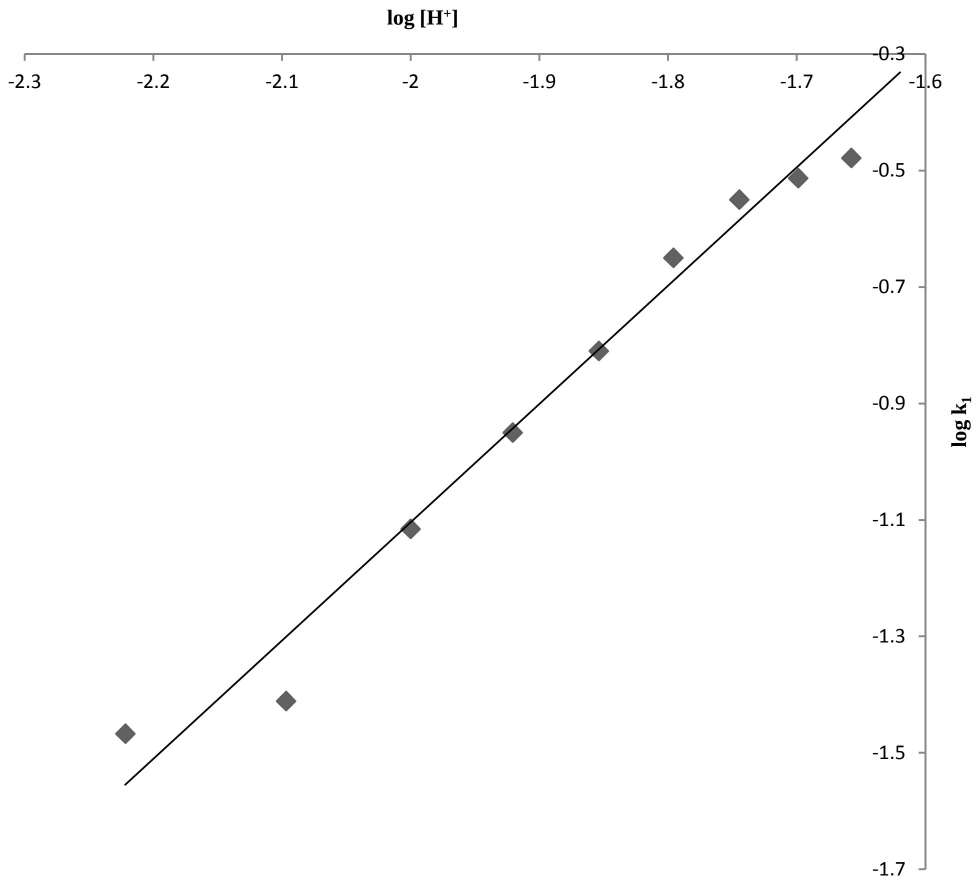

Fig. 4: Plot of log $k_1$versus log $[H^+]$ for the redox reaction of hexamethylpararosaniline chloride and bromate ion at $[HPR^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-] = 8.0 \times 10^{-3}$ mol dm^{-3}, I=0.50 mol dm^{-3}and T= 30 ± 1 °C

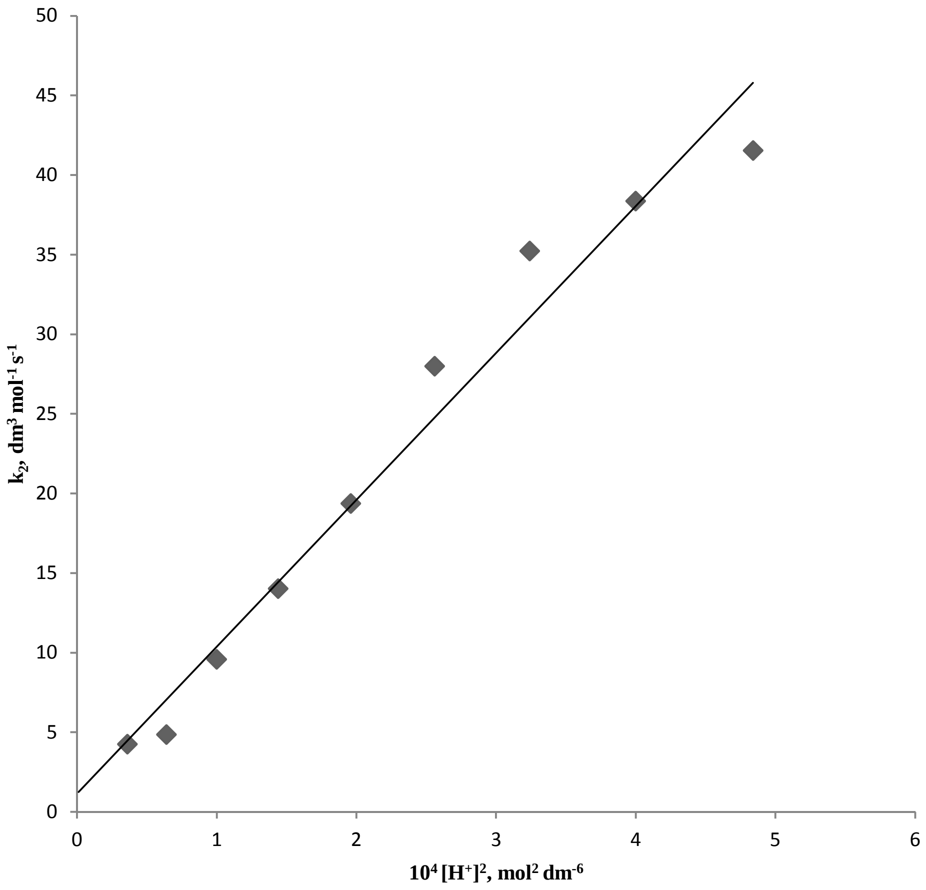

Fig. 5: Plot of k_2 versus $[H^+]^2$ for the redoxreaction of hexamethylpararosaniline chloride and bromate ion at $[HPR^+]$ = 1.0x10^{-5} mol dm^{-3}, $[BrO_3^-]$ = 8.0x10^{-3} mol dm^{-3}, I = 0.50 mol dm^{-3}and T = 30±1 ºC

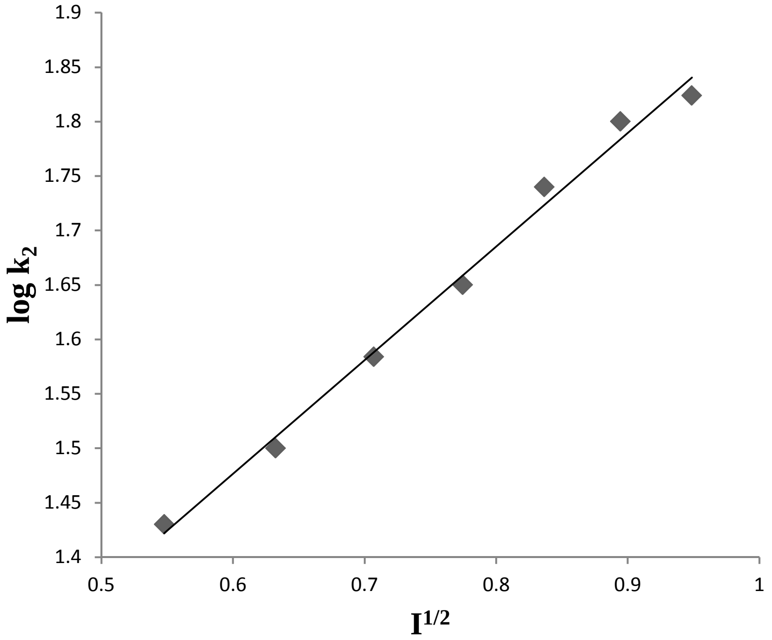

Fig. 6: Plot of k_2 versus $I^{1/2}$ for the redox reaction of hexamethylpararosaniline chloride and bromate ion at $[HPR^+]$ = 1.0x10^{-5} mol dm^{-3}, $[BrO_3^-]$ = 8.0x10^{-3} mol dm^{-3}, I=0.50 mol dm^{-3}, T= 30±1 ºC

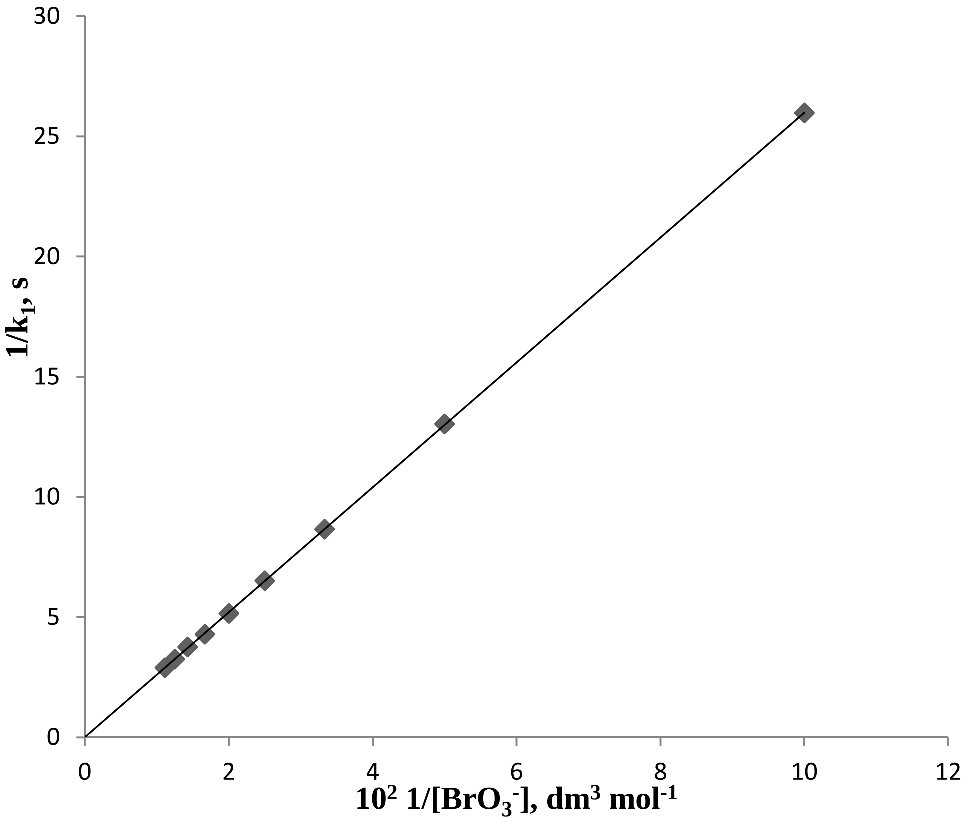

Fig. 7: Michaelis-Menten plot of $1/k_1$ versus $1/[BrO_3^-]$ for the redox reaction of crystal violet with bromate ion at $[HPR^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-2}$ mol dm^{-3}, I = 0.50 mol dm^{-3} and T= 30 ± 1 ºC

Reaction mechanism

On the basis of the data generated from our investigation, the following plausible mechanism is proposed:

$$BrO_3^- + 2H^+ \overset{K}{\rightleftharpoons} H_2BrO_3^+ \tag{5.1}$$

$$BrO_3^- + HPR^+ \xrightarrow[slow]{k_2'} HPR^{2+} + BrO_3^{2-} \tag{5.2}$$

$$H_2BrO_3^+ + HPR^+ \xrightarrow[slow]{k_3'} HPR^{2+} + BrO_2 + H_2O \tag{5.3}$$

$$BrO_3^{2-} + 2H^+ \xrightarrow{k_4'} BrO_2 + H_2O \tag{5.4}$$

$$2HPR^{2+} + 2BrO_2 + 8H^+ \xrightarrow{k_5'} Products + 2Br^- \tag{5.5}$$

$$2Br^- + BrO_3^- + 6H^+ \xrightarrow{k_6'} 3/2\ Br_2 + 3H_2O \tag{5.6}$$

With equations (5.2) and (5.3) as the rate determining step, the equation for the reaction can be written as:

$$Rate = k_2'[HPR^+][BrO_3^-] + k_3'[HPR^+][H_2BrO_3^+] \tag{5.7}$$

From equation (5.1)

$$[H_2BrO_3^+] = K[BrO_3^-][H^+]^2 \tag{5.8}$$

Substitution of equation (5.8) into (5.7) leads to:

$$Rate = (k_2' + k_3'K[H^+]^2)[HPR^+][BrO_3^-] \tag{5.9}$$

$$= (a + b[H^+]^2)\ [HPR^+][BrO_3^-] \tag{5.10}$$

Equation (5.10) agreess with the experimentally observed rate law(equatio 4)

where $a = k_2' = 9.22$ dm^6 mol^{-2} s^{-1} and $b = k_3'K = 1.16$ dm^9 mol^{-3} s^{-1}

Conclusion

The redox reaction of hexamethylpararosaniline chloride with bromate ion in aqueous acidic medium showed a stoichiometry of 2:3. The reaction was second order overall. The rate of the reaction was found to increase with increase in concentration of hydrogen ions. Both kinetic and spectroscopic investigations support the absent of intermediate complex formation. Based on the results obtained, outersphere mechanism is proposed as the mechanistic pathway for the reaction.

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