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Kinetics and Mechanism of the Oxidation of 3,7-Bis(dimethylamino) Phenothionium Chloride (Methylene Blue) by Bromate Ion in Aqueous Hydrochloric Acid Medium

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Abstract

The stoichiometry, kinetics and mechanism of the oxidation of 3,7–bis(dimethylamino) phenothionium chloride (methylene blue) by bromate ion, BrO_3^- was investigated in aqueous hydrochloric acid medium. The reaction follows the empirical rate law:

$$-\frac{1}{2}\frac{d[MB^+]}{dt} = (a + b[H^+]^2)[MB^+][BrO_3^-]$$

Where a = 210 $dm^3\ mol^{-1}\ s^{-1}$, b = 1.6 $dm^9\ mol^{-3}\ s^{-1}$ at 29 ± 1°C.
$[H^+]$ = 0.175 – 0.30 mol dm^{-3}, I = 0.50 mol dm^{-3} (NaCl) and λ_{max} = 665 nm.
The rate law indicates that the reaction occur via two pathways, involving acid - independent and second – order acid – dependent pathways. The inhibition of the reaction rate by the presence of added $HCOO^-$ and SO_4^{2-}, the absence of both spectroscopic and kinetic evidences for the formation of a precursor binuclear intermediate prior to the electron transfer step are suggestive of the outer-sphere mechanism.

Keywords: *Acid–independent; Bromate ion; Electron–transfer; Methylene blue; Outer–sphere.*

1.0 INTRODUCTION

Bromate ion is an oxyanion (Idris *et al.* 2010) and a very strong oxidizing agent (Deepa and Chandramohan, 2012), having a redox potential of 1.45 V (Lurie, 1975). Although banned for use in baking bread as a flour improver due to its carcinogenic tendencies (Khan et. al., 2011), it oxidizes both metal ion complexes (Birk, 1973; Birk and Kozub, 1973; Birk and Kozub, 1978; Iyun *et al*., 1992; Nikumbh and Rathi, 2014;

Thompson, 1971; 1978) and organic compounds (Journalagadda *et al.,* 1995; Lohidip *et al*., 1995; Lohidip and Iyun, 1993; Ravikant et al., 2014; Srivastava, and Srivastava, 2010) and it is also employed for aromatic bromination (Schatz, 1996).

Just like most other oxyanions (Ayoko *et. al.*, 1993; Birk and Kozub, 1973; Edwards, 1954; Xie et. al., 1999), the rates of the redox reactions of bromate ions were found to depend strongly on the hydrogen ion concentration of the solution (Ayoko *et al.,* 1993; Birk and Kozub 1978; Idris *et al.* 2014).

We have previously studied the kinetics and mechanisms of methylene blue (MB^+) with peroxydisulphate ion (Busari *et al.,* 2008) and sulphite ion (Busari *et al.,* 2012) respectively. MB^+ is an important biological stain and a redox indicator (Busari *et al.,* 2012) which a number of researchers (Burger and Field, 1984; Ukoha and Iyun, 2000; Yulia and Wei-Fang, 2008; Prasetyo and Mufakhir, 2011; Osunlaja *et al.,* 2012) have worked on. In the present study, in order to gain more insight into the redox characteristics of MB^+, a study of its oxidation by BrO_3^- was undertaken.

2.0 MATERIALS AND METHODS

Methylene blue (BDH, Analar) with maximum wavelength of absorption (λ_{max}) of 660–665 nm and $KBrO_3$ (BDH, Analar) were both used without further purification. HCl (BDH, Analar) was used to investigate the effect of hydrogen ion on rate of the reaction while NaCl (BDH, Analar) was used in maintaining constant ionic strength at 0.50 mol dm^{-3}. Unless otherwise stated, all other regents were used as received.

2.1 Kinetic Measurements

All kinetic measurements where made under pseudo–first order condition with [BrO_3^-] in at least 210 fold excess over [MB^+] (Idris *et al.,* 2014). Under the conditions indicated on Table 1, pseudo-first order rate constants were obtained from plot of log (A_t–A_∞) versus time (A_t and A_∞, are absorbances at time, t and at the end of the reaction respectively). The plots were linear to more than 60% extent of the reactions.

2.2 Stoichiometric Study

The stoichiometry of the reaction was determined by spectrophotometric titration (Ayoko *et al.,* 1991; Lohdip and Iyun, 1993; Mohammed *et al.,* 2009). Reaction mixtures containing [MB^+] = 2.0 x 10^{-3} mol dm^{-3} and various BrO_3^- concentrations in the range 1.0 x 10^{-5}–1.1 x 10^{-4} mol dm^{-3} at constant [H^+] = 0.20 mol dm^{-3} and I = 0.50 mol dm^{-3} were allowed to stand until the reaction had gone to completion.

The absorbance of the solutions were then measured at 665 nm, the absorption maximum of methylene blue (Conn, 1961), using corning colorimeter 256, and the stoichiometry determined from plot of absorbance versus [BrO_3^-]/ [MB^+].

3.0 RESULTS

3.1 Stoichiometry and Product Analysis

The result of stoichiometry showed that two moles of methylene blue were consumed by three moles of BrO_3^- according to equation (I).

$$2MB^+ + 3BrO_3^- \rightarrow Product + \frac{3}{2}Br_2 \qquad (1)$$

A colourless solution obtained at the end of the reaction indicated destruction of the quinoid chromophore group. Also the organic product gave a yellow precipitate with 2,4-dinitrophenylhydrazine, confirming the presence of carbonyl group. The inorganic product of the reaction was confirmed, qualitatively using cyclohexene, to be bromine. Also the red heavy liquid of bromine was noticed to settle at the bottom of the test-tube, when the solution was kept for a long time. The formation of bromine is a common feature of redox reaction of bromate ion (Ayoko *et al.,* 1991; Lohdip *et al.* 1995; Lohdip and Iyun, 1993).

3.2 Kinetics

The linearity of the pseudo–first order plots of log (A_t–A_∞) versus time indicated that the reaction was first order with respect to methylene blue. At [H^+] = 0.20moldm^{-3} and 29 ± 1^{o}C, a plot log k_{obsd} verse log [BrO_3^-] using kinetic data in Table 1, was linear (r = 0.985) with a slope of 1.08, suggesting that the reaction was also first order with respect to BrO_3^-. Thus, the rate law can be express by Equation 2:

$$\frac{1}{2}\frac{d[MB^+]}{dt} = k_2[MB^+][BrO_3^-] \quad \text{----------(2)}$$

Plot of k_2 versus $[H^+]^2$ (Figure 1) fitted the equation

$$k_2 = a + b[H^+]^2 \quad \text{----------(3)}$$

Table 1: Pseudo–first and second order rate constant for the redox reaction of methylene blue and bromate $[MB^+] = 1.87 \times 10^{-5}$ mol dm^{-3}, T = 29 ± 1°C, and λ_{max} = 665 nm.

10^3 [BrO_3^-], mol dm^{-3}	[H^+], mol dm^{-3}	I(NaCl), mol dm^{-3}	10^2 k_{obsd}, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
6	0.20	0.50	6.15	10.25
7	0.20	0.50	6.91	9.87
8	0.20	0.50	8.24	10.30
9	0.20	0.50	9.21	10.23
10	0.20	0.50	10.20	10.20
11	0.20	0.50	11.10	10.09
8	0.175	0.50	6.29	7.86
8	0.20	0.50	8.24	10.30
8	0.225	0.50	9.90	12.38
8	0.25	0.50	11.50	14.38
8	0.275	0.50	13.80	17.25
8	0.30	0.50	16.60	20.75
8	0.20	0.50	6.59	8.24
8	0.20	0.40	7.60	9.50
8	0.20	0.45	8.24	10.30
8	0.20	0.55	8.54	10.68
8	0.20	0.60	9.44	11.80
8	0.20	0.65	10.80	13.50
8	0.20	0.70	11.70	14.63

TABLE 2: Anion dependent rate constants for the methylene blue–bromate reaction. $[MB^+] = 1.87 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-] = 7.0 \times 10^{-3}$ mol dm^{-3}, $[H^+]$ = 0.20 mol dm^{-3}, I = 0.60 mol dm^{-3} [NaCl], I = 29 ± 1 °C, and λ_{max} = 665 nm.

X	10^2 [X], mol dm^{-3}	10^2 k_{obsd}, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
$HCOO^-$	0.0	6.91	9.81
	1.0	6.68	9.54
	2.0	6.22	8.89
	3.0	5.64	8.06
	4.0	4.49	6.41
	5.0	3.45	4.93
SO_4^{2-}	0.0	6.91	9.87
	1.0	6.91	9.87
	2.0	5.30	7.57
	3.0	4.26	6.09
	4.0	3.68	5.26

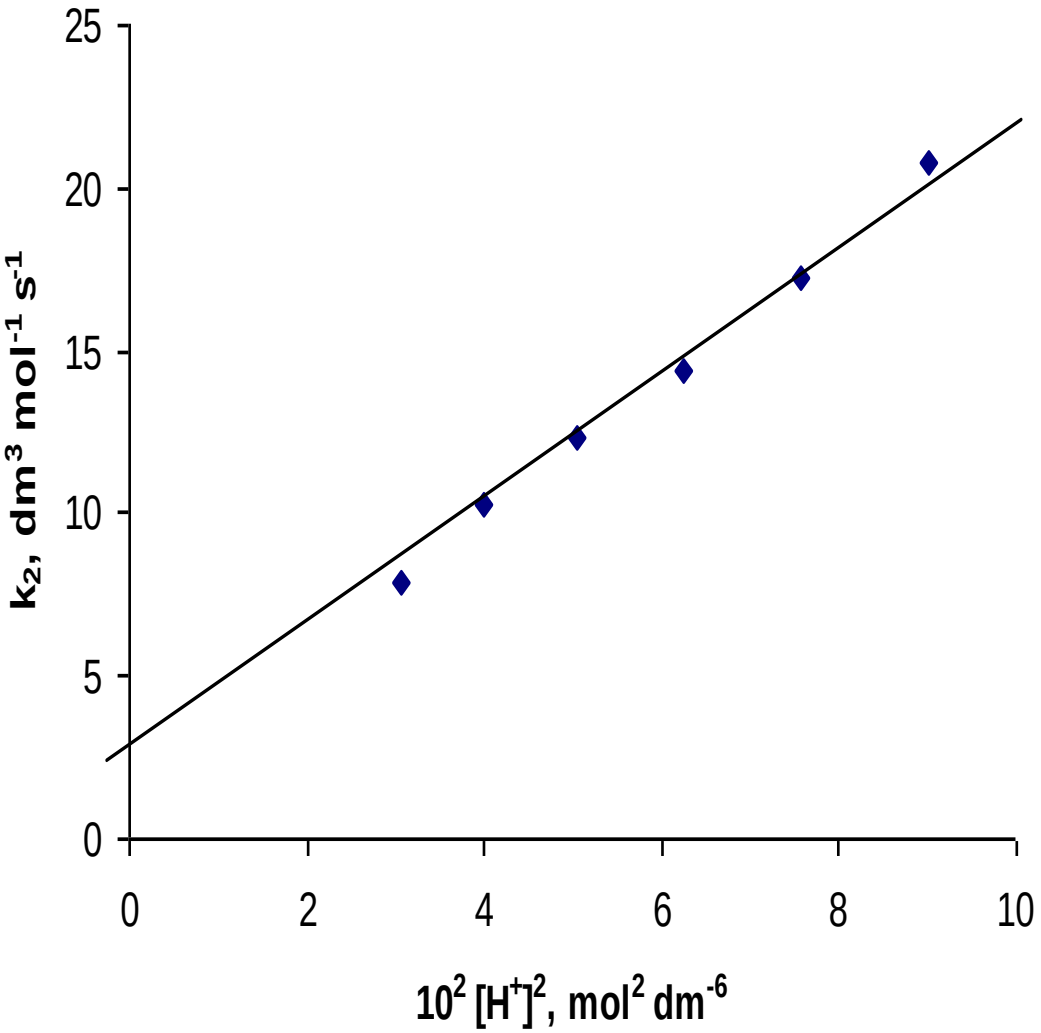

Figure 1: Plot of k_2 versus $[H^+]^2$ for the reaction of MB^+ and BrO_3^-.

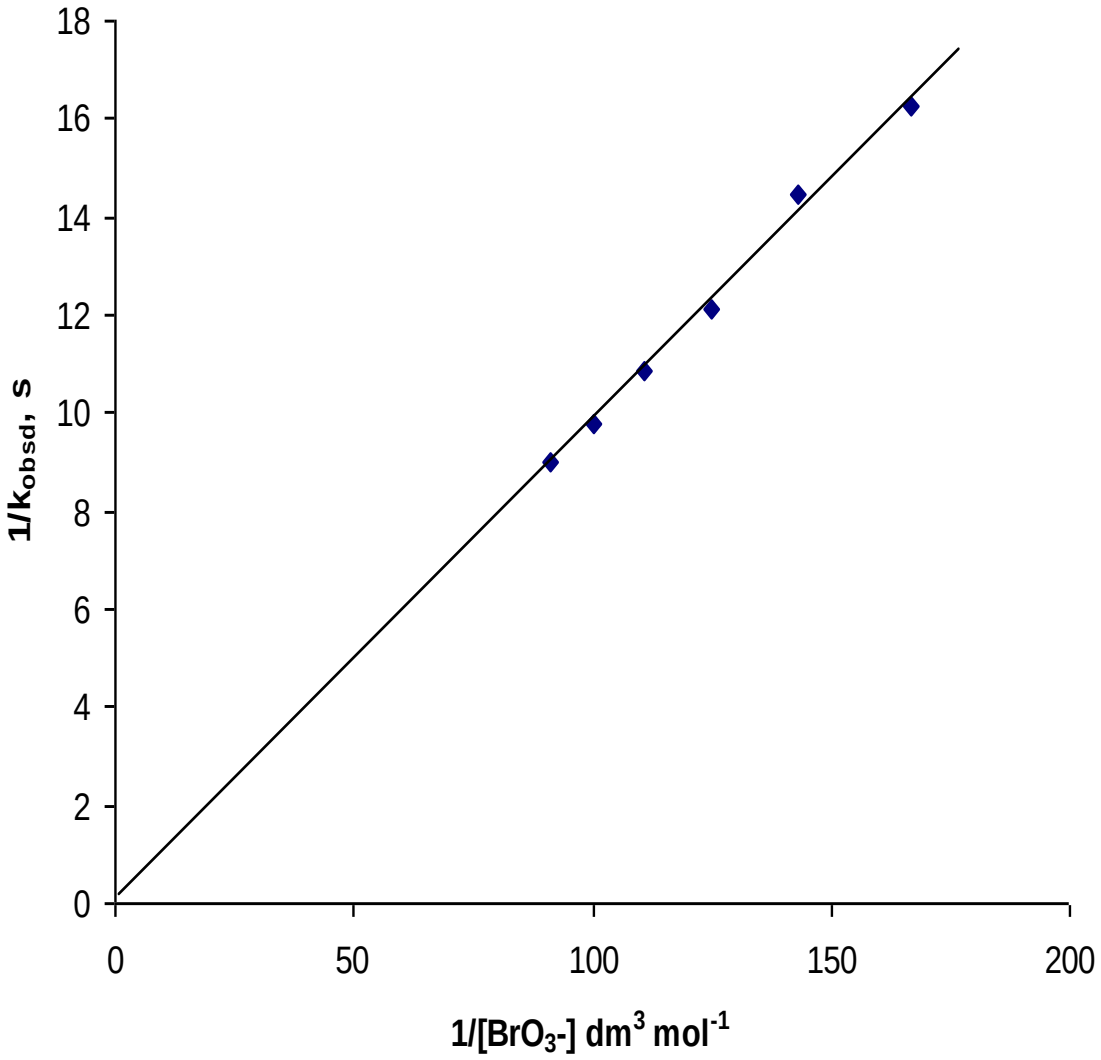

Figure 2. Michaelis–Menten plot for the reaction of MB^+ and BrO_3^-.

4.0 DISCUSSION

As with most reactions of BrO_3^-, it seems that parallel reactions of both protonated and unprotonated species of BrO_3^- occurred (Birk, 1973; Birk and Kozub, 1973; Lohdip and Iyun, 1993). The second order $[H^+]$ dependence term was rationalized in terms of the pre-equilibrium protonation of BrO_3^- to give $H_2BrO_3^+$ (Ayoko *et al.*, 1991; Birk 1973; Idris et. al., 2010; Iyun *et al.*, 1992; Thompson and Knight, 1973). It is thought that the protons serve to weaken the bonds between the oxygen atoms and central-bromine atom (Edwards, 1964), thereby facilitating the reducibility of the later. Since MB^+ is positively charged, the possibility of

$H_2BrO_3^+$ in the medium is supported by the positive Bronsted–Debye salt effect observed for the reaction.

Lack of spectrophotometric evidence for the formation of intermediate complex is an indication of outer-sphere mechanism. Michaelis–Menten plot as reported by Atkins and De Paula (2003), of 1/ k_{obsd} versus 1/ $[BrO_3^-]$, was linear (r = 0.997) with negligible intercept (Figure 2), further suggesting the absence of pre-electron transfer complex formation in this reaction. This view is reinforced by the observed anion inhibition (Table 2), which is a characteristic of outer-sphere mechanism (Adegite *et al.*, 1977; Lohdip and Iyun, 1993; Osunlaja *et al.*, 2012; Przystas and Sutin, 1973). On the bases of the above results, we proposed that the titled reaction occurred via the outer mechanistic pathway as shown below.

4.1 Mechanism

$$BrO_3^- + 2H^+ \xrightarrow{K_3} H_2BrO_3^+ \text{ ---------- (4)}$$

$$BrO_3^- + MB^+ \xrightarrow{k_4} MB^{2+} + BrO_3^{2-} \text{ ---------- (5)}$$

$$H_2BrO_3^+ + MB^+ \xrightarrow{k_5} MB^{2+} + BrO_2 + H_2O \text{ ---------- (6)}$$

$$BrO_3^{2-} + 2H^+ \xrightarrow{k_6} BrO_2 + H_2O \text{ ---------- (7)}$$

$$2MB^{2+} + 2BrO_2 + 8H^+ \xrightarrow{k_7} Product + 2Br^- + 4H_2O \text{ ---------- (8)}$$

$$2Br^- + BrO_3^- + 3H^+ \xrightarrow{k_8} \frac{3}{2}Br_2 + \frac{3}{2}H_2O + \frac{3}{4}O_2 \text{ ---------- (9)}$$

Reactions in equation (9), occurs only in the presence of excess bromine.

With equation (5) and (6) as the rate determining step, the equation for the reaction can be written as;

$$-\frac{1}{2}\frac{d[MB^+]}{dt} = k_4[MB^+][BrO_3^-] + k_5[MB^+][H_2BrO_3^+] \text{ ---------- (10)}$$

When substitution is made for $H_2BrO_3^+$ from equation (4), then equation (10) becomes

$$-\frac{1}{2}\frac{d[MB^+]}{dt} = (k_4 + k_5K_3[H^+]^2)[MB^+][BrO_3^-] \text{ ---------- (11)}$$

k_4 = a = 210 $dm^3\ mol^{-1}\ s^{-1}$ and k_5K_3 = b = 1.6 $dm^9\ mol^{-3}\ s^{-1}$ at 29 ± 1°C

5.0 CONCLUSION

A stoichiometry of 2 to ratio 3 was obtained for the redox reaction between methylene blue and bromate ion in aqueous hydrochloric acidic medium. The reaction was found to be first–order with respect to both methylene blue and bromate ion concentrations and second–order dependence in hydrogen ion concentration.

The rate of reaction was observed to increases with increase in acid concentration and ionic strength of the reaction medium with added anions retarding the reaction rate. Lack of spectrophotometric evidence for the formation of intermediate complex as well result of Michaelis – Menten plot suggests the absence of pre-electron transfer complex formation in this reaction.

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