Bromate ion oxidation of Pyrocatechol Violet in aqueous hydrochloric acid: Kinetics and mechanism

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ABSTRACT

The kinetics of the oxidation of pyrocatechol violet hereafter (refered to PCVH) by bromate ions has been carried out in aqueous hydrochloric acid medium at λ_{max} of 440nm, $T = 26 \pm 0.1^o C$, $I = 0.50$ mol dm^{-3} (NaCl) and $[H^+] = 0.10$ mol dm^{-3} (HCl). The reaction is first order with respect to oxidant and reductant concentration. The reaction obeyed a general rate law

$$\frac{d[PCVH]}{dt} = k_2[PCVH][BrO_3^-][H^+]^2$$

with $k_2 = 2.74$ $dm^{-3}mol^{-1}s^{-1}$. The reaction rate is affected by changes in the concentration of hydrogen ions and in the ionic strength of reaction medium. Added cation and anion inhibited the reaction rate respectively. The results of spectroscopic and kinetic investigation show that no intermediate complex is formed in the course of this reaction.

Key words: Pyrocatechol violet, bromate ion, kinetics, mechanism.

INTRODUCTION

Numerous reactions involving different organic and inorganic substrate and acidic bromate are known[1]. Considerable effort has been devoted towards the understanding of the chemistry of bromate ions in aqueous acid and to the elucidation of the mechanism of the oscillating closed chemical systems[2]. Bromate is a precursor to HOBr, an oxidizing species in the physiological environment [3].

PCVH has been reported as an excellent hair dye used in various cosmetics formulation[4]. When used in a rinse-off application, such as hair dyes may not present a hazard concern if pyrocatechol and its derivative are completely oxidized. It was concluded that there are insufficient data to support the safety assessments of PCVH. The data needed to complete the safety assessment include the extent and rate of oxidation when used in hair dying[4]. This requirement is the motivation for this work. It has the structure show bellow
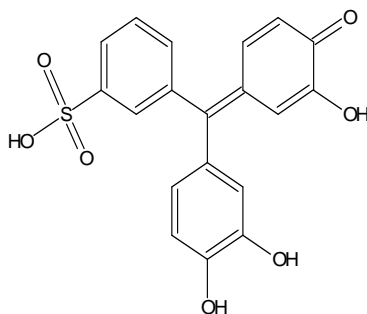
In this paper we report our findings on the kinetics of the oxidation of PCVH by bromate ions with a view to providing some information on the oxidation characteristic of this reactant.

MATERIALS AND METHODS

Experimental
The chemicals used were of analytical grade and were used without further purification. Standard solution of PCVH = 1×10^{-3} mol dm^{-3} was prepared by dissolving 3.863×10^{-3} mol dm^{-3} of PCVH in 10ml distilled water. Sodium bromate and hydrochloric acid solution were also prepared. Hydrochloric acid was standardized titrimetrically. Stock of NaCl, HCOONa, and CH$_3$COONa were prepared by dissolving accurately weighed quantities in a known volumes.

Determination of Stoichiometry
The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method[5]. Under the condition, [H$^+$] = 0.10 mol dm^{-3}, [PCVH] = 4×10^{-5} mol dm^{-3}, I = 0.50 mol dm^{-3}, λ_{max} = 440nm, T = 26 ± 0.1^{o}C and [BrO$_3^-$] = $0.10 - 1.20 \times 10^{-4}$ mol dm^{-3} were used. Reaction mixtures containing reductant and oxidant solutions were allowed to stand until the reaction went to completion. This was observed by measuring the absorbance of the solutions until the completion of the reaction as indicated by steady absorbance value over a period of two days[6]. The stoichiometry was evaluated from the plot of absorbance versus [reductant]/[oxidant].

Kinetics
A Corning 252 colorimetry spectrophotometer was used to follow the decrease in absorbance of the reaction mixture at λ_{max} = 440nm. The kinetics runs were usually conducted under pseudo-first order conditions with [BrO$_3^-$] always in more than a 10-fold excess over [PCVH]. Under this conditions, pseudo-first order rate constant were obtained from plots of log (A$_t$-A$_\infty$) versus time (A$_t$ and A$_\infty$ are absorbances at time t and at the end the reaction respectively) which were linear to greater than 80% of the reaction. The reaction was carried out at 26 ± 0.1^{o}C with [H$^+$] = 0.10 mol dm^{-3} and I = 0.50 mol dm^{-3} (NaCl) unless otherwise stated. The results are presented in Table 1.

The effect of [H$^+$] on the rate
The effect of [H$^+$] on the rate was investigated using hydrochloric acid in the range $(0.4 - 1.5) \times 10$ mol dm^{-3} while the [PCVH] and [BrO$_3^-$] were kept constant[7]. The reaction was carried out at 26 ± 0.1^{o}C and I = 0.50 mol dm^{-3} (NaCl). The results are presented in Table 1.

The effect of ionic strength
The effect of ionic strength on the rate of the reaction was investigated in the range $(3.0 - 9.0) \times 10$ mol dm^{-3} (NaCl) while the concentrations of other reagents were kept constant. The results are presented in Table 1

RESULTS AND DISCUSSION

The stoichiometry of the oxidation of PCVH by BrO_3^- ions is 1:2 as determined by spectrophotometry titration.

$$PCVH + 2BrO_3^- + nH^+ \longrightarrow \text{Pr} oducts \qquad\qquad 1$$

A similar stoichiometry was reported with respect to bromate ion concentration in the redox reaction between catechol and bromated[8].

The linearity of pseudo-first order plot to more than 80% reaction suggests first order dependence with respect to [PCVH].

The plot of $\log k_{obs}$ versus $\log[BrO_3^-]$ gave a gradient of 1.00 with correlation $R^2 = 0.98$ showing that the reaction is first order with respect to $[BrO_3^-]$ (Figure 1). Thus, the rate equation for the reaction is;

$$\frac{d[PCVH]}{dt} = k_2[PCVH][BrO_3^-] \qquad\qquad 2$$

It has been reported that the kinetics plot for the oxidation of BrO_3^- ion with indigo camine gave a fairly straight line with a gradient of 1.04 ± 0.1 indicating a first order dependence of the reaction rate on bromate concentration[1].

Similarly, first-order rate has been reported in the reaction between catechol and bromate ion[8].

The result in Table 1 shows that the rate constant increases with increase in $[H^+]$. Plot of $\log k_{obs}$ against $\log[H^+]$ gave a slope of 2.20 with correlation $R^2 = 0.99$ indicating the reaction is second order with respect to $[H^+]$ (Figure 3). This conforms to the equation:

$$k_2 = a[H^+]^2 \qquad\qquad 3$$

Plot of k_2 versus $[H^+]^2$ gave a straight line that passes through the origin (Figure 4). A graph of this nature indicates equilibrium between the protonated forms of reactant prior to the rate determining step[9]. Only the protonated is reactive.

The result in Table 1, shows that the rate of reaction was found to increase with increase in the ionic strength of reaction medium. A plot of $\log k2$ versus $\sqrt{I}$ gave a linear graph with a slope of 1.93 showing positive Bronsted-Debye salt effect[10]. This suggests that the charges on the reactants in the activated complex is either positive-positive or negative-negative.
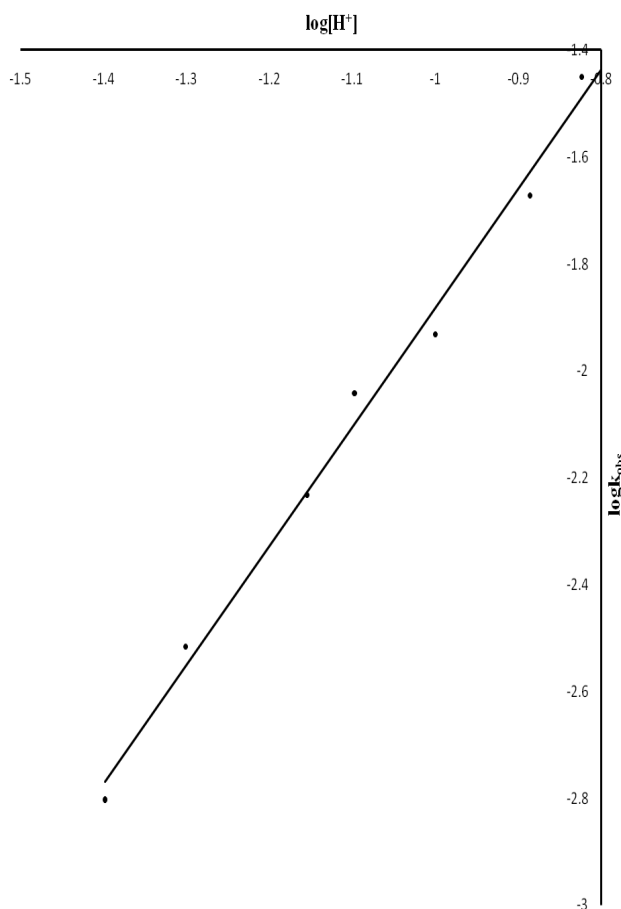
The effect of added ions Mg^{2+}, $Ca^{2+,}$ CH_3OO^- and $HCOO^-$ on the reaction was studied and was found to decrease in rate by both cation and anion as reflected in the values of the rate constant in Table 2. The presence of the cation and anion decrease the rate indicating that the outer-sphere electron transfer may be important in this reaction.
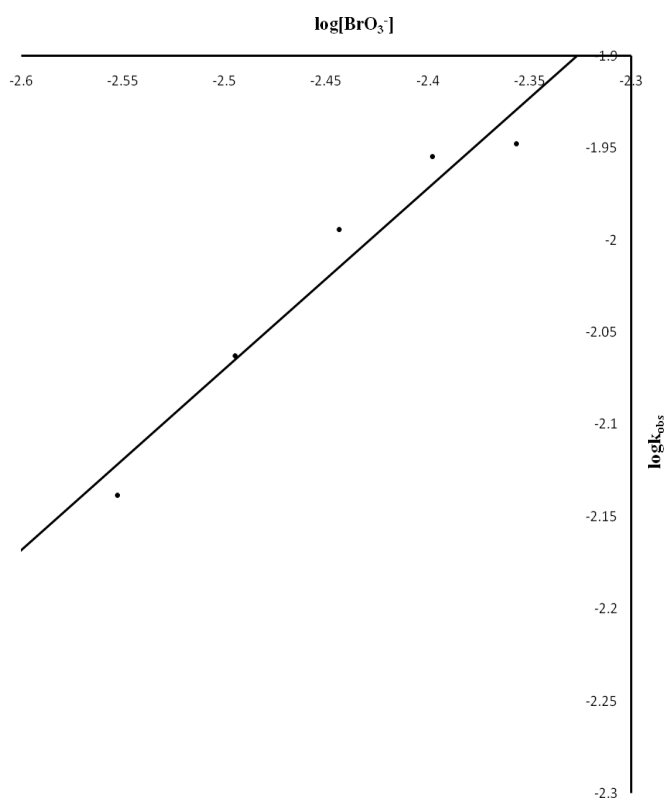
Figure 1: Plot of logk$_{obs}$ versus log[BrO$_3^-$] for the reaction of PCVH and BrO$_3^-$
[PCVH] = 4 x 10^{-5} mol dm^{-3}, [BrO$_3^-$] =2.0 x 10^{-3} – 4.4 x 10^{-3} mol dm^{-3}
[H$^+$] = 1.0 x 10^{-1} mol dm^{-3}, I = 0.5 mol dm^{-3} (NaCl), λ$_{max}$ = 440nm.
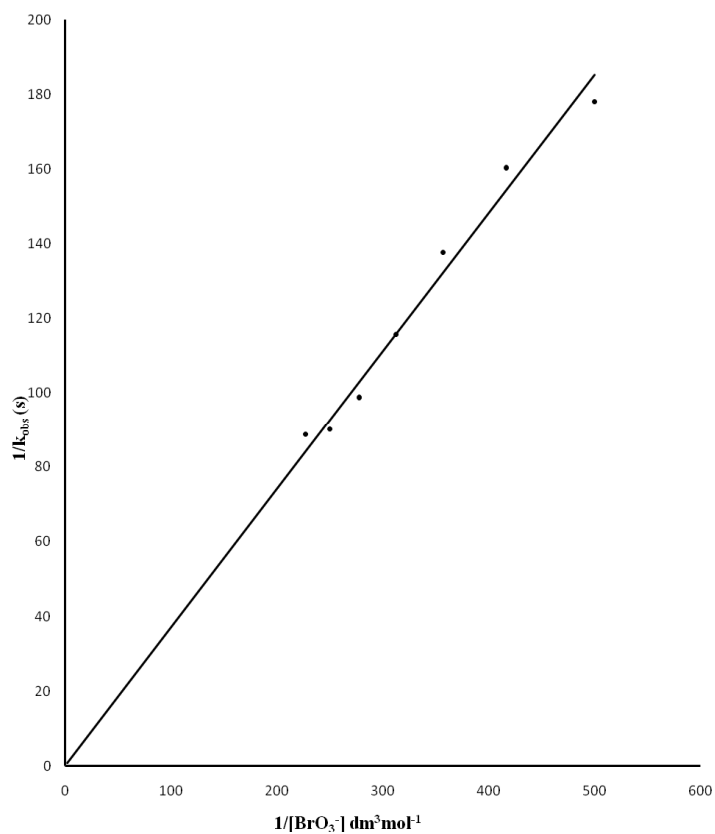
Figure 2: Plot of 1/k$_{obs}$ (s) versus 1/[BrO$_3^-$] (dm^{3}mol^{-1})

Figure 3: Plot of logk$_{obs}$ versus log[H$^+$] for PCVH-BrO$_3^-$ system.
[PCVH] = 4 x10^{-5} mol dm^{-3}, [BrO$_3^-$] = 4.0 x 10^{-3} mol dm^{-3}, λ_{max} = 440nm
[H$^+$] = 1.0 x 10^{-1} mol dm^{-3} , I = 0.5 mol dm^{-3} (NaCl).

Addition of a solution of acrylamide to the partially reacted mixture did not give a gel in the presence of excess methanol indicating the probably absence of free radicals in the reaction mechanism. The plot of 1/k$_{obs}$ versus 1/[BrO$_3^-$] was linear without intercept and spectroscopic studies indicate no significant shifts from the absorption maximum characteristic (Figure 2). These observations suggest absence of intermediate complex prior to the electron transfer in the reaction.

Reaction Mechanism
On the basis of the results, the following mechanism has been proposed for this reaction;

$$BrO_3^- + 2H^+ \overset{K_1}{\rightleftharpoons} H_2BrO_3^+ \qquad\qquad 4$$

$$PCVH + H_2BrO_3^+ \overset{K_2}{\rightleftharpoons} [PCVH, H_2BrO_3^+] \qquad\qquad 5$$

$$[PCVH, H_2BrO_3^+] \overset{k_3}{\longrightarrow} \text{Pr}\,oducts \qquad\qquad 6$$

$$Rate = k_3[PCVH, H_2BrO_3^+] \qquad\qquad 7$$

181
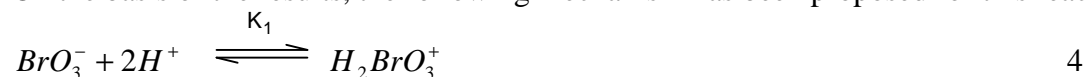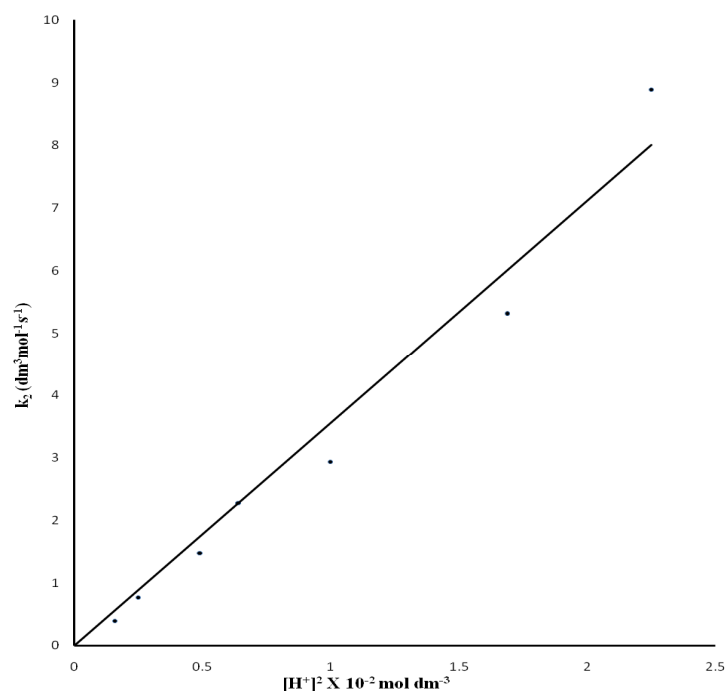
Figure 4: Plot of k_2 ($dm^3 mol^{-1} s^{-1}$) versus $[H^+]^2$ ($mol^2 dm^{-6}$) for PCVH-BrO$_3^-$ sysetm.
[PCVH] = 4 x 10^{-5} mol dm^{-3}, [BrO$_3^-$] = 4.0 x 10^{-3} mol dm^{-3}, λ$_{max}$ = 440nm
[H$^+$] = 1.0 x 10^{-1} mol dm^{-3}, I = 0.5 mol dm^{-3} (NaCl).

Table 1: **Pseudo-first order and Second order rate constant for the oxidation of PCVH by BrO$_3^-$ ion in aqueous HCl medium λ$_{max}$ = 440nm. T = 26 ± 0.1^{o}C, [PCVH] = 4 x 10^{-5} mol dm^{-3}**

10^3 [BrO$_3^-$] (mol dm^{-3})	10 [H$^+$] (mol dm^{-3})	10 [I] (mol dm^{-3})	10^3 k$_{obs}$ (s^{-1})	k$_2$ (dm^{-3}mol^{-1}s^{-1})
2.0	1.0	5.0	5.62	2.81
2.4	1.0	5.0	6.24	2.60
2.8	1.0	5.0	7.27	2.59
3.2	1.0	5.0	8.65	2.70
3.6	1.0	5.0	10.13	2.81
4.0	1.0	5.0	11.10	2.77
4.4	1.0	5.0	11.28	2.56
4.0	0.4	5.0	1.57	0.39
4.0	0.5	5.0	3.05	0.76
4.0	0.7	5.0	5.87	1.47
4.0	0.8	5.0	9.09	2.27
4.0	1.0	5.0	11.70	2.93
4.0	1.3	5.0	21.30	5.32
4.0	1.5	5.0	35.50	8.89
3.6	1.0	3.0	3.50	0.98
3.6	1.0	4.0	6.48	1.80
3.6	1.0	5.0	10.10	2.80
3.6	1.0	6.0	14.20	3.95
3.6	1.0	7.0	16.60	4.62
3.6	1.0	8.0	22.00	6.10
3.6	1.0	9.0	26.40	7.35

But $[PCVH, H_2BrO_3^+] = K_2[PCVH][H_2BrO_3^+]$ 8

Substituting equation 8 into equation 7

$Rate = k_3 K_2[PCVH][H_2BrO_3^+]$ 9

182

From equation 4,

$$[H_2BrO_3^+] = K_1[BrO_3^+][H^+]^2 \qquad\qquad 10$$

Substituting equation 10 into equation 9

$$Rate = K_1 K_2 k_3 [PCVH][BrO_3^+][H^+]^2$$

Table 2: Rate constants for the effect of cation and anion in the oxidation reaction between pyrocatechol violet and bromate ion at [PCVH] = 4 x 10^{-5} mol dm^3, [BrO_3^-] = 3.6 x 10^{-3} mol dm^{-3}, [H^+] = 0.10 mol dm^{-3}, I = 0.50 mol dm^{-3}

10^3 [Mg^{2+}] (mol dm^{-3})	10^3 k_{obs} (s^{-1})	k_2 ($dm^3 mol^{-1} s^{-1}$)
10	9.15	2.54
40	8.19	2.27
80	7.23	2.01
100	7.10	1.97
10^3 [Ca^{2+}] (mol dm^{-3})		
10	9.09	2.53
40	8.15	2.26
80	7.34	2.04
100	6.13	1.70
10^3 [$CHCOO^-$] (mol dm^{-3})		
5.0	9.53	2.65
15.0	7.73	2.15
25.0	7.24	2.01
30.0	7.07	1.96
10^3 [$HCOO^-$] (mol dm^{-3})		
5.0	5.91	1.64
15.0	4.54	1.26
25.0	3.83	1.06
30.0	3.02	0.84

CONCLUSION

The redox reaction of pyrocatechol violet and bromate ion in aqueous hydrochloric acid medium showed a stoichiometry of 1:2, a first order with respect to pyrocatechol violet and bromate ions respectively. The rate of reaction increased with increase in both hydrogen ion concentration and ionic strength of the reaction medium respectively with a second order dependence on hydrogen ion concentration. On the basis of the result obtained in this study, the outer-sphere mechanism is probably operating in this reaction

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