



Kinetics and mechanism of oxidation of pyrocatechol violet by iodate ion in aqueous hydrochloric acid

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Received: 6th October, 2010 ; Accepted: 16th October, 2010

ABSTRACT

The kinetic and mechanism of the oxidation of pyrocatechol violet (hereafter referred to as PCVH) by iodate ion (IO_3^-) have been studied in aqueous hydrochloric acid at ionic strength = 0.5 mol dm^{-3} (NaCl), $[\text{H}^+] = 5 \times 10^{-5} \text{ mol dm}^{-3}$ (HCl), $T = 27 \pm 0.1^\circ\text{C}$. The reaction is first order in both [PCVH] and $[\text{IO}_3^-]$. The redox reaction displayed a stoichiometry of 1:1 and obey the rate law: $\frac{d[\text{PCVH}]}{dt} = (a + b[\text{H}^+])[\text{PCVH}][\text{IO}_3^-]$ where $a = 0.03 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $b = 280.24 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. The second order rate constant increases with increase in acid concentration and ionic strength respectively. This system displayed positive salt effect while spectroscopic investigation and Michaelis-Menten plot showed no evidence of intermediate complex formation. A plausible mechanism has been proposed for the reaction.

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KEYWORDS

Pyrocatechol violet;
Iodate ions;
Kinetics;
Mechanism.

INTRODUCTION

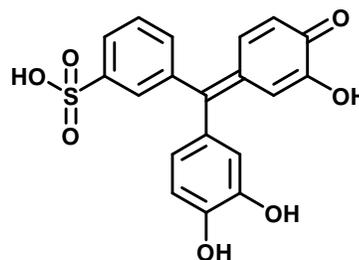
Pyrocatechol violet is a sulphonephthalien dye made from condensing two moles of pyrocatechol with one mole of o-sulfone benzoic acid anhydride. It has an indicator properties and forms complexes with metal ions, making it a useful chelating reagent^[5]. It has been reported that Pyrocatechol violet is used primarily in hair dye and also in skin care preparation. When Pyrocatechol violet was first reviewed it was concluded that this chemical was safe for use in the formulation of cosmetics for skin and hair at concentration up to 1.0%^[2].

A few works have been done on the redox reaction of pyrocatechol violet hereafter designated as PCVH. In determining the concentration of phosphate

and phosphate analogs, metal complexation reaction between ytterbium (Yb^{3+}) and pyrocatechol violet was studied. Stoichiometry of 2:1 (Yb^{3+})–PCVH complex was reported^[10].

It was later reported that the stoichiometry of ytterbium-PCV complex is 1:1^[4].

Pyrocatechol violet has been reported as a chelat-



Structure of Pyrocatechol violet

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ing agent for cupric ions in the characterization of liposomal membrane permeability^[12]. After cupric ions was added to PCVH liposomes, free PCVH turned into its chelate (PCVH-Cu) and encapsulated PCVH was stable since liposomal membrane prevented metal ions from permeating. After the light scattering background of liposome and the absorbance of PCVH were eliminated by the first-order derivative spectrophotometric method, free PCVH in liposome suspensions could be determined without separation. Because PCVH release is relevant to liposomal membrane permeability, PCVH becomes a marker to characterize the membrane permeability.

It has been found that the kinetics of the iodide-iodate reaction in acid medium have been of interest due to the various overall orders reported in literature and due to its key role in a number of oscillatory reaction^[7].

Given the importance of pyrocatechol violet as an indicator and part of skin care formulation, adequate understanding of the mechanism of its redox reaction is important for extending its uses. We herein report our finding on the redox reaction of pyrocatechol violet with iodate ion.

EXPERIMENTAL

All reagents used were Analar grade. Stock solution of PCVH and iodate ions were prepared by dissolving a known amount of each reagent and making up to a known solution volume with distilled water. The λ_{\max} (440nm) for PCVH was determined by reading the electronic spectrum of the solution of PCVH in the wavelength range 400-550nm.

A stock solution of hydrochloric acid was made by diluting commercial acid (36%, specific gravity 1.8) and standardizing the solution using trioxocarbonate (IV). Stock solutions of sodium chloride, magnesium chloride, calcium chloride, sodium nitrate, and sodium sulphate were prepared and standardized gravimetrically.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titrations using the mole ratio method. The reaction mixture containing $[\text{PCVH}] = 4 \times 10^{-5} \text{ mol dm}^{-3}$ and varied concentration of Iodate ion

at $[\text{H}^+] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ and $I = 0.50 \text{ mol dm}^{-3}$ (NaCl) were allowed to stand until the reaction went to completion. The absorbance of the solutions was measured until the completion of the reaction as indicated by steady absorbance value over a period of two days^[11]. The absorbances of the solutions were then measured at 440nm. The stoichiometry was evaluated from the plot of absorbance versus $[\text{PCVH}]/[\text{IO}_3^-]$.

Kinetic measurement

The rate of the reaction of PCVH with iodate ions was studied by observing the decrease in absorbance of PCVH at 440nm on a Corning 252 colorimeter. All kinetic measurements were carried out under pseudo-first order conditions with iodate ions concentration in excess of 10-fold over the PCVH concentration at $27 \pm 0.1^\circ\text{C}$ and 0.50 mol dm^{-3} (NaCl) ionic strength. The pseudo-first order plots of the $\log(A_t - A_\infty)$ versus time were made. From the gradient of the plots, the pseudo-first order rate constant, k_{obs} , were determined. The second-order rate constant, k_2 , were obtained from k_{obs} as $k_{\text{obs}}/[\text{IO}_3^-]$, (TABLE 1).

Acid dependence

The influence of $[\text{H}^+]$ on the reaction rate was investigated using hydrochloric acid in the range $(1.0-14.0) \times 10^{-3} \text{ mol dm}^{-3}$ while the $[\text{PCVH}]$ and $[\text{IO}_3^-]$ were kept constant. The reaction was carried out at 27°C and $I = 0.50 \text{ mol dm}^{-3}$ (NaCl), (TABLE 1).

The effect of ionic strength

The effect of ionic strength on the rate of the reaction was investigated in the $I = (1.0-8.0) \times 10^{-3} \text{ mol dm}^{-3}$ (NaCl) while the concentrations of the other reagents were kept constant (TABLE 1).

RESULTS

The stoichiometry of this reaction using mole/ratio concept was found to be in ratio of 1:1 with respect to both $[\text{PCVH}]$ and $[\text{IO}_3^-]$.

Kinetics measurement

The pseudo-first order plots of $\log(A_t - A_\infty)$ versus time for the reaction were linear for about 70% of the reaction. The linearity of these plots shows that this reaction is first order with respect to $[\text{PCVH}]$. The plot

TABLE 1 : Pseudo-first order and second order rate constant for the reaction of PCV and IO_3^- . At $[\text{PCVH}] = 4 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$ (NaCl), $T = 27 \pm 0.1^\circ\text{C}$ and $\lambda_{\text{max}} = 440\text{nm}$

$10^3[\text{IO}_3^-]$ (mol dm^{-3})	$10^3[\text{H}^+]$ (mol dm^{-3})	$10[\text{I}]$ (mol dm^{-3})	$10^3 k_{\text{obs}}$ (s^{-1})	k_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
4.0	5.0	5.0	5.52	1.38
4.8	5.0	5.0	6.41	1.33
5.6	5.0	5.0	7.73	1.38
6.4	5.0	5.0	8.99	1.40
7.2	5.0	5.0	9.87	1.37
8.0	5.0	5.0	11.18	1.39
8.8	5.0	5.0	12.28	1.39
9.6	5.0	5.0	13.37	1.39
6.4	1.0	5.0	1.72	0.27
6.4	3.0	5.0	6.08	0.95
6.4	5.0	5.0	9.02	1.41
6.4	7.0	5.0	12.20	1.90
6.4	9.0	5.0	17.27	2.69
6.4	12.0	5.0	21.49	3.35
6.4	14.0	5.0	25.33	3.95
6.4	5.0	1.0	6.84	1.06
6.4	5.0	2.0	7.23	1.13
6.4	5.0	3.0	8.06	1.25
6.4	5.0	4.0	8.33	1.30
6.4	5.0	5.0	8.99	1.40
6.4	5.0	6.0	9.43	1.47
6.4	5.0	7.0	9.65	1.50
6.4	5.0	8.0	10.74	1.67

of $\log k_{\text{obs}}$ versus $\log[\text{IO}_3^-]$ gave a slope of 1.02 with correlation $R^2 = 99.7\%$ indicating first order with respect to $[\text{IO}_3^-]$ (Figure 1). The overall rate law for this reaction can therefore be given as:

$$\frac{d[\text{IO}_3^-]}{dt} = k_2[\text{PCVH}][\text{IO}_3^-] \quad (1)$$

Effect of hydrogen Ion on the rate

The result in TABLE 1 shows that the rate constant increases with increase in $[\text{H}^+]$. Plot of $\log k_{\text{obs}}$ against $\log[\text{H}^+]$ gave a slope of 0.94 with correlation $R^2 = 98\%$ indicating that the reaction is first order with respect to $[\text{H}^+]$ (Figure 3). Plot of k_2 (second-order rate constant of acid dependence) versus $[\text{H}^+]$ gave a linear plot with an intercept (Figure 4). The acid dependence rate constant can be represented by the equation.

$$K_2 = a + b[\text{H}^+] \quad (2)$$

Substituting eq. (2) into (1)

TABLE 2 : Dependence of observed first order and second order rate constant for redox reaction of pyrocatechol violet with IO_3^- on cation and anion concentration $[\text{PCVH}] = 4 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{IO}_3^-] = 6.4 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 5 \times 10^{-3} \text{ mol dm}^{-3}$

$10^3[\text{Mg}^{2+}]$ (mol dm^{-3})	$10^3 k_{\text{obs}}$ (s^{-1})	k_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
80	8.88	1.38
120	9.04	1.41
160	8.88	1.38
$10^3 [\text{Ca}^{2+}]$ (mol dm^{-3})		
100	9.02	1.41
120	8.88	1.39
160	9.21	1.44
$10^3 [\text{NO}_3^-]$ (mol dm^{-3})		
80	8.22	1.28
120	7.73	1.20
160	7.23	1.13
$10^3 [\text{SO}_4^{2-}]$ (mol dm^{-3})		
40	3.29	0.59
80	1.91	0.29
100	1.42	0.22

The rate equation can be written:

$$\frac{d[\text{IO}_3^-]}{dt} = (a + b[\text{H}^+])[\text{PCVH}][\text{IO}_3^-] \quad (3)$$

where $a = 0.03 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$, $b = 280.24 \text{ dm}^6 \text{mol}^{-2} \text{s}^{-1}$

Effect of ionic strength

Ionic strength was varied from $(1.0-8.0) \times 10 \text{ mol dm}^{-3}$ (NaCl) at constant concentration of iodate ions, $[\text{PCVH}]$ and hydrogen ions concentration. The rate of reaction was found to increase with increase in ionic strength. The plot of $\log k_2$ versus \sqrt{I} gives a slope = 0.34.

DISCUSSION

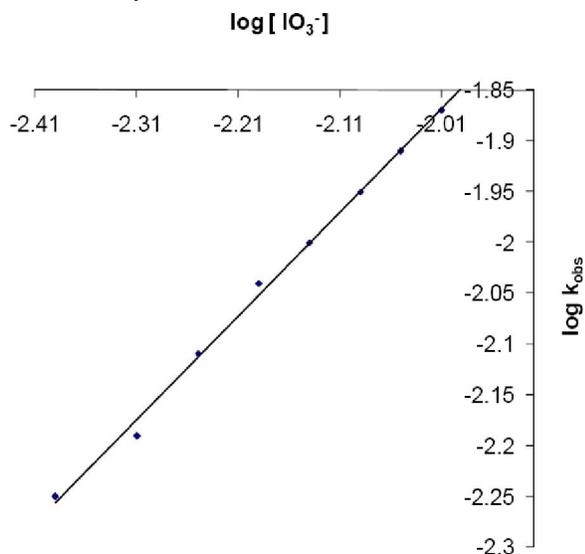
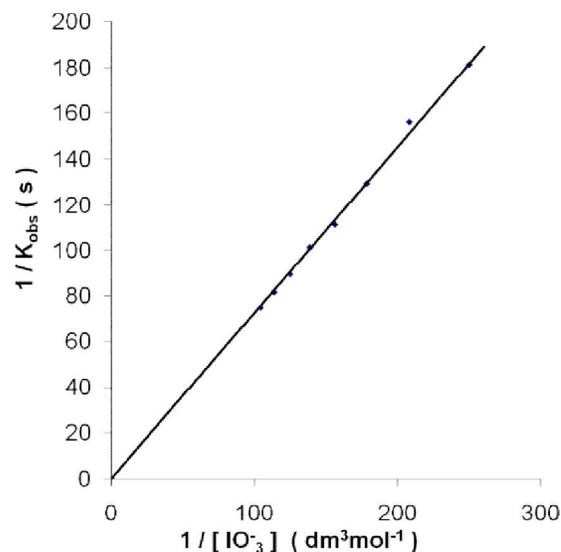
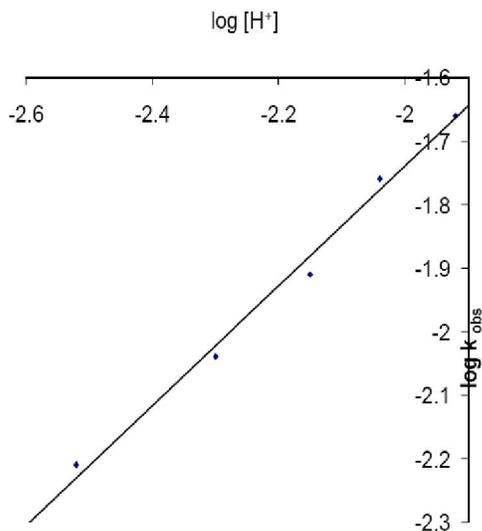
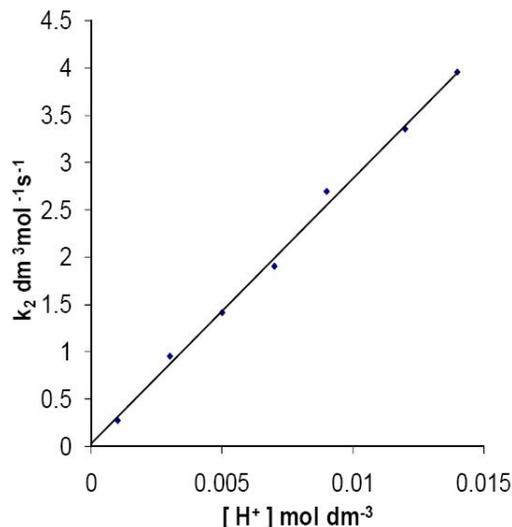
The stoichiometry obtained in this work is ratio 1:1. Hence the overall equation for the title reaction can be written as,



Kinetics studies of the reaction showed that the reaction is first order with respect to PCVH concentration and IO_3^- concentration. This is consistent with what has been reported in the reaction between iodate and 1,3-dihydroxybenzene in aqueous perchloric acid medium^[8].

It has been reported that the bulk of iodate-based oxidation are borne by the reactive oxyiodine species

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Figure 1 : Plot of $\log k_{\text{obs}}$ versus $\log [\text{IO}_3^-]$ Figure 2 : Plot of $1/k_{\text{obs}}$ (s) versus $1/[\text{IO}_3^-]$ ($\text{dm}^3 \text{mol}^{-1}$)Figure 3 : Plot of $\log k_{\text{obs}}$ versus $\log [\text{H}^+]$ Figure 4 : Plot of $k_2 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ versus $[\text{H}^+] \text{mol dm}^{-3}$

HIO_2 , IO_2 , and HOI as well as molecular iodine, I_2 ^[3,9]. These species can be generated in acidic iodate condition and the rate of iodate oxidations are usually controlled by the rate at which these reactive species are generated. Investigations of Briggs-Rauscher and Brayliebhafsky reaction have suggested that the nucleophilic species is the trace amount of iodide ions that are contained in normal iodate solution^[1].



The $\text{H}_2\text{I}_2\text{O}_3$ species formed above can then break down in the rate-determining step to produce the reactive species, HIO_2 , and HOI ^[9].

After the oxidation product has been formed, the iodide produced is fed back into the reaction medium to facilitate further oxidation of the reaction species. With this, we may accept iodosic acid as a viable oxidant, it, however, rapidly reacts with iodide to produce more hypoiodous acid^[3].

The acid dependence studies showed a non-zero intercept when k_2 was plotted against $[\text{H}^+]$. A graph of this nature indicates that there are two pathways prior to the rate determining steps: the protonated path and the unprotonated path^[6,11]. Also, the first order with respect to $[\text{H}^+]$ obtained in this work is in consistence with already reported redox reaction between IO_3^- and 1,3-dihydroxybenzene^[8].

TABLE 1 shows that change in concentration of ionic strength affect the rate of reaction.

If pure coulomb interaction were the sole determinant of the observed effect, one would have expected a negative salt effect. This result indicates that there is a positive salt effect in the reaction at the activated complex. It means that the charges on the reactant ions in the activated complex may be either positive-positive or negative-negative.

This suggest inner-sphere mechanism and is supported by the lack of dependence on rate constant obtained by changing the concentration of cation (TABLE 2).

Spectroscopic studies indicate no significant shifts from the absorption maximum of PCVH. This suggests absence of intermediate complex formation prior to electron transfer in the reaction. This is further supported by analysis of Michaelis-Menten plot (plot of $1/k_{\text{obs}}$ (s) versus $1/[\text{IO}_3^-]$ ($\text{dm}^3 \text{mol}^{-1}$)) which gives no intercept (Figure 2).

The plausible mechanism consistent with the result is:



$$\text{Rate} = k_3[\text{PCVH}_2^+, \text{IO}_3^-] + k_5[\text{PCVH}, \text{IO}_3^-] \quad (12)$$

From eq. (8) and (10)

$$[\text{PCVH}_2^+, \text{IO}_3^-] = K_2[\text{PCVH}_2^+][\text{IO}_3^-] \quad (13)$$

and

$$[\text{PCVH}, \text{IO}_3^-] = K_4[\text{PCVH}][\text{IO}_3^-] \quad (14)$$

Substituting eq. (13) and (14) into (12)

$$\text{Rate} = K_2 k_3 [\text{PCVH}_2^+][\text{IO}_3^-] + K_4 k_5 [\text{PCVH}][\text{IO}_3^-] \quad (15)$$

From eq. (7)

$$[\text{PCVH}_2^+] K_1 [\text{PCVH}][\text{H}^+] \quad (16)$$

Substituting eq. (16) into eq. (15)

$$\text{Rate} = K_1 K_2 k_3 [\text{PCVH}][\text{IO}_3^-][\text{H}^+] + K_4 k_5 [\text{PCVH}][\text{IO}_3^-] \quad (17)$$

Addition of a solution of acrylamide to partially re-

acted mixture did not give a gel in the presence of excess methanol indicating the probable absence of free radical in the reaction mechanism.

CONCLUSION

The redox reaction of pyrocatechol violet and iodate ion in aqueous acidic medium showed a stoichiometry of 1:1, a first order with respect to pyrocatechol violet and iodate ions respectively. The rate of reaction increased with increase in both hydrogen ion concentration and ionic strength of the reaction medium, with a first order dependence on hydrogen ion concentration. An intermediate complex was not implicated in the course of the reaction.

Based on these results, the reaction is most probably occurring through the outer-sphere mechanism.

ACKNOWLEDGEMENT

We acknowledge all the staff of Chemistry department, Ahmadu Bello University, Zaria for their immeasurable support during the course of this work.

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