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Kinetics and mechanism of oxidation of Pyrocatechol Violet by chlorite ion in aqueous hydrochloric acid

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ABSTRACT

At $I = 0.50 \text{ mol dm}^{-3}$ (NaCl), $T = 21 \pm 1^\circ\text{C}$, $[H^+] = (0.6-1.8) \times 10^{-2} \text{ mol dm}^{-3}$, the oxidation-reduction reaction between pyrocatechol violet (hereafter referred to PCVH) and chlorite ions have been studied and has a stoichiometry of 1:1. The reaction is second-order overall, first-order in both oxidant and reductant. The reaction occurs by parallel acid independent and acid-dependent pathways suggesting HClO^- and ClO_2^- as the principal reactant chlorite species. The second order rate constant increases with increase in acid concentration and decrease with an increase in ionic strength of the reaction medium. The reaction rate was mildly reduced by anions SO_4^{2-} and HCOO^- . The test for free radicals was negative. The kinetic data are consistent with the following equation:

$$\frac{d[\text{ClO}_2^-]}{dt} = (a + b[H^+])[\text{PCVH}][\text{ClO}_2^-]$$

The experimental results are in favour of the outer-sphere mechanisms

Key Words: Pyrocatechol violet, Chlorite ions, Kinetic, Mechanism.

INTRODUCTION

Chlorite is very reactive. Oxidation reaction of chlorite ions with dyes such as triphenylmethane, malachite green and crystal violet have been reported with stoichiometry 1:2 respectively [1]. Redox reaction of chlorite ion with formaldehyde and ethanol have been studied. In these reactions an order of one was obtained for the [oxidant] and [reductant] respectively. The reaction also occurred by a two-step mechanism, with the chlorite-formaldehyde reaction having a stoichiometry of 1:2.

It has been suggested that the reaction between the chlorine oxide oxidant and certain metal ions proceed via an inner sphere path [2]. This oxidant can be reduced in both one- and two-electron

steps. For example, in the reduction of chlorate ions to chloride ion in acid solution, chlorine dioxide, chlorous acid, hypochlorous acid and chlorine are possible intermediate. These intermediates can either interact with one another or they in turn be reduced ultimately to chloride ions if the rate of their further reduction are faster than the rate of their self-interaction. It has been reported that PCVH is used primarily in hair dye and also in skin care preparation. When PCVH was first reviewed it was concluded that it was safe for use in the formulation designed for discontinuous, brief use, followed by rinsing from the skin and hair at concentration of up to 1.0% [3].

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

MATERIALS AND METHODS

Pyrocatechol violet (B.D.H, analar grade) stock solution was prepared by weighing a known amount and dissolving in a known volume of distilled water. A stock solution of hydrochloric acid was prepared by diluting 36% HCl. The solution was then standardized using sodium carbonate as primary standard. Stock solution of sodium chloride, sodium sulphate and sodium formate were prepared and standardized titrimetrically.

Kinetic Measurements

The rate of the reaction was monitored on Corning Spectronic 252 colorimeter. The rate of the reaction of the oxidant with reductant was studied by monitoring the decrease in absorbance of the oxidant at wavelength $\lambda_{\max} = 440\text{nm}$, characteristic of the reductant. All kinetic measurements were carried out under pseudo-first order conditions with respect to oxidant at least 10-fold in excess over the reductant concentration at 21°C and 0.50 mol dm^{-3} (NaCl) ionic strength. The pseudo-first order rate constant k_{obs} were determined from the slope of the plots. The results are presented in Table 1.

Effect of Hydrogen ion on the rate

The influence of acid on the rate of the reaction was investigated in the acid range $(0.6-1.8) \times 10^{-2}\text{ mol dm}^{-3}$, while the [PCVH] mol dm^{-3} and $[\text{ClO}_2^-]$ mol dm^{-3} were kept constant at $4 \times 10^{-5}\text{ mol dm}^{-3}$ and $3.6 \times 10^{-3}\text{ mol dm}^{-3}$ respectively. The reaction was carried out at $T = 21 \pm 0.1^\circ\text{C}$ and $I = 0.50\text{ mol dm}^{-3}$ (NaCl).

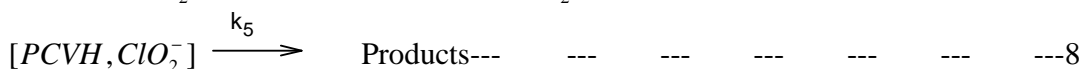
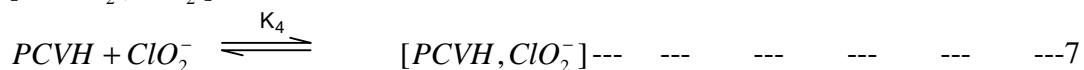
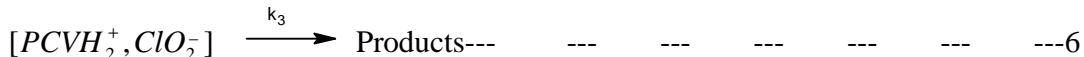
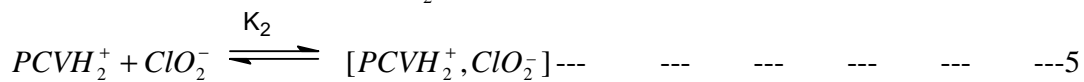
Effect of ionic strength

The effect of ionic strength on the rate of the reaction was investigation in the range of $I = (1.0-8.0) \times 10^{-3}\text{ mol dm}^{-3}$ (NaCl) while the [PCVH] = $4 \times 10^{-5}\text{ mol dm}^{-3}$, $[\text{ClO}_2^-] = 3.6 \times 10^{-3}\text{ mol dm}^{-3}$ and $[\text{H}^+] = 1.0 \times 10^{-2}\text{ mol dm}^{-3}$ were kept constant. The rate of the reaction was found to decrease with increase in ionic strength. The results are presented in Table 1.

Effect of Added Anion / Cation

While the concentrations of all other reactant were kept constant and at ionic strength of 0.50 mol dm^{-3} (NaCl), the effect of added cation and anion on the rate of the reaction was investigated over the range $(10-70) \times 10^{-3}\text{ mol dm}^{-3}$ respectively. The results are presented in the Table 2.

The dependence of rate on anion concentration is a common feature of reactions proceeding by the outer sphere pathway. The outer sphere mechanism has been reported for the reaction of catechol, a precursor compound to pyrocatechol violet [8]. On the basis of the results obtained in this investigation the following mechanisms is proposed,



$$\text{Rate} = k_3 [PCVH_2^+, ClO_2^-] + k_5 [PCVH, ClO_2^-] \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \quad \text{---} 9$$

From equation 5 and 7

$$[PCVH_2^+, ClO_2^-] = K_2 [PCVH_2^+] [ClO_2^-] \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \quad \text{---} 10$$

and

$$[PCVH, ClO_2^-] = K_4 [PCVH] [ClO_2^-] \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \quad \text{---} 11$$

Substituting equation 10 and 11 into equation 9

$$\text{Rate} = K_2 k_3 [PCVH_2^+] [ClO_2^-] + K_4 k_5 [PCVH] [ClO_2^-] \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \quad \text{---} 12$$

From equation 4

$$[PCVH_2^+] = K_1 [PCVH] [H^+] \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \quad \text{---} 13$$

Substituting equation 13 into equation 12

$$\text{Rate} = K_1 K_2 k_3 [PCVH] [ClO_2^-] [H^+] + K_4 k_5 [PCVH] [ClO_2^-]$$

Addition of a solution of acrylamide to a partially reacted mixture of these reactants did not give a gel in the presence of excess methanol, indicating the probable absence of free radical in the reaction medium.

Table 1: Pseudo-first order and Second order rate constant for the reaction of pyrocatechol violet and chlorite ions: $[PCVH] = 4 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$ (NaCl), $T = 21 \pm 0.1^\circ \text{C}$, $\lambda_{\text{max}} = 440 \text{ nm}$

$10^3 [\text{NaClO}_2^-]$ (mol dm^{-3})	$10^2 [\text{H}^+]$ (mol dm^{-3})	$10 [I]$ (mol dm^{-3})	$10^3 k_{\text{obs}}$ (s^{-1})	k_2 ($\text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$)
2.0	1.0	5.0	3.94	1.97
2.4	1.0	5.0	4.60	1.91
2.8	1.0	5.0	5.75	2.05
3.2	1.0	5.0	6.21	1.94
3.6	1.0	5.0	6.90	1.92
4.0	1.0	5.0	7.52	1.88

4.4	1.0	5.0	7.98	1.81
4.8	1.0	5.0	9.02	1.88
3.6	0.6	5.0	4.86	1.35
3.6	0.8	5.0	5.83	1.62
3.6	1.0	5.0	6.90	1.92
3.6	1.2	5.0	7.69	2.13
3.6	1.4	5.0	8.63	2.39
3.6	1.6	5.0	9.40	2.61
3.6	1.8	5.0	10.36	2.89
3.6	1.0	1.0	12.50	3.47
3.6	1.0	2.0	10.52	2.92
3.6	1.0	3.0	9.54	2.65
3.6	1.0	4.0	7.56	2.10
3.6	1.0	5.0	6.90	1.92
3.6	1.0	6.0	5.59	1.55
3.6	1.0	7.0	4.60	1.28
3.6	1.0	8.0	4.44	1.23

Table 2: Dependence of observed first order and second order rate constant for redox reaction of pyrocatechol violet with ClO_2^- on cation and anion concentration

$10^3[\text{SO}_4^{2-}]$ (mol dm^{-3})	$10^3 k_{\text{obs}}$ (s^{-1})	k_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
10	6.25	1.73
30	4.77	1.33
50	3.55	0.98
70	2.13	0.59
$10^3[\text{Ca}^{2+}]$ (mol dm^{-3})		
10	8.25	2.29
30	9.02	2.51
50	10.59	2.94
70	12.09	3.36

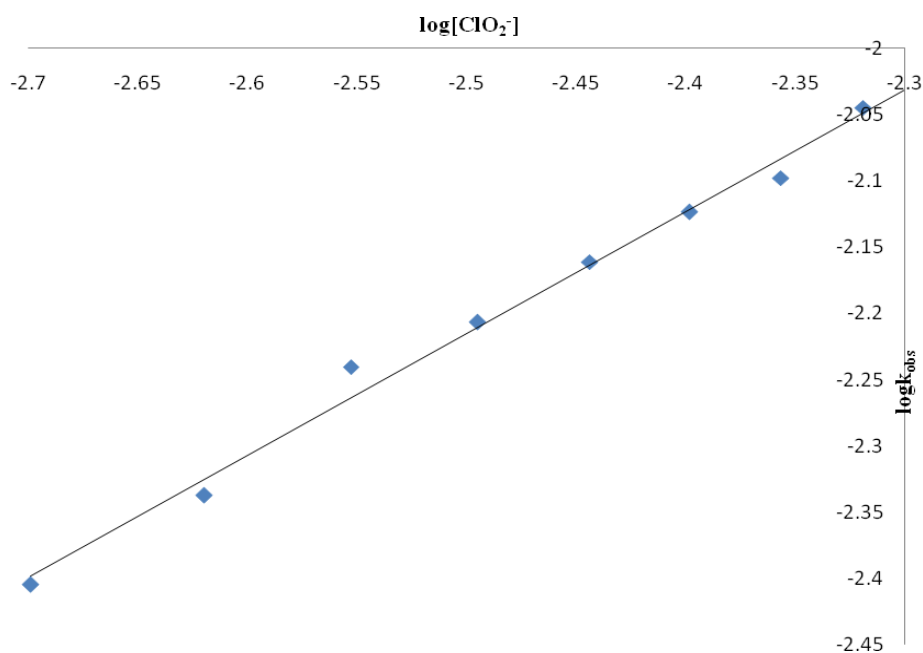


FIGURE 1: Plot of $\log k_{\text{obs}}$ versus $\log[\text{ClO}_2^-]$ for PCVH- ClO_2^- system

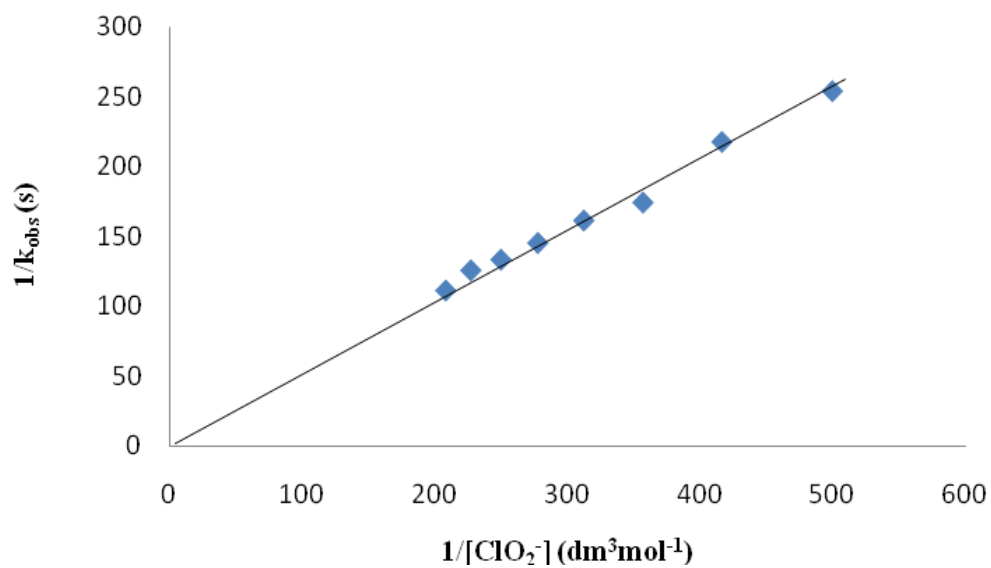


FIGURE 2: Plot of $1/k_{\text{obs}}$ (s) versus $1/[\text{ClO}_2^-]$ ($\text{dm}^3\text{mol}^{-1}$) for PCVH- ClO_2^- system

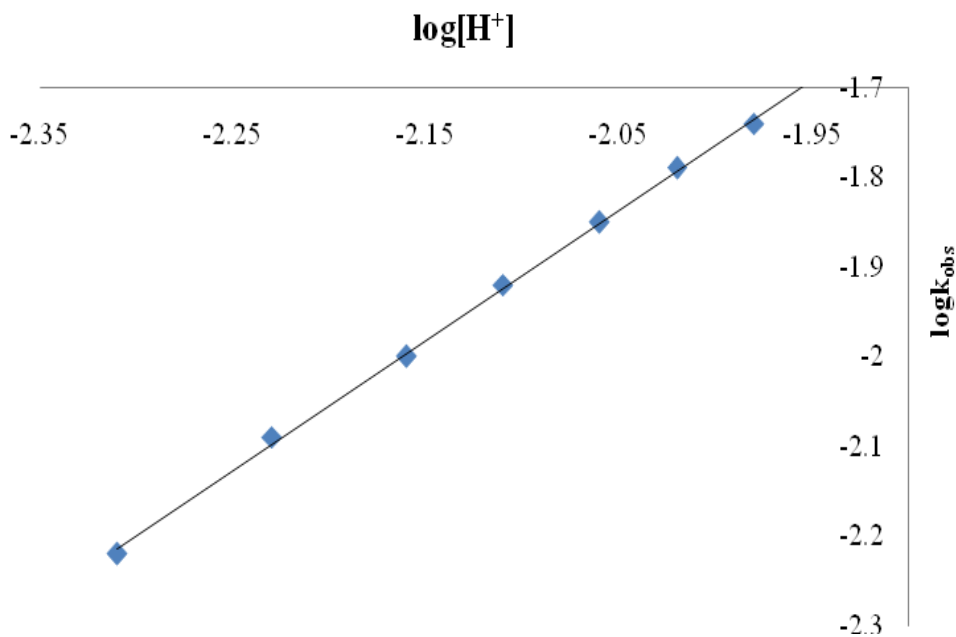


FIGURE 3: Plot of $\log k_{\text{obs}}$ versus $\log[\text{H}^+]$ for PCVH- ClO_2^- system

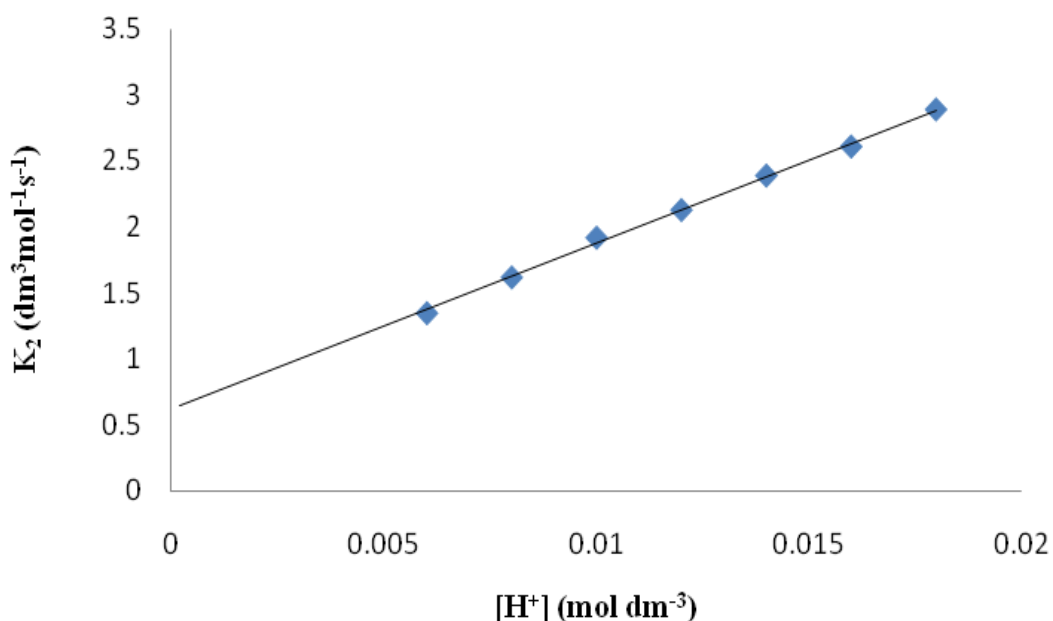


FIGURE 4: Plot of k_2 ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$) versus $[\text{H}^+]$ (mol dm^{-3}) for PCVH- ClO_2^- system

CONCLUSION

The redox reaction of pyrocatechol violet and chlorite ion in aqueous acidic medium showed a stoichiometry of 1:1, a first order with respect to pyrocatechol violet and chlorite ions respectively. The rate of reaction increased with increase in both hydrogen ion concentration and

decrease with increase in ionic strength of the reaction medium. With a first order dependence on hydrogen ion concentration. On the basis of the results obtained in this study, the outer-sphere mechanism is probably operating in this reaction.

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