

## Kinetic Approach to the Mechanism of Redox Reaction of Pyrocatechol Violet and Nitrite Ion in Aqueous Hydrochloric Acid

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**Abstract:** The kinetics of the oxidation of Pyrocatechol violet (PCVH) by nitrite ion ( $\text{NO}_2^-$ ) in aqueous acidic medium has been studied at  $24 \pm 1^\circ\text{C}$ ,  $I = 0.50 \text{ mol}/\text{dm}^3$ (NaCl),  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol}/\text{dm}^3$ . The reaction is first order to [PCVH] and half order to  $[\text{NO}_2^-]$ . The redox reaction displayed a 1:1 stoichiometry and obeys the rate law:  $d[\text{PCVH}]/dt = (a + b[\text{H}^+]) [\text{PCVH}][\text{NO}_2^-]^{1/2}$ . The second-order rate constant increases with increase in acid concentration and ionic strength. This system displayed positive salt effect while spectroscopic investigation and Michaelis-Menten plot showed evidence of intermediate complex formation in the course of the reaction. A plausible mechanism has been proposed for the reaction.

**Key words:** Kinetics, mechanism, nitrite ion, pyrocatechol violet

### INTRODUCTION

Oxidation-reduction reaction involving nitrite ion ( $\text{NO}_2^-$ ) is well known (Onu and Iyun, 1998). The studied of reduction of  $\text{Pt}[\text{Co}-\text{phenylene-bis-dimethylarsin Br}_2]^{2+}$  by  $\text{NO}_2^-$  in anhydrous MeOH has been reported (Nicholas and Stanley, 1981). It was found that the reaction proceeded through a two steps inner-sphere mechanism which involves the transfer of two electrons from the reductant to the oxidant. In the reduction of riboflavin by  $\text{NO}_2^-$ ,  $\text{H}_2\text{O}_2$  was obtained as the product while  $\text{NH}_3$  was the product formed for the reaction involving ascorbic acid (Gurevich and Trubachev, 1964). Pyrocatechol violet (hereafter referred as PCVH) is predominantly used as hair dyes. It was reported that if PCVH were completely oxidized prior to the application of oxidative hair dyes, the concerns regarding the carcinogenic/cocarcinogenic potential would be alleviated; however no data regarding the extent and rate of oxidation were available (Andersen, 1997). The kinetics studies of the redox reactions of the PCVH is therefore necessary for understanding its safety assessment when use in cosmetic formulation. PCVH has the structure shown in Fig. 1.

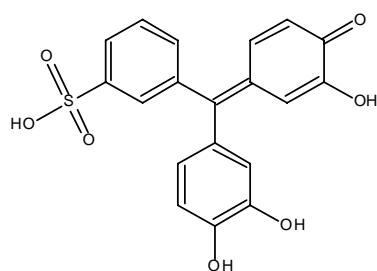


Fig. I: PCVH structure

In this study we report our findings on the kinetics of reduction of PCVH by  $\text{NO}_2^-$  ion under the stipulated experimental conditions.

### EXPERIMENTAL

Chemicals used were of analytical grades and were therefore used without further purification. Standard solutions of PCVH and Sodium chlorite were prepared by dissolving a known amount into distilled water and making it up to a known solution volume.  $1 \text{ mol}/\text{dm}^3$  hydrochloric acid solution was also prepared. Hydrochloric acid was standardized titrimetrically using Sodium trioxocarbonate (IV). Stock solutions of  $1 \text{ mol}/\text{dm}^3$  NaCl,  $\text{NaNO}_3$ , and  $\text{Na}_2\text{SO}_4$  were also prepared respectively by dissolving accurately weighed quantities in a known volume of distilled water.

**Stoichiometry:** The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method (Idris *et al.*, 2005). Under the condition,  $[\text{H}^+] = 1 \times 10^{-3} \text{ mol}/\text{dm}^3$  and  $I = 0.50 \text{ mol}/\text{dm}^3$  (NaCl), reaction mixtures containing reductant and oxidant solution at  $[\text{H}^+] = 1 \times 10^{-3} \text{ mol}/\text{dm}^3$  and  $I = 0.50 \text{ mol}/\text{dm}^3$  were allowed to stand until the reaction went to completion. This was ascertained by a steady absorbance value over a period of two days (Babatunde, 2008). The absorbance of the solutions were then measured at  $\lambda_{\text{max}} = 440 \text{ nm}$  of reaction products. The stoichiometry was evaluated from the plot of absorbance versus  $[\text{PCVH}]/[\text{NO}_2^-]$ .

**Kinetics:** A Corning 252 colorimeter was used to follow the decrease in absorbance of the reaction mixture at

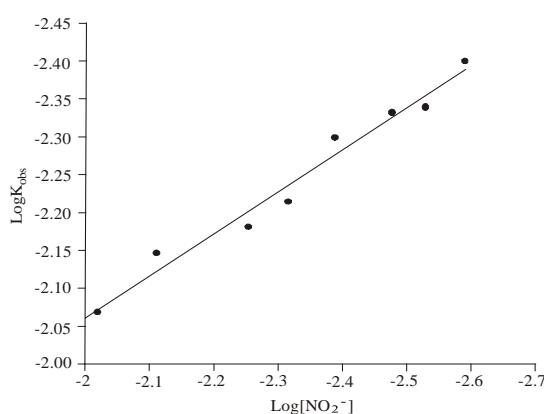


Fig. 2: Plot of  $\log k_{\text{obs}}$  versus  $\log[\text{NO}_2^-]$  for the reaction of PCVH and  $\text{NO}_2^-$  [PCVH] =  $3.8 \times 10^{-5}$  mol/dm $^3$ ,  $[\text{NO}_2^-] = 2.28 \times 10^{-3} - 9.50 \times 10^{-3}$  mol/dm $^3$   $[\text{H}^+] = 1.0 \times 10^{-3}$  mol/dm $^3$ , I = 0.5 mol/dm $^3$  (NaCl),  $\lambda_{\text{max}} = 440$  nm

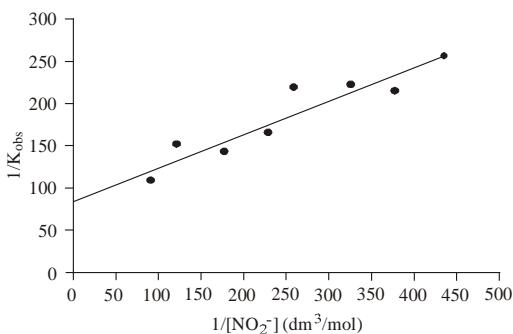


Fig. 3: Plot of  $1/k_{\text{obs}}$  (s) versus  $1/[\text{NO}_2^-]$  (per dm $^3$  . mol) for the PCVH- $\text{NO}_2^-$  system

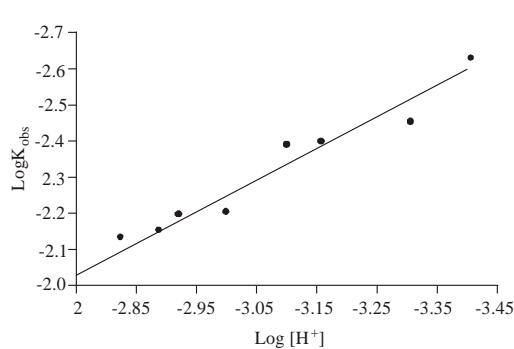


Fig. 4: Plot of  $\log k_{\text{obs}}$  versus  $\log[\text{H}^+]$  for PCVH- $\text{NO}_2^-$  system, [PCVH] =  $3.8 \times 10^{-5}$  mol/dm $^3$ ,  $[\text{NO}_2^-] = 4.56 \times 10^{-3}$  mol/dm $^3$ ,  $\lambda_{\text{max}} = 440$  nm, I = 0.5 mol/dm $^3$  (NaCl)

$\lambda_{\text{max}} = 440$  nm, The kinetics runs were conducted under pseudo-first order conditions with nitrite ion concentration always in more than a 10-fold excess over [PCV]. Under

this conditions, pseudo-first order rate constants 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 of the reaction respectively) which were linear to greater than 80% of the reaction. The reaction was carried out at  $24 \pm 1^\circ\text{C}$  with  $[\text{H}^+] = 1 \times 10^{-3}$  mol/dm $^3$  (HCl) and  $I = 0.50$  mol/dm $^3$  (NaCl) unless otherwise stated. The results are presented in Table 1.

**The effect of  $[\text{H}^+]$  on the rate:** The effect of  $[\text{H}^+]$  on the rate was investigated using hydrochloric acid in the range  $(0.4-1.6) \times 10$  mol/dm $^3$  while the [PCVH] and  $[\text{NO}_2^-]$  were kept constant (Onu and Iyun, 2000). The reaction was carried out at  $24 \pm 1^\circ\text{C}$  and  $I = 0.50$  mol/dm $^3$  (NaCl). The results are presented in Table 1.

## RESULTS AND DISCUSSION

The overall stoichiometry of the oxidation of PCVH by  $\text{NO}_2^-$  ion is determined by spectrophotometry titration and it was found to displayed 1:1 stoichiometry



The pseudo-first order plots of  $\log(A_t - A_\infty)$  versus time for these reaction were linear for about 70% of the reaction. ( $A_t, A_\infty$  are the absorbances of the complex at times t and the end of the reaction respectively). The linearity of these plots indicates that the reaction is first order with respect to [PCVH]. Plot of  $\log k_{\text{obs}}$  versus  $\log[\text{NO}_2^-]$  gave a slope of 0.52 with correlation  $R^2 = 0.97$ , showing that the reaction is half-order with respect to  $[\text{NO}_2^-]$  (Fig. 2). Thus the rate equation for the reaction is:

$$\frac{d[\text{PCVH}]}{dt} = k_2 [\text{PCVH}] [\text{NO}_2^-]^{1/2} \quad (2)$$

The order of half obtained in this reaction does not conforms to already reported order for the redox reactions involving  $\text{NO}_2^-$  (Suthakaran *et al.*, 1980; Fraser *et al.*, 1967).

The rate constant of the reaction increased with increase in acid concentration as shown in Table 1. The order with respect to  $[\text{H}^+]$  was found to be 0.92 with correlation  $R^2 = 0.98$  meaning that it is first order with respect to  $[\text{H}^+]$  (Fig. 4). The plot of  $k_2$  versus  $[\text{H}^+]$  is linear with a finite intercept (Fig. 5). The acid dependent rate constant  $k_2$  is given as:

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

The overall rate equation in the acid range investigated is given by equation:

Table 1: First and second-order rate constant for the oxidation of PCVH by  $\text{NO}_2^-$  ion in aqueous HCl medium  $\lambda_{\max} = 440 \text{ nm}$ .  $T = 24 \pm 1^\circ\text{C}$ ,  $[\text{PCVH}] = 3.8 \times 10^{-5} \text{ mol/dm}^3$

$10^3[\text{NO}_2^-] (\text{mol}/\text{dm}^3)$	$10^3[\text{H}^+] (\text{mol}/\text{dm}^3)$	$10[\text{I}] (\text{mol}/\text{dm}^3)$	$10^3k_{\text{obs}} (\text{s}^{-1})$	$k_2 (\text{dm}^3/\text{mol.s})$
2.28	1.0	5.0	3.91	0.082
2.66	1.0	5.0	4.49	0.087
3.04	1.0	5.0	4.60	0.084
3.80	1.0	5.0	4.95	0.080
4.56	1.0	5.0	6.04	0.089
5.32	1.0	5.0	6.52	0.089
7.60	1.0	5.0	7.10	0.081
9.50	1.0	5.0	8.54	0.088
4.56	1.0	5.0	2.30	0.034
4.56	1.0	5.0	3.45	0.051
4.56	1.0	5.0	3.91	0.058
4.56	1.0	5.0	4.03	0.060
4.56	1.0	5.0	6.14	0.090
4.56	1.0	5.0	6.33	0.094
4.56	1.0	5.0	6.90	0.102
4.56	1.0	5.0	7.29	0.108
4.56	1.0	5.0	9.78	0.144
4.56	1.0	1.0	3.21	0.048
4.56	1.0	2.0	3.59	0.053
4.56	1.0	3.0	4.39	0.065
4.56	1.0	4.0	4.67	0.069
4.56	1.0	5.0	6.33	0.093
4.56	1.0	6.0	6.42	0.095
4.56	1.0	7.0	8.34	0.124
4.56	1.0	8.0	9.21	0.136
4.56	1.0	9.0	9.49	0.140

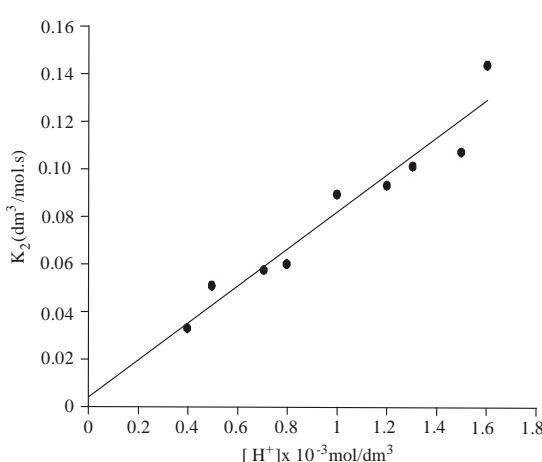


Fig. 5: Plot of  $k_2 (\text{dm}^3/\text{mol.s})$  versus  $[\text{H}^+] \text{ mol}/\text{dm}^3$  for PCVH- $\text{NO}_2^-$  system.  $[\text{PCVH}] = 3.8 \times 10^{-5} \text{ mol}/\text{dm}^3$ ,  $[\text{NO}_2^-] = 4.56 \times 10^{-3} \text{ mol}/\text{dm}^{-3}$ ,  $\lambda_{\max} = 440 \text{ nm}$ ,  $I = 0.5 \text{ mol}/\text{dm}^3$  (NaCl)

$$\frac{d[\text{PCVH}]}{dt} = (a + b[H^+])[\text{PCVH}][\text{NO}_2^-]^{1/2} \quad (4)$$

The nature of acid dependence observed implies that there are two pathways, one which depends on acid and the other which does not depend on acid. This result shows that both the protonated and unprotonated forms of the reactant are reactive. It has been reported that the

equilibria below have been established for  $\text{NO}_2^-$  in aqueous media (Onu and Iyun, 1998).



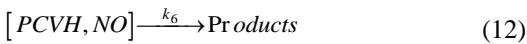
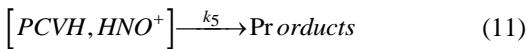
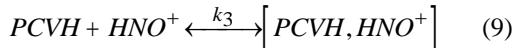
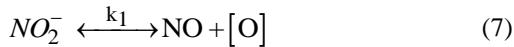
The result in Table 1, shows that the rate of reaction increased with increase in ionic strength. A plot of  $\log k_2$  versus  $\sqrt{I}$  gave a linear graph with a slope of 0.95 showing positive salt effect. This suggests that the product of the charges on the reactants in the activated complex is either positive-positive or negative-negative (Iyun and Kabir, 1996; Babatunde, 2008).

The effects of added cations and anions were studied and were found to affect the rate of reaction Table 2. Cations increase the rate while anions decrease the rate. The effect of cation and anion catalysis indicates that the outer-sphere electron transfer may be important in this reaction.

The results of the spectroscopic studies indicate slight shifts from the absorption maximum characteristic of the PCVH. This suggests the presence of intermediate complex formation prior to electron transfer in the reaction. The plot of  $1/k_{\text{obs}}$  versus  $1/[\text{NO}_2^-]$  was linear with non-zero intercept (Fig. 3). These are strong evidence in favour of the inner-sphere mechanism which is probably operating in the  $\text{NO}_2^-/\text{PCVH}$  reaction.

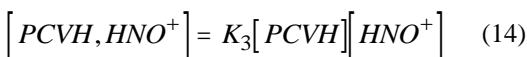
$10^3 [\text{Mg}^{2+}] (\text{mol}/\text{dm}^3)$	$10^3 k_{\text{ob}} (\text{s}^{-1})$	$k_2 (\text{dm}^3/\text{mol.s})$
10	6.90	0.102
50	7.48	0.111
110	11.20	0.166
$10^3 [\text{Ca}^{2+}] (\text{mol}/\text{dm}^3)$		
10	7.48	0.111
50	8.73	0.129
110	9.59	0.142
$10^3 [\text{SO}_4^{2-}] (\text{mol}/\text{dm}^3)$		
10	4.26	0.063
50	3.16	0.047
110	2.13	0.032
$10^3 [\text{NO}_3^-] (\text{mol}/\text{dm}^3)$		
10	4.37	0.065
50	3.12	0.046
110	2.47	0.036

The following mechanism is proposed for this reaction:



$$\text{Rate} = k_5 [\text{PCVH}, \text{HNO}^+] + k_6 [\text{PCVH}, \text{NO}] \quad (13)$$

From Eq. (9) and (10)



Substituting Eq. (14) and (15) into Eq. (13) gives:

$$\text{Rate} = K_3 k_5 [\text{PCVH}] [\text{HNO}^+] + K_4 k_6 [\text{PCVH}] [\text{NO}] \quad (16)$$

From Eq. (8):

$$[\text{HNO}^+] = K_2 [\text{NO}] [\text{H}^+] \quad (17)$$

Substituting Eq. (17) into Eq. (16) gives:

$$\text{Rate} = K_2 K_3 k_5 [\text{PCVH}] [\text{NO}] [\text{H}^+] + K_4 k_6 [\text{PCVH}] [\text{NO}] \quad (18)$$

But  $K_1 = [\text{NO}_2^-] / [\text{NO}] [\text{O}]$ , Assuming that  $[\text{NO}] = [\text{O}]$

$$K_1 = [\text{NO}_2^-] / [\text{NO}]^2$$

$$[\text{NO}] = [\text{NO}_2^-]^{1/2} / K^{1/2} \quad (19)$$

Substituting Eq. (19) into (18):

$$\begin{aligned} \text{Rate} &= \frac{K_2 K_3 K_5}{K^{1/2}_1} [\text{PCVH}] [\text{NO}_2^-]^{1/2} [\text{H}^+] \\ &\quad + \frac{K_4 K_6}{K^{1/2}_1} [\text{PCVH}] [\text{NO}_2^-]^{1/2} \end{aligned} \quad (20)$$

## CONCLUSION

The redox reaction of pyrocatechol violet and nitrite ion in aqueous hydrochloric acid medium showed a stoichiometry of 1:1, a first order with respect to pyrocatechol violet and half order with respect to  $[\text{NO}_2^-]$ . The rate of reaction increased with increase in both hydrogen ion concentration and ionic strength of the reaction medium respectively with a first order dependence on hydrogen ion concentration. On the basis of the result obtained in this study, an inner-sphere mechanism is probably operating in this reaction

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