
Kinetics and Stoichiometry of the Reduction of 2, 6-Dichlorophenol Indophenol with Sulphite Ion in Aqueous Medium

By

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ABSTRACT

The reduction of 2,6-dichlorophenol indophenol (DCPIP) by sulphite ion in aqueous medium under pseudo-first order condition was studied at ionic strength (I) 0.20 mol dm^{-3} (NaCl), $T = 28 \pm 1^\circ\text{C}$ and λ_{max} of 600 nm. The stoichiometry showed that one mole of DCPIP was consumed by one mole of sulphite ion. The reaction was first order with respect to DCPIP, Zero order with respect to sulphite ion and first order overall. The reaction was insensitive to change in ionic strength of the reaction medium and added ion showed catalysis of reaction rate. The overall reaction conform to the rate law

$$\frac{d[\text{DCPIP}]}{dt} = k_1[\text{DCPIP}]$$

Evidences in this paper showed that the reaction occurred through the outer-sphere mechanism.

INTRODUCTION

Large degree of aromatic compound are present in dyes, which are harmful to human health. 2,6-Dichlorophenol-Indophenol with a molecular formula of $\text{C}_{12}\text{H}_7\text{Cl}_2\text{NO}_2$ belongs to the quinone-imine class of dyes (Lillie, 2002). It is widely used in industries, pharmaceutical and biological stain for the study of bacteria and related microorganisms (Kramer *et al.*, 2011). Its stability and long degradation time in the environment is cause of concern. Effect like toxicity of the water and general change in ecosystem especially on microorganism is inevitable (Hamad *et al.*, 2015; Jackeline *et al.*, 2012). Possible treatment of these dyes in our environment are chemical oxidation, adsorption and electrochemical degradation (Rammel *et al.*, 2011). Sulphite ion are powerful reducing agent used as preservative and antioxidant additive in food and pharmaceutical industries (Hassan and Neil, 2012). There is paucity of report on the redox reaction of 2,6-Dichlorophenol-Indophenol with Sulphite. It is hoped the kinetic data generated and proposed mechanisms for the redox reactions of 2,6-dichlorophenol indophenol with sulphite would contribute to the conceptual development of inorganic reaction mechanisms.

EXPERIMENT

The reagents used were of analytical grade. Stock solutions of DCPIP, SO_3^{2-} and NaCl were prepared by dissolving accurately weighed amount of each in known volume of distilled water. The stock solution of the DCPIP was standardized by titrating with freshly prepared vitamin C solution.

The λ_{\max} of 600 nm was determined by running the electronic spectrum of the solution of DCPIP in the wavelength range of 400-780 nm using Cary 100 series UV-Vis Spectrophotometer.

Stoichiometry Determination

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method by keeping the concentration of the dye constant at $1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.2 \text{ mol dm}^{-3}$, $\lambda_{\max} = 600 \text{ nm}$, $T = 28 \pm 1$ and $[\text{SO}_3^{2-}]$ was varied from $0.25 - 3.5 \times 10^{-4} \text{ mol dm}^{-3}$. The absorbance of the reacting mixture was measured at 600 nm after the reaction had gone to completion indicated by steady absorbance value (figure 1). A point of inflexion on the curve of absorbance versus mole ratio plot indicates the stoichiometry of the reaction (Onu *et al.*, 2015)

Kinetic Measurement

The kinetics of the reaction was monitored under pseudo first order condition using Sherwood colorimeter model 254 at $28 \pm 1^\circ\text{C}$ and $I = 0.2 \text{ mol dm}^{-3}$. Progress of the reaction was monitored by observing the change in absorbance of the dye at 600 nm. The pseudo first order plots of $\log (A_\infty - A_t)$ versus time were linear up to 70% of the reaction (figure 2). From the slope of the plots, the pseudo-first order rate constant (k_{obs}) was determined. The first order rate constant (k_1) was obtained from the relation:

$$k_1 = k_{\text{obs}} / [\text{SO}_3^{2-}]$$

The result is represented in table 1. The influence of ionic strength on the rate was investigated within the range $0.05 - 0.5 \text{ mol dm}^{-3}$ using NaCl.

The Effect of added ion on the reaction rate

The effect of added cations and anions were investigated for $[X] = 10.0 - 60.0 \times 10^{-3} \text{ mol dm}^{-3}$ ($X = \text{Ca}^{2+}, \text{Mg}^{2+}, \text{SO}_4^{2-}, \text{NO}_3^-$) and the concentration of other reactants were kept constant at $28 \pm 1^\circ\text{C}$ and ionic strength of 0.20 mol dm^{-3} (table 2)

Free Radical Test

Acrylamide was added to a partially oxidized reaction mixture containing various concentration of oxidant and reductant. Followed by addition of large excess of methanol and to each of the reactant separately.

Product Analysis

The spectrum of the reaction mixture was obtained few minutes after the commencement of the reaction. This was compared with the spectrum of the dye alone over a wavelength range of 400 -780 nm. FTIR (Fourier transform infrared spectroscopy) of the product was obtained using Cary 630 FTIR spectrophotometer to predict the possible structure of the product.

RESULT AND DISCUSSION

The spectrophotometric titration showed one mole of Dye was consumed by one mole of sulphite ion. This conform to the equation

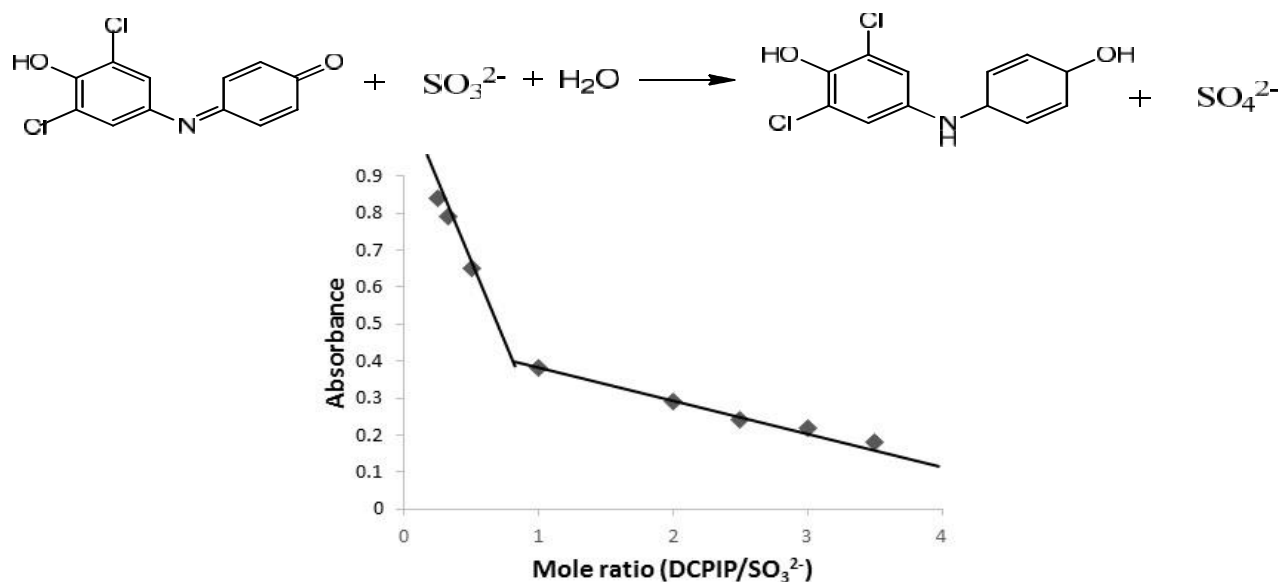


Figure 1: Plot of absorbance versus mole ratio for the redox reaction of 2,6 -dichlorophenol Indophenol with sulphite ion at [DCPIP] = 1.0×10^{-4} mol dm⁻³, I = 0.20 mol dm⁻³ and T = 28 ± 1 °C

The stoichiometry 1:1 is similar to the ones obtained for the reaction of the [DCPIP] with two electron reductant. DCPIP is a two electron acceptor but can take part in one electron transfer reaction catalyzed by oxidoreductases (christaian *et al*, 2005; Dupuy *et al*, 1990). The stoichiometry obtained is consistent with the SO₄²⁻ product. The product was confirmed qualitatively by the observation of white insoluble precipitate (Vogel, 1996) of BaCl₂ solution followed by dilute HCl to the solution at the end of the reaction involving stoichiometric amount of the reactants. FTIR spectrum of the organic product gave peak at 3600 cm⁻¹ and 3480 cm⁻¹ corresponding to O-H and N-H bond respectively. This further support the two electron transfer to the oxidant.

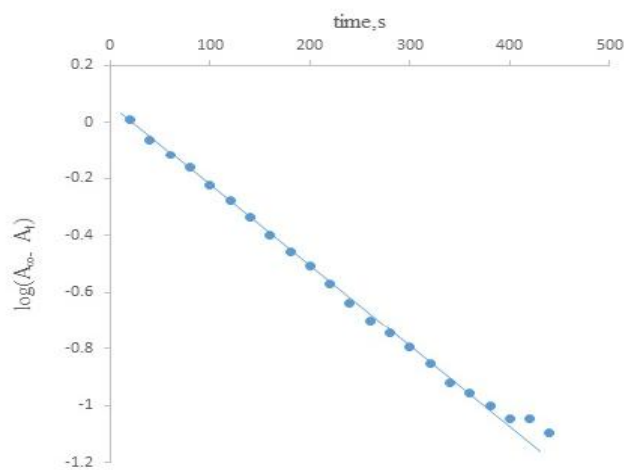


Figure 2: Typical pseudo-first order plot for the redox reaction of 2,6-dichlorophenol indophenol with sulphite ions at [DCPIP] = 1.0×10^{-4} mol dm⁻³, [SO₃²⁻] = 4.0×10^{-2} mol dm⁻³, I = 0.20 mol dm⁻³ and T = 28 ± 1 °C

The pseudo-first order of $\log (A_{\infty} - A_t)$ versus time, t for these reactions were linear for about 70% of the reaction. The linearity of these plots indicates that these reactions are first order with respect to [DCPIP].

Table 1: Pseudo-first order and second order rate constants for the redox reaction of 2,6-dichlorophenol Indophenol with sulfite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm⁻³, [SO₃²⁻] = 3.0×10^{-2} mol dm⁻³, T = 28 ± 1 °C and λ_{\max} = 600 nm

$10^2[\text{SO}_3^{2-}]$, mol dm ⁻³	I, mol dm ⁻³	10^2k_{obs} , s ⁻¹	10^2k_1 , s ⁻¹
3	0.2	1.78	1.78
4	0.2	1.79	1.79
5	0.2	1.78	1.78
6	0.2	1.79	1.79
7	0.2	1.79	1.79
8	0.2	1.78	1.78
9	0.2	1.78	1.78
10	0.2	1.78	1.78
3	0.05	1.79	1.79
3	0.1	1.79	1.79
3	0.15	1.78	1.78
3	0.2	1.79	1.79
3	0.3	1.79	1.79
3	0.4	1.78	1.78
3	0.5	1.78	1.78

The plot of $\log k_{\text{obs}}$ vs $\log [\text{DCPIP}]$ gave a slope of 0.001. Showing the reaction is zero order with respect to [SO₃²⁻]. The rate of the equation is

$$\frac{d[\text{DCPIP}]}{dt} = k_1[\text{DCPIP}]$$

Increase in ionic strength of the reaction medium has no effect on the rate of the reaction (table 1). Plot of $\log k_2$ vs \sqrt{I} give a straight line with a slope of 0.006. This suggest that the activated complex consist of neutral specie (Benson, 1969).

Detection of free radical

Addition of acrylamide to the partially oxidized reaction mixture followed by excess methanol lead to the formation of gelatinous precipitate. This suggests that free radicals are involved in this process of the reaction (Hamza, 2012).

Table 2: Pseudo-first order and second order rate constants for the effect of added ions on the redox reaction of 2,6-dichlorophenol Indophenol with sulfite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm⁻³, [SO₃²⁻] = 3.0×10^{-2} mol dm⁻³, T = 28 ± 1 °C and $\lambda_{\text{max}} = 600$ nm

	$10^2[\text{SO}_3^{2-}]$, mol dm ⁻³	I, mol dm ⁻³	10^2k_{obs} , s ⁻¹	10^2k_1 , s ⁻¹
Ca ²⁺	0	0.2	1.78	1.78
	10	0.2	1.78	1.78
	20	0.2	1.79	1.79
	30	0.2	1.79	1.79
	40	0.2	1.78	1.78
	50	0.2	1.78	1.78
	60	0.2	1.78	1.78
NO ₃ ⁻	0	0.2	1.78	1.78
	10	0.2	1.86	1.86
	20	0.2	1.92	1.92
	30	0.2	1.96	1.96
	40	0.2	1.98	1.98
	50	0.2	2.02	2.02
	60	0.2	2.08	2.08

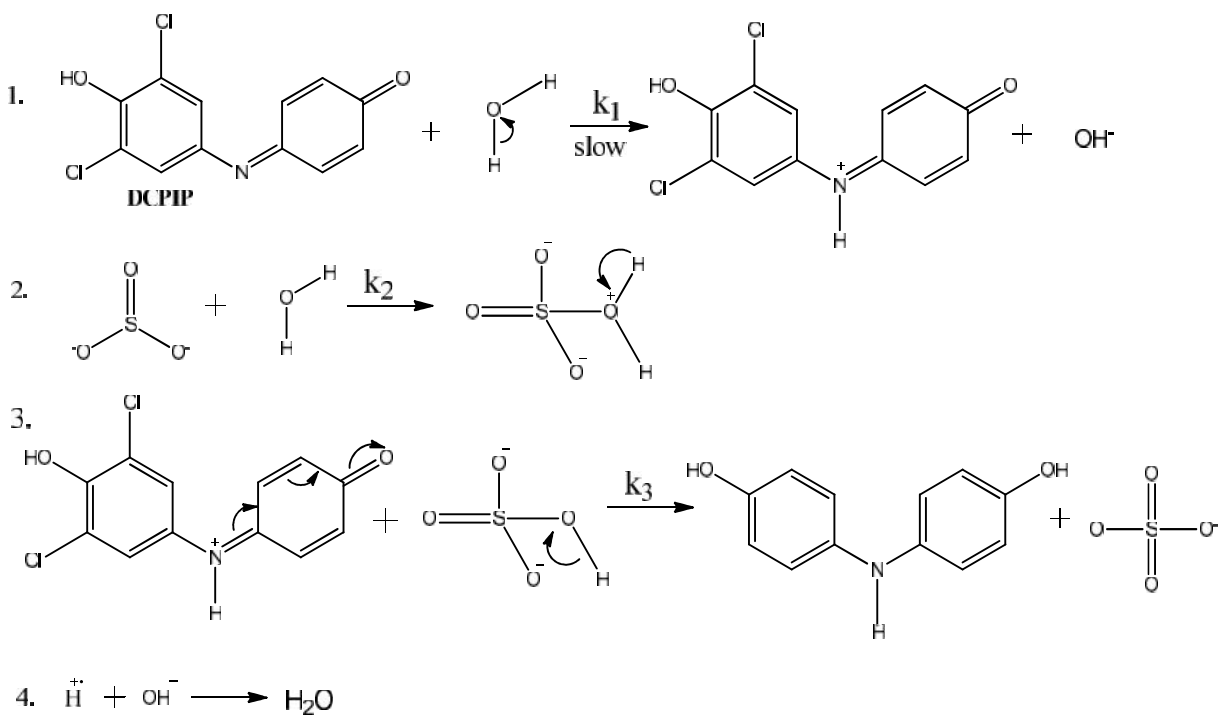
Effect of added ions

Addition of Ca²⁺ ion have no effect on the rate of reaction. However, NO₃⁻ ion decreased the rate constant. This may further explain the nature of the activated complex by suggesting a charge and neutral specie in the activated complex. This observation is characteristics of reaction occurring via outer-sphere mechanism (Babatunde, 2013).

Intermediate Complex Formation

The spectroscopic studies indicated no shift from the absorption maxima of 600 nm of the DCPIP dye. This further suggests that the formation of bridged intermediate complex in the reaction is absent. There by, supporting the operation of outer-sphere mechanism for this reaction (Babatunde, 2013).

On the basis of the result obtained. The following plausible mechanism is proposed



From the slow step

$$\text{Rate} = k_1[\text{DCPIP}][\text{H}_2\text{O}]$$

$$[\text{H}_2\text{O}] = 1$$

$$\text{Rate} = k_1[\text{DCPIP}]$$

CONCLUSION

Redox reaction of 2,6-dichlorophenol indophenol with sulphite ion showed stoichiometry of 1:1 with respect to both reactant. Analysis of other kinetic data under the pseudo first order condition gave overall order of one; zero order with respect to the concentration of the reductant and first order with respect to the concentration of the oxidant. Evidence from the study showed that the reaction occurred through outer-sphere mechanism and a plausible mechanism has been proposed in respect to the experimental data generated.

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