Kinetics and Mechanism of the Redox Reaction of Indigo Carminewith Sulphite Ions in Aqueous Acidic Medium

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Abstract: The redox reaction between indigo carmine [IC] and sulphite ions shows a first order dependence on both [IC] and [SO_3^{2-}]. Hydrogen ions concentration has no effect on the rate of the reaction. Added cations and anions exerted no effect on the rate of the reaction. Results of the Michaelis-Menten analysis gave evidence of intermediate complex formation. Based on the results obtained in this study, the inner sphere mechanism is proposed for the IC- SO_3^{2-} reaction.

Key words: Indigo Carmine · Sulphite · Kinetics · Mechanism

INTRODUCTION

Indigo carmine (3,3'-dioxo-2,2'-bis-Indolyden-5,5'-disulfonic acid disodium salt) here and thereafter referred to as IC, is primarily used as a redox indicator [1]. It is blue at a pH of 11.4 and yellow at 13 [2], it is also used as a dye in the manufacture of capsules and as a diagnostic dye [3]. Several investigations have been conducted to verify the efficiency of processes used to promote indigo carmine degradation. Zinal and co-workers [4] studied its degradation in aqueous solution by using TiO_2 immobilised on the inner surfaces of a quartz pipe submitted to continuous exposure to UV light. From total organic carbon (TOC) measurements, the authors found a mineralization rate of 83% after a photodegradation period of 4.5h. Ali and co-workers [5] investigated the degradation of indigo carmine promoted by hydrogen peroxide catalyzed by homogeneous systems comprised of several transition metal complexes. The authors observed that, in addition to the colour removal, the catalytic system was able to promote almost complete dye mineralization whereas its activity depended on several parameters, mainly the redox potential of the centre metal ion and the nature of the ligands.

Indigo carmine has been used as a homogeneous mediator on a glassy carbon electrode in investigating the electro-catalytic oxidation of hydroxylamine [5]. The homogeneous catalytic activity of transition metal ions for the oxidation reaction of IC and their kinetic determination has also been studied.

Sulphite ions have received a lot of attention as a powerful reductants in the past few decades [6] and were observed to reduce metal ions and other oxidants by a variety of mechanisms with varying stochiometry [6]. This has allowed a distinction to be made between its uses as a one equivalent and a two equivalent oxidizing agent. Reports show that the free SO_3^{2-} is always oxidized to SO_4^{2-} without $S_2O_6^{2-}$ or with a very negligible amount of $S_2O_6^{2-}$ [6].

The present work aims at studying the kinetics and mechanism of the reaction between IC and sulphite ions.

EXPERIMENTAL

A 1.0×10^{-3} mol dm^{-3} stock solution of indigo carmine (Analar grade), was prepared by dissolving 4.66g in 100 cm^3 volumetric flask using distilled water and sodium sulphite was prepared by dissolving known quantities in distilled water. The $\lambda_{max} = 610$nm of IC was determined by running the electronic spectrum of solution of IC in the wavelength range of 440-700 nm. H_2SO_4 was used to furnish H^+ to the reaction; Na_2SO_4 was used to maintain a constant ionic strength for each run. All other reagents used were of analar grade.

Stoichiometry: The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method [7]. The concentration of indigo carmine (IC) was kept constant at 2.8×10^{-5} mol dm^{-3}, [H^+] = 2.0×10^{-5} mol dm^{-3} and I = 1.0 mol dm^{-3},

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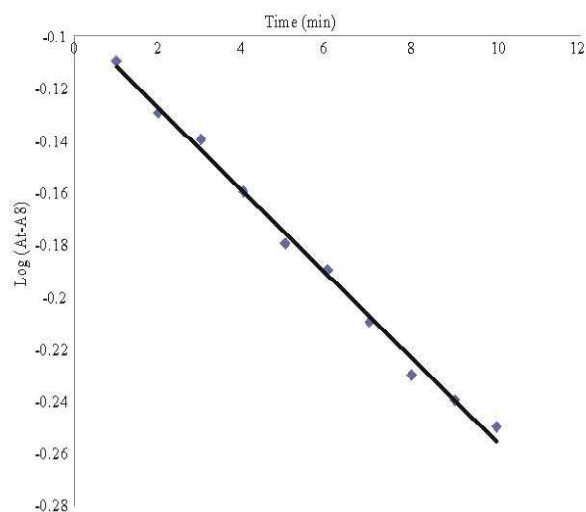E-mail: joshuaedos@yahoo.com

Fig. 1: Typical pseudo-first order plot for the redox reaction of Indigo Carmine with SO_3^{2-} [IC] = 2.8×10^{-5} mol dm^{-3}, [SO_3^{2-}] = 0.168 mol dm^{-3}, [H$^+$] = 2.0×10^{-5} mol dm^{-3}, I = 1.0 mol dm^{-3}, λ = 610nm and T = 29 ± 1°C

λ_{max} = 610nm while that of sulphite ion was varied in the range (0.76- 2.8) $\times 10^{-5}$ mol dm^{-3}. The absorbance of the reacting mixtures was measured after the reaction had gone to completion as indicated by steady zero absorbance value observed over a period of two days. A point of inflexion on the curve of the absorbance versus mole ratio corresponds to the stoichiometry of the reaction.

Kinetic Measurements: The kinetic of the reaction was monitored using a Corning Colorimeter Model. 252 at [IC] at 29 ± 1°C, I = 1.0 mol dm^{-3} (Na$_2$SO$_4$) and [H$^+$] = 2.0×10^{-5} mol dm^{-3}, (H$_2$SO$_4$). The progress of the reaction was monitored by following the decrease in absorbance of the dye at 610 nm. All the kinetic measurements were carried out under pseudo-first order conditions with the concentration of periodate ions at least 3000 folds greater than that of the dye. The pseudo-first order plots of log (A$_t$- A$_8$) versus time, were made (where A$_8$ and A$_t$ are the absorbance at the end of the reaction at time, t) and from the slope of the plots, the pseudo-first order rate constant (k$_1$) was determined [8]. The second order rate constant (k$_2$) was obtained from k$_1$ as k$_2$ / [SO$_3^{2-}$]. A typical pseudo- first order plot is presented in Fig. 1.

Effect of Changes in [H$^+$] on the Reaction Rate: The effect of changes in [H$^+$] was investigated by keeping the [IC] and [SO$_3^{2-}$] constant while varying the [H$^+$] in the range (0.2-600)$\times 10^{-5}$ mol dm^{-3} at constant ionic strength of I =1.0 mol dm^{-3} and the reaction was carried out at 29±1°C. The results are presented in Table 1.

Effect of Ionic Strength: The effect of ionic strength of the rate of the reaction was investigated in the range of 0.6- 1.5 mol dm^{-3} (NaCl) while the concentration of other reactants was kept constant at 29±1°C. The result is presented in Table 1.

Table 1: Pseudo first order and second order rate constant plot for the reaction of Indigo Carmine and SO_3^{2-}. [IC] = 2.8×10^{-5} mol dm^{-3}, λ = 610nm and T = 29 ± 1°C

[SO$_3^{2-}$], mol dm^{-3}	10^1 I, mol dm^{-3}	10^5[H$^+$], mol dm^{-3}	10^2 k$_1$, min^{-1}	k$_2$, dm^3 mol^{-1} min^{-1}
0.140	1.0	2.0	2.65	0.19
0.168	1.0	2.0	2.88	0.17
0.196	1.0	2.0	3.12	0.16
0.224	1.0	2.0	3.84	0.17
0.252	1.0	2.0	4.24	0.17
0.280	1.0	2.0	4.61	0.16
0.196	1.0	2.0	3.20	0.16
0.196	1.0	0.2	3.20	0.16
0.196	1.0	2.0	3.22	0.16
0.196	1.0	6.0	3.39	0.17
0.196	1.0	60.0	2.73	0.14
0.196	1.0	200.0	3.06	0.16
0.196	1.0	600.0	3.25	0.17
0.196	0.6	2.0	3.00	0.15
0.196	0.7	2.0	3.20	0.16
0.196	0.8	2.0	2.73	0.14
0.196	0.9	2.0	3.17	0.16
0.196	1.0	2.0	3.20	0.16
0.196	1.2	2.0	3.38	0.17
0.196	1.5	2.0	3.11	0.16

Test for Intermediate Complex: The spectra of the reaction mixture were obtained after two minutes. The spectra of the dye alone were compared over a range of wavelength 420 nm and 700 nm to test for the possibility of any intermediate complex formation. Michaelis-Mentens plot of $1/k_1$ versus $1/[IO_4^-]$ was made (Fig. 3).

RESULTS AND DISCUSSION

Stoichiometry and Product Analysis: The results of the spectrophotometric titration revealed that one mole of IC consumed one mole of SO_3^{2-} to yield the product. The overall reaction is given by equation 1

$$\text{[structure]} + SO_3^{2-} + H_2O \longrightarrow \text{Products} \dots\dots\dots\dots \quad (1)$$
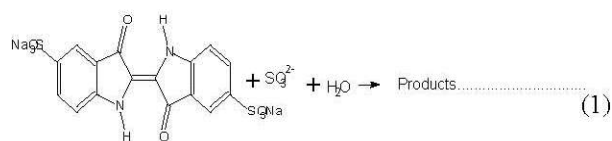
Similar stoichiometry has been reported for the reaction of sodium hypochlorite and indigo carmine [9] The presence of SO_4^{2-} was confirmed by the addition of $BaCl_2$ and HCl solution [10]. This gave a white precipitate, insoluble in excess HCl suggesting the presence of SO_4^{2-} as one of the reaction products.

Kinetics: The linearity of the pseudo-first order plots suggested that there is no inhibition by the product of the reaction and that the order with respect to $[SO_3^{2-}]$ is one. The plot of log $[SO_3^{2-}]$ versus log k_1 shows an order of one with respect to [IC] (Fig. 2). Values of the rate constants obtained by varying the concentrations of the reductant and hydrogen ion are presented in Table 1. Therefore

$$-d[IC]/dt = k_2[IC][SO_3^{2-}] \quad (2)$$

Effect of [H⁺] on the Rate of the Reaction: As illustrated by the data in Table 1, values of $k_2 = k_1/[SO_3^{2-}]$ are [H⁺] independent in the $(0.2\text{-}600) \times 10^{-2}$ mol dm^{-3} acid range. This independence is in accord with the fact that neither the oxidants nor the reductant undergo significant protonation changes under the reaction conditions. Similar result have also been reported by Rao [11].

Effect of Ionic Strength: The effect of ionic strength on the rate of the reaction was investigated in the range 0.6-1.5 mol dm^{-3} of the reaction medium by adding
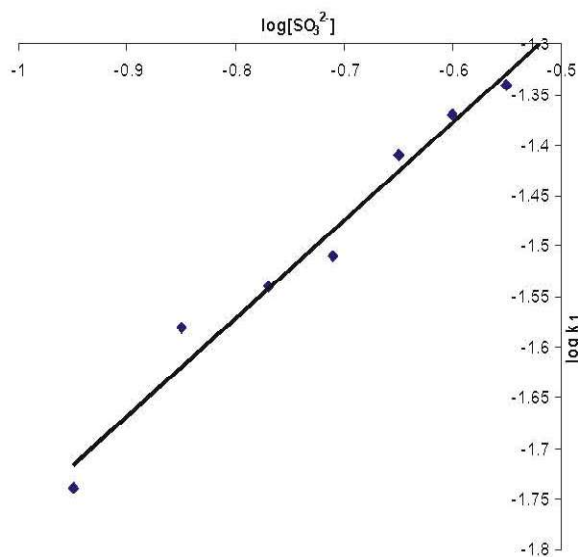

Fig. 2: Plot of the redox reaction of log k_1 versus log $[SO_3^{2-}]$

Na_2SO_4. The results reported in Table 1 show that the second order rate constants were independent of the charges in the ionic strength of the reaction medium. The lack of dependence on ionic strength observed in this investigation suggests that the product of the charges on the reactant ions in the activated complex is zero. The activated complex from this reaction therefore either involves a charged ion and uncharged specie or two uncharged ions. This is a common feature of most reactions of indigo carmine [9, 12-14].

Free Radical Test: 5.0 cm^3 of 10% (w/v) acrylamide was added to the reaction mixture containing [IC] = 2.8 x 10^{-3} mol dm^{-3} at 29 $\pm$ 1°C, I = 1.0 mol dm^{-3} (Na_2SO_4) and [H⁺] = 2.0×10^{-5} mol dm^{-3}, (H_2SO_4). The total volume was adjusted to 10cm^3 with distilled water and the formation of polyacrylamide was noticed upon adding a large excess of methanol. No polymerization was observed in the control experiments with either IC or SO_3^{2-}. The observed polymerization indicates the presence of free radicals. Free radicals were earlier confirmed in reactions involving sulphite ion [15].

Intermediate Complex Formation: The absorption spectra of solutions containing the dye alone and the solution of the reaction mixture under similar condition were compared between 420 and 700 nm. There was no observable difference with respect to λ_{max}. This suggests that the formation of an intermediate complex is unlikely.

Table 2: Rate data for the effect of added cations and anions on the redox reaction of indigo carmine with sulphite ion, at I = 1.0 mol dm^{-3}. λ_{max} = 610nm, T = 29±1°C [IC] = 2.8×10^{-5} mol dm^{-3}, [SO$_3^{2-}$] = 0.196 mol dm^{-3}, [H$^+$] = 2.0×10^{-5} mol dm^{-3}

10^3 [Mg^{2+}], mol dm^{-3}	10^{3}k$_1$, s^{-1}	k$_2$, dm^3 mol^{-1}s^{-1}
20	3.16	0.16
40	3.23	0.16
60	2.78	0.14
80	2.89	0.15
100	2.84	0.15
10^3[Ca^{2+}], mol dm^{-3}		
15	3.13	0.16
45	3.21	0.16
75	2.76	0.14
100	2.89	0.15
10^3[CH$_3$COO], mol dm^{-3}		
20	3.16	0.16
40	3.23	0.16
60	2.78	0.14
80	2.89	0.15
100	3.21	0.16
10^3[HCOO], mol dm^{-3}		
20	3.13	0.16
40	3.21	0.16
60	2.76	0.14
100	3.12	0.16

Effect of Added Cations and Anions: Added Ca^{2+}, Mg^{2+}, HCOO$^-$ and NO$_3^-$ did not affect the rate of the reaction. This lack of ion catalysis suggests that an inner-sphere mechanism is probably in operation. Results are shown in Table 2.

Michaelis-Menten Plot: The Michaelis-Menten's plot of 1/k$_1$ min versus 1/ [SO$_3^{2-}$] dm^3 mol^{-1} (Fig. 3) did not pass through the origin suggesting the presence of an intermediate complex formation. Therefore an inner-sphere mechanism is likely to be operating in the IC-SO$_3^{2-}$ reaction.

Although the spectroscopic studies suggest an outer-sphere mechanism since there is no observeable shift in λ_{max} of the reaction mixture proceeding via inner-sphere mechanism since there is lack of ion catalysis, presence of gel formation and the Michaelis-Menten's plot of 1/ k$_1$ versus 1/ [SO$_3^{2-}$] has a positive intercept.

Reaction Scheme:

IC + SO$_3^{2-}$ [IC-SO$_3^{2-}$]   Slow (3)

[IC-SO$_3^{2-}$] + H$_2$O Product + SO$_4^{2-}$ + H$^+$ Fast (4)

Based on equation 3 the rate law can be written as
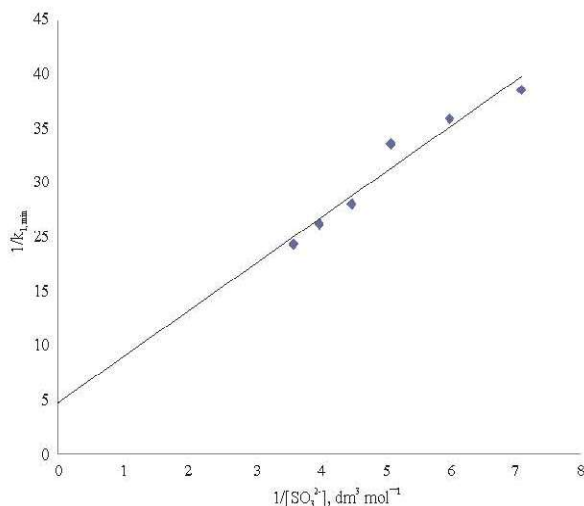
Fig. 3: Michaelis-Menten's plot of 1/k$_1$ min versus 1/ [SO$_3^{2-}$] dm^{-3} mol^{-1}

$$Rate = k_1[IC][SO_3^{2-}] \qquad (5)$$

Here k$_1$ is the second order rate constant. In excess [SO$_3^{2-}$] equation (5) reduces to equation (6)

$$Rate = k'[IC] \qquad (6)$$

Where:

$$k' = k[SO_3^{2-}] \qquad (7)$$

Equation (5) is consistent with the experimentally obtained order. The agreement with the experimentally results supports the proposed mechanism as the probable mechanism.

CONCLUSION

The redox reaction of indigo carmine with sulphite ions in aqueous acidic medium showed a stoichiometry of 1:1, a first order was observed with respect to both reactants respectively. The rate was unaffected with increase in acid ion concentration, changes in ionic strength and added cations and anions. An intermediate complex was implicated in the course of the reaction.

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