



A kinetic study of the redox reaction of indigo carmine by nitrite ion in aqueous hydrochloric acid medium

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ABSTRACT

The kinetics of oxidation of indigo carmine (hereafter referred to as IC) by nitrite ions have been studied in aqueous hydrochloric acid under the pseudo – first order condition of excess $[\text{NO}_2^-]$ at $27 \pm 1^\circ\text{C}$, $[\text{H}^+] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ and ionic strength $I = 0.5 \text{ mol dm}^{-3}$. The stoichiometry of the reaction was observed to be 1:1 mole ratio of IC to nitrite ions. The reaction is first order with respect to both the $[\text{IC}]$ and $[\text{NO}_2^-]$. The overall reaction conforms to the rate law $-\text{d}[\text{IC}]/\text{dt} = a [\text{NO}_2^-] [\text{IC}] [\text{H}^+]^{0.39}$, ($a = 1.30 \times 10^{-2} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$). © 2011 Trade Science Inc. - INDIA

KEYWORDS

Indigo carmine;
Kinetics;
Order;
Nitrite;
Mechanism.

INTRODUCTION

Indigo carmine ($\text{C}_{16}\text{H}_8\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$), is one of the oldest dyes and still one of the most important. Its major industrial application is the dyeing of clothes (blue jeans) and other blue denim^[1]. The primary use of indigo carmine is as redox indicator in analytical chemistry^[2]. It is blue at a pH of 11.4 and yellow at 13.0. Indigo carmine turns yellow upon reduction. It is used as a dye in the manufacturing of capsules^[3]. It is also a dark blue powder with coppery luster used as a dye in testing kidney function and as a reagent in detecting chlorate and nitrate is synthetically produced from the sulphonation of indigo^[4]. Indigo carmine is not readily metabolized but rather freely filterable by the kidneys. Giving intravenous injection of indigo carmine for intra-cytopscopy is a safe technique that can

detect otherwise undetected intra-operative comprise of the urinary tract^[5]. It also contributes to intra-vital staining for contrasting and accentuating changed mucosal process^[6,7].

The oxidation of indigo carmine dye by hydrogen peroxide in the presence of some sulfur compounds such as sulfides and thiourea has been studied^[1].

Nitrite ion has been reported to act either as oxidant or as reductant in redox reactions^[8,9]. Consequently, the knowledge of the kinetics and mechanisms that characterize the redox reaction of IC with nitrite ions is highly desirable so as to enhance its applicability in the textile industry.

This paper reports on the kinetics and mechanism of reduction of IC by nitrite ions in aqueous acid medium.

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EXPERIMENTAL

Materials and reagents

A $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ stock solution of indigo carmine (Analar grade), was prepared by dissolving 4.66g in 100 cm^3 volumetric flask using distilled water. Sodium nitrite was prepared by dissolving known quantity in distilled water. The λ_{max} of IC was determined by running the electronic spectrum of the solution in the wavelength range of 420nm-700nm. A 1.0 mol dm^{-3} stock solution of hydrochloric acid was made by diluting commercial acid (36%, specific gravity = 1.8) and standardizing the solution using sodium trioxocarbonate (IV). All other reagents used were of analar grade without further purification.

Stoichiometry

The stoichiometry of the reaction was determined spectrophotometrically using the mole ratio method^[10]. This was done by keeping the concentration of indigo carmine (IC) constant at $2.8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}^+] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ and $I = 0.5 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 610 \text{ nm}$ and varying the concentrations of the nitrite ion in the range $(0.76-2.8) \times 10^{-5} \text{ mol dm}^{-3}$. The absorbance of the reacting mixtures was taken after the reaction had gone to completion as indicated by steady absorbance value over a period of four days. The stoichiometry was evaluated from the plot of absorbance versus $[\text{NO}_2^-]$.

Kinetic measurement

The kinetic runs were performed under pseudo-first order conditions with the concentration of nitrite ion at least 60 folds greater than that of IC. The rate was monitored by following the absorbance of the dye at $\lambda_{\text{max}} = 610 \text{ nm}$ using Corning Colorimeter 252 (10). For each run the temperature was kept constant at $27 \pm 1^\circ \text{C}$, $[\text{H}^+] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ and the required amount of NaCl were added to maintain a total ionic strength of 0.5 mol dm^{-3} . The pseudo-first order plots of $\log(A_t - A_\infty)$ versus time, which were linear to about 90% at various reactant concentrations were made (where A_∞ and A_t are the absorbance at the end of the reaction at time, t respectively). A typical pseudo-first order plot is presented in figure 1.

Absorption studies

The absorption spectra of solutions containing the

dye alone and the solution of the reaction mixture under similar conditions were compared between 420nm and 700nm to test for the possibility of the presence of any free radical formation. There was no observable difference in both spectra with respect to the λ_{max} .

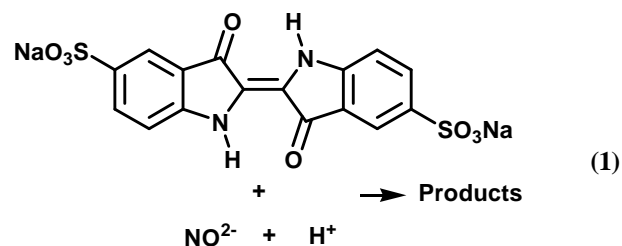
Effect of $[\text{H}^+]$ on the rate

The effect of $[\text{H}^+]$ on the rate was investigated using hydrochloric acid in the range $(1-15) \times 10^{-2} \text{ mol dm}^{-3}$ while $[\text{NO}_2^-]$ and $[\text{IC}]$ were kept constant. The reaction proceeded at $27 \pm 1^\circ \text{C}$ with $I = 0.5 \text{ mol dm}^{-3}$ (NaCl). The results are presented in TABLE 1.

RESULTS AND DISCUSSION

Stoichiometry

The results of the spectrophotometric titration revealed that one mole of IC consumed one mole of NO_2^- to yield the product. The overall reaction is given by the equation below,



Similar stoichiometry has been reported for the reaction of sodium hypochlorite and indigo carmine^[11].

Kinetics

The pseudo-first order plots of $\log(A_t - A_\infty)$ versus time were linear to about 90% extent of reaction, indicating that the reaction is first order in $[\text{IC}]$ under the experimental condition. The pseudo-first order rate constant was determined at different initial concentration of NO_2^- . Plot of $\log k_1$ versus $\log [\text{NO}_2^-]$ at $[\text{H}^+] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ gave a slope of 1.0 (Figure 2). This suggests a first order dependence on $[\text{NO}_2^-]$. The value of second order rate constant, k_2 ($k_2 = k_1/[\text{NO}_2^-]$) were fairly constant (TABLE 1) suggesting that the reaction is also first order in $[\text{IC}]$ and that the reaction is second order overall.

Effect of acid on the rate of the reaction

From the result in TABLE 1, it is observed that the

TABLE 1 : Pseudo-first order and second order rate constants for the IC - NO₂⁻ reaction at [IC] = 2.8×10⁻⁵ mol dm⁻³, T = 27 ± 1°C

10 ³ [NO ₂ ⁻], mol dm ⁻³	10 ² [H ⁺], mol dm ⁻³	10 ¹ I, mol dm ⁻³	10 ³ k ₁ , s ⁻¹	k ₂ , dm ³ mol ⁻¹ s ⁻¹
1.68	5.0	5.0	2.02	1.20
1.96	5.0	5.0	2.53	1.29
2.24	5.0	5.0	2.83	1.26
2.52	5.0	5.0	3.22	1.28
2.80	5.0	5.0	3.41	1.22
3.08	5.0	5.0	3.75	1.22
3.36	5.0	5.0	4.12	1.23
3.64	5.0	5.0	4.40	1.21
3.90	5.0	5.0	4.74	1.22
4.20	5.0	5.0	5.20	1.24
3.36	1.0	5.0	3.73	1.10
3.36	3.0	5.0	4.03	1.20
3.36	5.0	5.0	4.17	1.24
3.36	7.0	5.0	4.61	1.37
3.36	9.0	5.0	5.18	1.54
3.36	11.0	5.0	5.76	1.71
3.36	13.0	5.0	5.85	1.74
3.36	15.0	5.0	6.31	1.83
3.36	5.0	1.0	4.15	1.24
3.36	5.0	2.0	4.12	1.23
3.36	5.0	4.0	4.21	1.25
3.36	5.0	5.0	4.17	1.24
3.36	5.0	6.0	4.35	1.29
3.36	5.0	7.0	4.31	1.28
3.36	5.0	10.0	4.32	1.29

value of the reaction rate constant of the reaction increasing with increase in [H⁺], plot of log k_H versus [H⁺] shows an order of 0.39 with respect to [H⁺]. Plot of k₂ versus [H⁺] was linear with a positive intercept in the acid concentration range investigated and can be represented by the equation,

$$k_2 = b[\text{H}^+]^{0.39} \quad (2)$$

This observation suggests that the oxidation occurs via one pathway involving only the protonated specie reacting to give the products.

Effect of ionic strength on the rate of the reaction

Changes in ionic strength in the range (0.1 - 1.0) mol dm⁻³ of the reaction medium had no effect on the rate of the reaction. The observed zero Brownsted-Debye salt effect suggests that charged and neutral

TABLE 2 : Rate data for the effect of added cations and anions on the redox reaction of indigo carmine with nitrite ion, at I = 0.5 mol dm⁻³, λ_{max} = 610nm, T = 27 ± 1°C, at [IC] = 2.8×10⁻⁵ mol dm⁻³, [NO₂⁻] = 3.36×10⁻³ mol dm⁻³, [H⁺] = 0.5×10⁻² mol dm⁻³

	10 ³ k ₁ , s ⁻¹	k ₂ , dm ³ mol ⁻¹ s ⁻¹
10³[K⁺], mol dm⁻³		
20	4.38	1.31
80	4.56	1.36
100	4.19	1.25
150	4.35	1.30
10³[Ca²⁺], mol dm⁻³		
40	4.35	1.30
80	4.49	1.34
100	4.65	1.38
200	4.42	1.32
10³[CH₃COO⁻], mol dm⁻³		
20	4.01	1.19
80	3.11	0.93
100	1.67	0.50
150	0.26	0.08
10³[HCOO⁻], mol dm⁻³		
40	3.57	1.06
80	1.70	0.57
100	0.88	0.26
200	0.38	0.13

specie is reacting at the rate determining step. The result is presented on TABLE 1.

This is a common feature of most reactions of indigo carmine^[12-15].

Effect of added cations and anions on the rate of the reaction

The effect of Added Ca²⁺ and Mg²⁺, CH₃COO⁻ and HCOO⁻ on the rate of the reaction was studied and the results are presented in TABLE 2. There was an inhibition of the rate of the reaction due to the presence of added anions. The inhibition of this reaction by the anions suggests the outer-sphere mechanism^[16,17].

Free radical test

Acrylamide solution was added to initiate polymerization if free radicals were present. The lack of polymerization even after adding excess methanol indicates the probable absence of free radicals in the reaction mixture. The acrylamide did not polymerize either the reactant alone or the reaction mixture. This suggests

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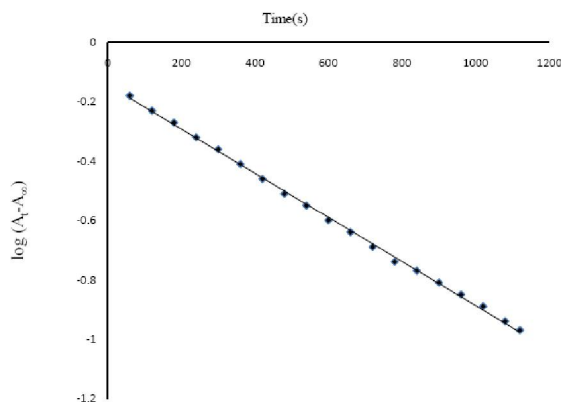


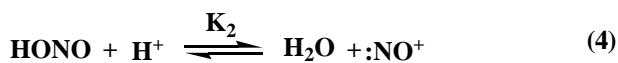
Figure 1 : Typical pseudo first order plot for the redox reaction of Indigo carmine with NO_2^- . $[\text{IC}] = 2.8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{NO}_2^-] = 3.64 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, $\lambda = 610 \text{ nm}$ and $T = 27 \pm 1^\circ \text{C}$

that the free radicals are not involved in this reaction and suggests an outer-sphere mechanism.

Intermediate complex formation

The results of the spectroscopic studies indicated no significant shift from the absorption maxima of 610nm characteristic of IC. This suggests that the formation of an intermediate complex during the course of this reaction is very unlikely. Plots of $1/k_1$ versus $1/[\text{NO}_2^-]$ gave a straight line which passed through the origin. (Figure 3) This further suggests the absence of the formation of intermediate complex thereby supporting the possibility of the outer-sphere mechanism.

Nitrite ion exists in acidic medium as HONO, NO^+ and forms the following equilibria (9):



REACTION SCHEME



From the rate determining step

$$\text{Rate} = k_3 [\text{IC}] [\text{HONO}] \quad (7)$$

Since eq. (3) is a fast rapid equilibrium, HONO is in equilibrium with NO_2^- and H^+ and corresponds to

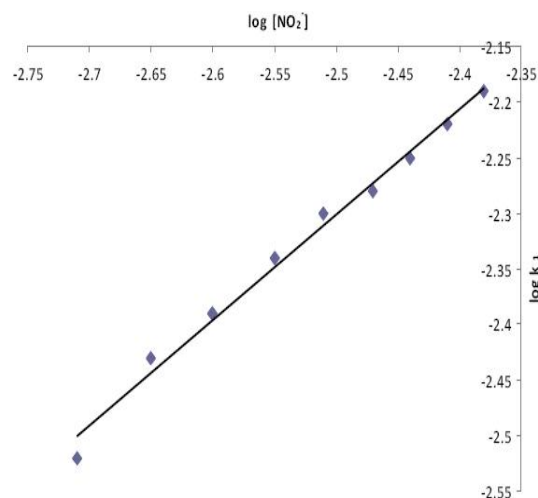


Figure 2 : Plot of $\log k_1$ versus $\log [\text{NO}_2^-]$

the arrhenius concept.

$$K_1 = \frac{[\text{HONO}]}{[\text{NO}_2^-][\text{H}^+]} \quad (8)$$

In this expression, the concentration NO_2^- i.e. $[\text{NO}_2^-]$ is not the total concentration of nitrite ion but the equilibrium concentration. Therefore if $[\text{NO}_2^-]_t$ represent the total concentration of nitrite ion, then,

$$[\text{NO}_2^-]_t = [\text{NO}_2^-]_e + [\text{HONO}] \quad (9)$$

From eq. (8),

$$[\text{HONO}] = K_1 [\text{NO}_2^-] [\text{H}^+] \quad (10)$$

$$[\text{NO}_2^-]_t = \frac{[\text{HONO}]}{K_1 [\text{H}^+]} \quad (11)$$

Substitute eq. (11) into (9).

$$[\text{NO}_2^-]_t = \frac{[\text{HONO}]}{K_1 [\text{H}^+]} + [\text{HONO}] \quad (12)$$

$$[\text{NO}_2^-]_t = \frac{[\text{HONO}] + K_1 [\text{H}^+] [\text{HONO}]}{K_1 [\text{H}^+]} \quad (13)$$

$$K_1 [\text{H}^+] [\text{NO}_2^-]_t = [\text{HONO}] (1 + K_1 [\text{H}^+]) \quad (14)$$

$$[\text{HONO}] = \frac{K_1 [\text{H}^+] [\text{NO}_2^-]_t}{1 + K_1 [\text{H}^+]} \quad (15)$$

Substitute eq. (15) into (7)

$$\text{Rate} = \left\{ \frac{k_3 K_1 [\text{H}^+] [\text{NO}_2^-]_t}{1 + K_1 [\text{H}^+]} \right\} [\text{IC}] \quad (16)$$

$$\text{Rate} = \left\{ \frac{k_3 K_1 [\text{H}^+]}{1 + K_1 [\text{H}^+]} \right\} [\text{NO}_2^-]_t [\text{IC}] \quad (17)$$

This rate law supports the experimental results: the

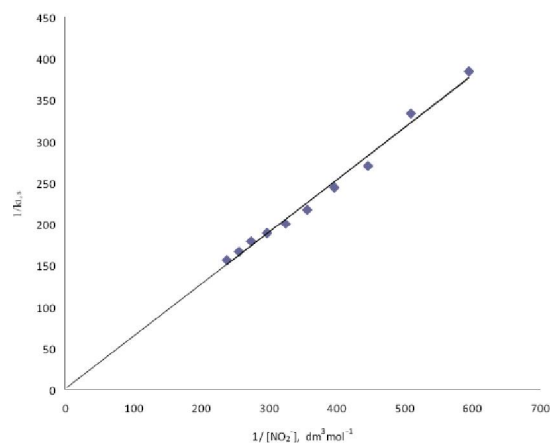


Figure 3 : Michaelis-Menten plot for the redox reaction between IC and NO_2^-

first order dependence of $[\text{IC}]$ and $[\text{NO}_2^-]$ and a fractional order in $[\text{H}^+]$ observed.

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