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Kinetics of Nitrite ION Catalysed Oxidation of Indigo carmine by Chloramine-T in Acidic Buffer (PH 5.8) Medium

Sayaji Rao[1],G. Poornachandra Rao[2]

Department of chemistry, Jayaprakash Narayana College of Engineering,
Mahabubnagar, A.P.

Abstract:

Indigocarmine or IC (5, 5′-indigodisulfonic acid, disodium salt) is a dye which is used as a redox indicator in analytical chemistry and as a microscopic pigment in biology. The chemistry of IC and its derivatives has been reviewed by Rodd. It is castoff as dye in the textile industry and manufacture of capsules. In surgery, circulatory indigocarmine is used to highlight the urinary tract. IC is sanctioned for use as a food colourant in the United States and Europian countries. Though indigocarmine in solution has been assessed with the help of organic haloamine and other substances. Only very rare kinetic studies are described in literature of this indole derivative.

Keywords — **Nitrite Ion, oxidation of indigocarmine Chloramine-T, Acidic Buffer Medium.**
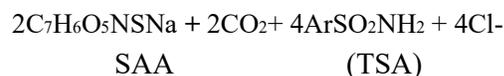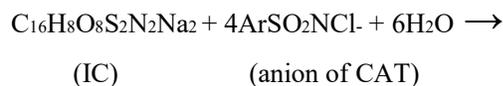
INTRODUCTION

Kinetics of nitrite ion catalysed oxidation of indigocarmine by chloramine-T has been stated spectrophotometrically at λmax= 610 nm in acidic buffer medium (pH = 5.8) in this segment.

Kinetic procedure:

Kinetic runs were completed under conditions of $[CAT]_0 >> [IC]_0$ at 27°C for each run, essential amounts of solutions of IC, $NaClO_4$, $NaNO_2$ and buffer of known pH were taken in a stoppered pyrex glass tube whose outer surfaces were coated black. The tube was thermostated in a water bath at a given temperature. The reaction was originated by adding a measured amount of pre-equilibrated CAT solution and shaken occasionally for uniform concentration. The course of the reaction was observed spectrophotometrically by calculating the absorbance at the λmax of 610 nm for IC at steady time intervals for three half-lives. The pseudo first order rate constants k′ calculated were reproducible within ± 3%. Ever since the total ionic strength preserved was 0.1 mol dm-3, molar concentrations were used in the expression of rate constants in its place of activities in first estimate, abandoning the activity coefficients. The regression analysis of the investigational data was carried out on origin 5.0 HP computer to attain the regression coefficient (r).

Reaction Stoichiometry

Fluctuating ratios of the oxidant (CAT) to IC in pH 5.8 buffer medium were equilibrated at 27°C for 12 hours. Aliquots of the reaction mixture were iodometrically titrated with a standard thiosulphate solution, using starch indicator, to regulate the concentrations of unmoved CAT. The analysis displayed that one mole of IC responded with four moles of oxidant; the stoichiometric reaction can be characterized as below.

$$C_{16}H_8O_8S_2N_2Na_2 + 4ArSO_2NCl_- + 6H_2O \longrightarrow$$

(IC)   (anion of CAT)

$$2C_7H_6O_5NSNa + 2CO_2 + 4ArSO_2NH_2 + 4Cl_-$$

SAA   (TSA)

Product Analysis

The existence of toluenesulphonamide or TSA, which is the reduction product of CAT, was noticed by paper chromatography. The oxidation product of IC, sodium salt of sulphonated anthranilic acid (SAA) was analysed. The SAA present in the reaction mixture was quantitatively dogged using a standard technique involving its precipitation as zinc(II) salt $Zn(C_7H_5O_5NSNa)_2$. The recovery of SAA from dissimilar reaction combinations in pH 5.8 buffer was in the variety 85-95%, additional product CO_2 was noticed by the conventional lime water test.

RESULTS

Effects of reactants on the rate:

Under pseudo first order situations of $[CAT]_0 \gg [IC]_0$ at constant $[CAT]_0$, $[NO_2-]$, pH and temperature, the plots of log $[OD]_0/[OD]_t$ versus time were linear (Table 1.1, Fig.1.1, r = 0.9987) signifying a first order dependency of the reaction rate of [IC], $[OD]_t$ is the absorbances of the reaction combination at time interval 't'. The pseudo-first order rate constants k' acquired at 27°C are independent of $[IC]_0$ additional authorizing the first order dependence on $[IC]_0$ (Table 1.2). At constant pH, $[NO_2-]$, $[IC]_0$, ionic strength and temperature the rate augmented with growing $[CAT]_0$ (Table 1.2). Additionally a plot of log k' versus log $[CAT]_0$ was linear (Table 1.3) with a slope of 2.0 displaying second order dependence on [CAT].

Effect of [NO₂-] on the rate:

The reaction rate upsurges with the rise in $[NO_2-]$ (Table 1.4, r = 0.9911) and the plot of log k' versus log $[NO_2-]$ was linear with a slope of 1.0 displaying first order dependence on $[NO_2-]$.

Effect of pH on the rate:

The reaction rate declined with growing pH of the medium (Table 1.5, r = 0.9928). A plot of log k' versus log $[H+]$ was linear with a slope of 0.8 displaying fractional order dependency on $[H+]$.

Effect of toluenesulphonamide concentration on the rate:

Toting of reaction product, TSA (2.0×10^{-5} to 20.0×10^{-5} mol dm^{-3}) to the reaction combination retarded the reaction rate (Table 1.6, r = 0.9991) A plot of log k' versus log [TSA] was linear with a slope of -1.0 displaying inverse first order.

Effect halide ion concentration on the rate:

Addition of chloride ion (2.0×10^{-4} to 20.0×10^{-4} mol dm$_{-3}$) has insignificant consequence on the reaction rate (Table 1.7).

Effect of ionic strength on the rate:

Ionic strength of the reaction medium diverse by tallying $NaClO_4$ (0.05 to 0.1 mol dm$_{-3}$) did not result on the rate (Tabled 1.8).

Effect of dielectric constant (D) of solvent on the rate:

The effect of D on the reaction rate was premeditated by variable MeOH content (0-20% v/v) in pH 5.8 buffer medium. The rate declined with an upsurge in MeOH content of the medium, additionally, a plot of log k' versus 1/D gave a straight line (Table 1.9, Fig.1.6, r = 0.9959) with a negative slope. This consequence is in conformity with the Amis concept for dipole-dipole or dipole-ion interactions.

Effect of temperature on the rate:

The reaction was calculated at dissimilar temperatures, 295 K to 313 K while observance the [CAT] and other conditions constant. The rate constants are obtainable in table 1.10. The activation parameters were calculated from the slopes and intercepts of the Arrhenius plots of log k' versus 1/T (Table 1.11, r = 0.9971).

Test for free radicals:

Tests accomplished for the existence of free radicals by adding the reaction blend to acrylonitrile solution were negative. The nonappearance of polymerization shows that free radical species *in situ* are not designed in reaction.

The blank experiments presented that no reaction is taking place amongst

(i) IC and Nitrite ion in the absence of CAT

(ii) Nitrite ion and CAT in the absence of IC and

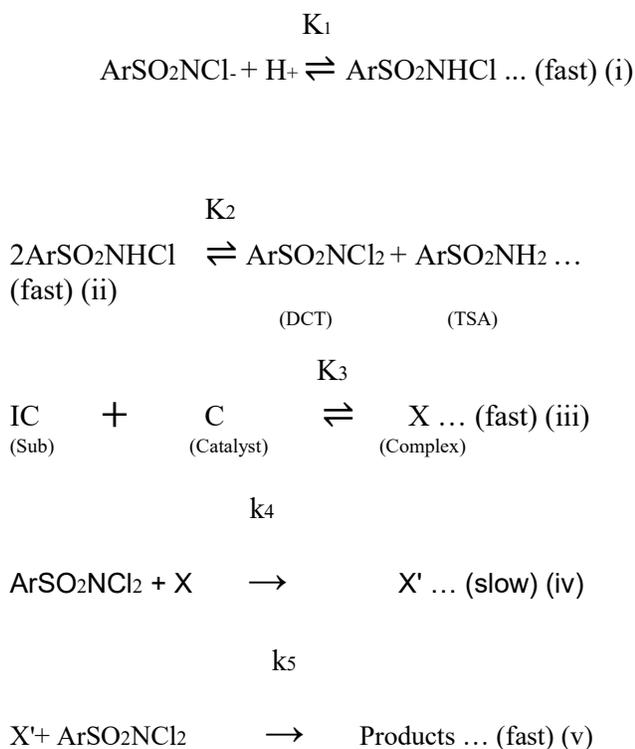(iii) Indigocarmine and NaCl in presence of NO_2- and in the absence CAT

DISCUSSION AND MECHANISM

Pryde and Sopper, Morries et al and Bishop and Jennings have publicized the presence of similar equilibria in acid medium. Chloramine-T ($ArSO_2NClNa$) or ($p-CH_3C_6H_4SO_2NClNa.3H_2O$) acts as a strong electrolyte in aqueous solution forming diverse species as shown in equation 1.2 to 1.6.

$$ArSO_2NClNa \rightleftharpoons ArSO_2NCl- + Na+ \dots (1.2)$$

$$ArSO_2NCl_- + H_+ \rightleftharpoons ArSO_2NHCl \ldots \quad (1.3)$$

$$2ArSO_2NHCl \rightleftharpoons ArSO_2NCl_2 + ArSO_2NH_2 \ldots (1.4)$$

$$ArSO_2NCl_2 + H_2O \rightleftharpoons ArSO_2NHCl + HOCl \ldots (1.5)$$

$$ArSO_2NHCl + H_2O \rightleftharpoons ArSO_2NH_2 + HOCl \ldots (1.6)$$

The likely reactive oxidizing species in acidified CAT solutions are therefore $ArSO_2NHCl$, $ArSO_2NHCl_2$ and HOCl. In the current study of IC oxidation, the reaction displays a second order in [CAT] and a retardation by the added TSA ($ArSO_2NH_2$) i.e., an inverse first order on $[TSA]_0$ designating the association of $ArSO_2NCl_2$ as the kinetically active species in a fast pre-equilibrium. Furthermore, the reaction rate shows requirements of a first order on [IC], a fractional order on [H+] and first order on catalyst [NO2-]. Based on the previous discussion, a mechanism (Scheme 1.1) is projected to account for the investigational observations.

$$\overset{K_1}{ArSO_2NCl_- + H_+ \rightleftharpoons ArSO_2NHCl} \ldots \text{(fast) (i)}$$

$$\overset{K_2}{2ArSO_2NHCl \rightleftharpoons ArSO_2NCl_2 + ArSO_2NH_2} \ldots$$
(fast) (ii)

(DCT)   (TSA)

$$\overset{K_3}{IC + C \rightleftharpoons X} \ldots \text{(fast) (iii)}$$
(Sub)   (Catalyst)   (Complex)

$$\overset{k_4}{ArSO_2NCl_2 + X \longrightarrow X' } \ldots \text{(slow) (iv)}$$

$$\overset{k_5}{X' + ArSO_2NCl_2 \longrightarrow Products} \ldots \text{(fast) (v)}$$

Scheme 1.1
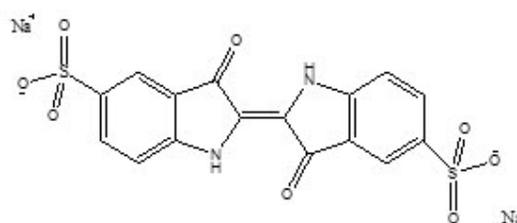

Fig 1. Molecular structure of indigo carmine

The value of enthalpy of activation ($\Delta H^{\neq}$) is helpful of the suggested machinery in Scheme-8.1. The highly negative entropy of activation ($\Delta S^{\neq}$) designates the formation of a transition state by an associative procedure.

TABLE 1.1
Effect of varying [CAT] on the rate of oxidation of indigocarmine:
(Representative run)
$[IC]_0 = 5.0 \times 10_{-5}$ mol dm-3; [CAT] = $1.6 \times 10_{-4}$ mol dm-3; [NO2-] = $2.0 \times 10_{-3}$ mol dm-3; λ_{max} = 610 nm; μ = 0.1 mol dm-3; pH = 5.8; T = 300K.

Time (min)	Optical density (OD)	log [OD]0/[OD]t
0	0.519	-
3.0	0.254	0.31

6.0	0.189	0.43
9.0	0.142	0.55
12.0	0.105	0.68
15.0	0.085	0.79
18.0	0.068	0.90
21.0	0.050	1.04
24.0	0.036	1.15

Plot of log $[OD]_0/[OD]_t$ versus time
 r = 0.9997 k′ = 17.5×10^{-4}(sec⁻¹)

TABLE 1.2
Effect of varying [IC] on the rate of reaction
[CAT] = 1.6×10^{-4} mol dm⁻³; [NO$_2$ ⁻] = 2.0×10^{-3} mol dm⁻³; λ_{max} = 610 nm; μ = 0.1 mol dm⁻³; pH = 5.8; T = 300K.

[IC] × 10⁵ (mol dm⁻³)	k′ × 10⁴ (sec⁻¹)
2.0	17.3
3.0	17.6
5.0	17.5
6.0	17.4
7.5	17.3

TABLE 1.3
Effect of varying [CAT] on the rate of reaction
[IC]$_0$ = 5.0×10^{-5} mol dm⁻³; [NO$_2$ ⁻] = 2.0×10^{-3} mol dm⁻³; λ_{max} = 610 nm; μ = 0.1 mol dm⁻³; pH = 5.8; T = 300K.

[CAT] × 10⁴ (mol dm⁻³)	4+log [CAT]	k′ × 10⁴ (sec⁻¹)	4+log k′
1.0	0.000	7.76	0.89
1.2	0.079	12.3	1.09
1.6	0.204	17.5	1.24
1.8	0.255	28.0	1.44
2.2	0.342	38.9	1.59
2.6	0.414	47.8	1.68

Plot of log k′ versus log [CAT] r = 0.9911 order = 2.0

TABLE 1.4
Effect of varying [NO$_2$ ⁻] on the rate of reaction
[IC]$_0$ = 5.0×10^{-5} mol dm⁻³; [CAT] = 1.6×10^{-4} mol dm⁻³;
λ_{max} = 610 nm; μ = 0.1 mol dm⁻³; pH = 5.8; T = 300K.

[NO$_2$⁻] × 10³ (mol dm⁻³)	3+log [NO$_2$⁻]	k′ × 10⁴ (sec⁻¹)	4+log k′
1.0	0.0000	10.0	1.00
2.0	0.3010	17.5	1.24
3.0	0.4771	26.3	1.42
4.0	0.6020	41.6	1.62
5.0	0.6989	50.1	1.70

Plot of log k′ versus log [NO$_2$⁻] r = 0.9923 order = 1.0

TABLE 1.5
Effect of varying pH on the rate of reaction
[IC]$_0$ = 5.0×10^{-5} mol dm⁻³; [CAT] = 1.6×10^{-4} mol dm⁻³; [NO$_2$ ⁻] = 2.0×10^{-3} mol dm⁻³; λ_{max} = 610 nm; μ = 0.1 mol dm⁻³; T = 300K.

pH	[H⁺] x 10⁶	6 + log [H⁺]	k′ × 10⁴ (sec⁻¹)	4+log k′
5.2	6.31	6.80	63.0	1.80
5.4	3.98	6.50	32.3	1.51
5.6	2.51	6.39	25.7	1.41
5.8	1.58	6.19	17.5	1.24
6.0	1.00	6.00	14.1	1.15

Plot of log k′ versus log [H⁺] r = 0.9928 order = 0.8

TABLE 1.6
Effect of varying [TSA] on the rate of reaction
[IC]$_0$ = 5.0×10^{-5} mol dm⁻³; [CAT] = 1.6×10^{-4} mol dm⁻³; [NO$_2$ ⁻] = 2.0×10^{-3} mol dm⁻³; λ_{max} = 610 nm; pH = 5.8; μ = 0.1 mol dm⁻³; T = 300K.

[TSA] × 10⁵ (mol dm⁻³)	5+log [TSA]	k′ × 10⁴ (sec⁻¹)	4+log k′
2.0	0.3010	81.2	1.91
5.0	0.6989	32.0	1.49
10.0	1.0000	16.6	1.22
16.0	1.2041	11.2	1.04
20.0	1.3010	9.59	0.98

Plot of log k′ versus log [TSA] r = 0.9991 order = -1.0

TABLE 1.7
Effect of varying [Cl⁻] ion on the rate of reaction
[IC]$_0$ = 5.0×10^{-5} mol dm⁻³; [CAT] = 1.6×10^{-4} mol dm⁻³; [NO$_2$ ⁻] = 2.0×10^{-3} mol dm⁻³; λ_{max} = 610 nm; pH = 5.8; μ = 0.1 mol dm⁻³; T = 300K.

[Cl⁻] × 10⁴ (mol dm⁻³)	k′ × 10⁴ (sec⁻¹)
2.0	17.4
5.0	17.5
10.0	17.1
15.0	17.6
20.0	17.3

TABLE 1.8

Effect of varying ionic strength on the rate of reaction

$[IC]_0 = 5.0 \times 10^{-5}$ mol dm^{-3}; $[CAT] = 1.6 \times 10^{-4}$ mol dm^{-3}; $[NO_2^-] = 2.0 \times 10^{-3}$ mol dm^{-3}; $\lambda_{max} = 610$ nm; pH = 5.8; T = 300K.

[NaClO$_4$] (mol dm^{-3})	k′ × 10^4(sec^{-1})
0.05	17.3
0.06	17.5
0.07	17.2
0.08	17.6
0.10	17.4

TABLE 1.9

Effect of varying dielectric constant of the medium on rate of reaction

$[IC]_0 = 5.0 \times 10^{-5}$ mol dm^{-3}; $[CAT] = 1.6 \times 10^{-4}$ mol dm^{-3}; $[NO_2^-] = 2.0 \times 10^{-3}$ mol dm^{-3}; $\lambda_{max} = 610$ nm; pH = 5.8; $\mu = 0.1$ mol dm^{-3}; T = 300K.

Methanol % (v/v)	D	10^2/D	k′ × 10^5(sec^{-1})	4+log k′
0	76.73	1.30	17.5	1.243
5	74.50	1.34	15.2	1.181
10	72.37	1.38	14.1	1.149
15	69.90	1.43	12.6	1.100
20	67.48	1.48	10.9	1.037

Plot of log k′ versus log [1/D] r = 0.9959

TABLE 1.10

Effect of varying temperature on the rate of reaction

$[IC]_0 = 5.0 \times 10^{-5}$ mol dm^{-3}; $[CAT] = 1.6 \times 10^{-4}$ mol dm^{-3}; $[NO_2^-] = 2.0 \times 10^{-3}$ mol dm^{-3}; $\lambda_{max} = 610$ nm; pH = 5.8; $\mu = 0.1$ mol dm^{-3};

Temperature(K)	10^3/T	k′ × 10^4 (sec^{-1})	4+log k′
295	3.38	12.5	1.099
300	3.33	17.5	1.243
303	3.30	19.4	1.287
308	3.24	28.1	1.448
313	3.19	46.7	1.669

Plot of log k′ versus log1/T r = 0.9889 Slope = -3000.0

TABLE 1.11

Activation parameters for the oxidation of indigocarmine by CAT in buffer medium

Ea (kJ mol^{-1})	ΔH$^{\neq}$ (kJ mol^{-1})	ΔS$^{\neq}$ (JK^{-1} mol^{-1})	ΔG$^{\neq}$ (kJ mol^{-1})
57.47	54.95	- 115.09	89.90

CONCLUSION

In this paper we reported oxidative decolorization of indigocarmine dye with chloramine-T catalysed by performing product analysis and the results have been presented for different reactants and then later discussed about mechanism of how they work (reactive oxidizing species in acidified CAT solutions) and finally effect of varying on the rate of oxidation of indigocarmine and other rate of reactions are tabulated with values. Thus we have shown the kinetics of nitrite ion catalysed oxidation of indigocarmine by chloramine-t in acidic buffer (ph 5.8) medium in details.

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