RESEARCH ARTICLE

OXIDATIVE DECOLORISATION OF INDIGOCARMINE DYE BY CHLORAMINE-T IN ACIDIC BUFFER (pH= 5.8) MEDIUM CATALYSED BY NITRITE ION: A KINETIC AND MECHANISTIC STUDY

[*1]Chandrashekar, [2]Radhika, R. T., [3]Venkatesha, B. M. and [4]Ananda, S.

[1]Department of Chemistry, PES College of Engineering Mandya-571401, Karnataka, India
[2]Department of Chemistry Maharani's Science College for Women, Mysore-570005, India
[3]Department of Chemistry, Yuvaraja´s College, University of Mysore, Mysore - 570005, India
[4]Department of Studies in Chemistry, Manasagangothri, University of Mysore, Mysore - 570006, India

ABSTRACT

Kinetics of oxidative decolorisation of indigocarmine(IC) dye by CAT in pH 5.8 buffer medium catalyzed by nitrite ion has been studied at 300K spectrophotometrically at $_{max}$= 610 nm. The reaction is first order with respect to [IC], [Nitrite ion] and second order with respect to [CAT]. It also shows an inverse first order on p-toluenesulphonamide concentration [TSA] and inverse fractional order on [H⁺]. The additions of the reaction product p-toluenesulphonamide and halide ions have no significant effect on the rate of the reaction. The variation of ionic strength of the medium did not affect the rate indicating that non ionic species are involved in the rate determining step. The dielectric effect is positive. The reaction was studied at different temperatures and the activation parameters have been deduced. Oxidation products were characterized. Test for free radicals was found to be negative. The derived rate law based on the proposed mechanism is in complete agreement with the observed kinetic data.

INTRODUCTION

Indigocarmine (IC) also known as indigotine. It is approved for use as a food colorant in the united states Summary of colour additives for use in united states in foods (1984). The primary use of indigocarmine is as a pH indicator. It is blue at pH 11.4 and yellow at 13.0. Indigocarmine is also a redox indicator, turning yellow upon reduction. The chemistry of IC and derivatives has been reviewed by Rodd (1960). It is used as dye in the textile industry and manufacture of capsules. In surgery, intravenous indigocarmine is used to highlight of urinary tract. Murthy *et al.* (1979) have reported the kinetics of oxidation of IC by potassium peroxydisulphate in presence of acid medium, kinetics of EDTA catalysed oxidation of IC by Vanadium (V) spectrophotometrically in presence of acid medium at 25⁰C reported by Rao *et al.* (1979) Ananda etal have reported the kinetics of oxidation of IC by chloramine-B and HOCl buffer medium (pH 2-6) at 30 C⁰. (1995), and kinetics of oxidation of indigocaramine by bromamine-T in acidic buffer medium Ananda *et al.* (1997). Venkatesha *et al.* (1995) have reported the oxidation of indigocaramine by chloramine-T and aqueous chlorine in acidic buffer medium. (1995), and oxidative decolourisation of indigocarmine dye with chloramine-T

catalysed by cobalt (II) venkatesha *et al.* (2011). Puttaswamy *et al.* (1991) have reported the kinetics of oxidation of IC by sodium hypohalites (NaOX) in alkaline buffer of pH= 9-11 spectrophotometrically. Srinivasa *et al.* (1982) have reported kinetics and mechanism of oxidation of IC by V(v) in presence of salicylic acid and substituted salicylic acids. Oxidation of kinetics of IC with potassium bromate in aqueous sulphuric acid reported by Sreekantha *et al.* (1988).

A prominent member of the class of N-haloarylsulfonamides is sodium N-chloro-p-toluenesulfonamide or chloramine-T (p-CH₃C₆H₄SO₂NClNa3H₂O or CAT), which is a byproduct in the manufacture of saccharin Campbell and Johnson (1978). CAT is the most widely studied haloamine containg positive chlorine which is implicated in the reaction of an array of functional groups of the substrates. Several studies on the mechanistic aspect of oxidation of diverse organic substrate including IC by aromatic haloamines have been reported by us (Ananda *et al.*, 1997; Venkatesha *et al.*, 1995; Venkatesha *et al.*, 2011; Saldanha *et al.*, 2002; Venkatesha *et al.*, 1994; Venkatesha *et al.*, 1992). However, there is no information available on the nitrite catalysed oxidation of IC by aromatic N-chloroamines. In the present paper, we report on the kinetic and mechanistic investigations of nitrite ion catalysed oxidative decolorisation of IC by chloramine-T.

*Corresponding author: Chandrashekar,
Department of Chemistry, PES College of Engineering Mandya-571401, Karnataka, India.

MATERIALS AND METHODS

Experimental

Aqueous solution of indigocarmine (Merck) was prepared using triply distilled water. Stock solution of chloramine-T (A.R. Thomas Baker India) was prepared in triply distlled water. An aqueous solution of CAT was standardized iodometrically and preserved in brown bottles to prevent photochemical degradation. Aqueous solution of indigocarmine (Merck) was prepared using triply distlled water. Standard buffer system (Acetic acid and sodium acetate) pH 5.8 was prepared and its pH value checked with a pH meter. All other chemicals were of analytical grade. Triply disitlled water was used for preparing aqueous solution. Ionic strength of reaction mixture was kept at a high value using concentrated solution of $NaClO_4$.

Kinetic Measurements

Kinetic runs were performed under pseudo-first order conditions of a large excess of the oxidant over IC at 300K. For each run, requisite amounts of solutions of IC, $NaNO_2$, $NaClO_4$, (to maintain a constant ionic strength) and buffer of known pH were mixed in a stoppered pyrex glass tube, whose outer surfaces were coated black. Required amount of buffer was added to maintain a constant volume. The tube was thermostated in a water bath at a given temperature. To this solution was added a measured amount of preequilibrated CAT solution to give a known overall concentration. The reaction mixture was shaken for uniform concentration. The course of the reaction was monitored spectrophotometrically by measuring the absorbance at the $_{max}$ =610 nm for IC at regular time intervals for three half lives. The pseudo first order rate constants k calculated were reproducible within ± 3%. Since the total ionic strength maintained was 0.1 mol dm^{-3}, molar concentrations were used in the expression of rate constants instead of activities in first approximation, neglecting the activity coefficients. The regression analysis of the experimental data was carried out on origin 5.0 HP computer to obtain the regression coefficient (r).

Reaction Stoichiometry

Varying ratios of the oxidant to IC in the presence of buffer pH 5.8 were equilibrated at 300 K for 12 hours. The unchanged oxidant in the reaction mixture was determined by iodometric titration. The analysis showed that one mole of IC reacted with four moles of oxidant, according to the following stoichiometry, forming sulphonated anthranilic acid (SAA).

$C_{16}H_8O_8S_2N_2Na_2$ + $4ArSO_2NCl^-$ + $6H_2O$ $\longrightarrow$
(IC)   (anion of CAT)
$2C_7H_6O_5NSNa$+$2CO_2$+ $4ArSO_2NH_2$ + $4Cl^-$... (1)
 SAA
Here Ar is p-CH_3-C_6H_4

Product Analysis

The reduction product of oxidant, toluenesulphonamide was detected by paper chromatography Feigl (1990). Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl in ethanol as spray reagent (Rf= 0.905). The oxidation product of IC, sodium salt of sulphonated anthranilic acid (SAA) was analysed Vogel (1978). Amounts of anthranilate present in the reaction mixture were quantitatively determined using a standard method involving its precipitation as zinc(II) salt $Zn(C_7H_5O_5NSNa)_2$ Vogel (1978). The recovery of the anthranilate from several reaction mixtures in pH 5.8 buffer was in the range 85-95%, another product CO_2 was detected by the conventional lime water test. Attempts to quantitative estimation of CO_2 evolved were unsuccessful.

RESULTS AND DISCUSSION

Effects of CAT and IC concentration on the reaction rate

Under pseudo first order conditions of $[CAT]_0 >>$ $[IC]_0$ at constant $[CAT]_0$, $[NO_2^-]$, pH and temperature, the plots of log $[OD]_0/[OD]_t$ versus time were linear indicating a first order dependence of the reaction rate of [IC], $[OD]_t$ is the absorbances of the reaction mixture at time interval 't'. The pseudo-first order rate constants k' obtained at 300K are independent of $[IC]_0$ further confirming the first order dependence on $[IC]_0$. At constant pH, $[NO_2^-]$, $[IC]_0$, ionic strength and temperature the rate increased with increasing $[CAT]_0$ (Table 1). Furthermore a plot of log k' versus log $[CAT]_0$ was linear with a slope of 2.0 showing second order dependence on [CAT] (Table 1, Figure 1, r = 0.9911).

Table 1.   Effect of varying reactant concentration on the rate
$[NO_2^-]$ = 2.0×10^{-3} mol dm^{-3}; $_{max}$ = 610 nm; μ = 0.1 mol dm^{-3}; pH = 5.8; T = 300K

[CAT] x 10^4 (mol dm^{-3})	10^5[IC] (mol dm^{-3})	10^4k´ (s^{-1})
1.0	5.0	7.76
1.2	5.0	12.3
1.6	5.0	17.5
1.8	5.0	28.0
2.2	5.0	38.9
2.6	5.0	47.8
1.6	2.0	17.3
1.6	3.0	17.6
1.6	5.0	17.5
1.6	6.0	17.4
1.6	7.5	17.3

Fig.1 Plot of logk´ versus log[CAT]
$[IC]_0$ = 5.0×10^{-5} mol dm^{-3}; $[NO_2^-]$ = 2.0×10^{-3} mol dm^{-3};

$_{max}$ = 610 nm; μ = 0.1 mol dm^{-3}; pH = 5.8; T = 300K.

Effect of [NO$_2^-$] on the reaction rate

The reaction rate increases with the increase in [NO$_2^-$] (Table 2, r = 0.9911) and the plot of log k versus log [NO$_2^-$] was linear with a slope of 1.0 showing first order dependence on [NO$_2^-$].

Table 2. 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};
$_{max}$ = 610 nm; μ = 0.1 mol dm^{-3}; pH = 5.8; T = 300K

[NO$_2^-$] × 10^3 (mol dm^{-3})	k´ × 10^4 (sec^{-1})
1.0	10.0
2.0	17.5
3.0	26.3
4.0	41.6
5.0	50.1

Effect of pH on the reaction rate

The reaction rate decreased with increasing pH of the medium (Table 3, r = 0.9928). A plot of log k versus log [H$^+$] was linear with a slope of 0.8 showing fractional order dependence on [H$^+$].

Table 3. 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}; $_{max}$ = 610 nm; μ = 0.1 mol dm^{-3}; T = 300K

pH	[H$^+$] x 10^6	k´ × 10^4 (sec^{-1})
5.2	6.31	63.0
5.4	3.98	32.3
5.6	2.51	25.7
5.8	1.58	17.5
6.0	1.00	14.1

Effect of reduction product, [TSA] on the reaction rate

The effect of the externally added reduction product, TSA on the rate at other constant conditions was studied in the range (2.0 x 10^{-5} to 20.0 x 10^{-5} mol dm^{-3}) to the reaction mixture retarded the reaction rate. A plot of log k versus log [TSA] was linear with a slope of -1.0 showing inverse first order (Figure 2, r = 0.9991).
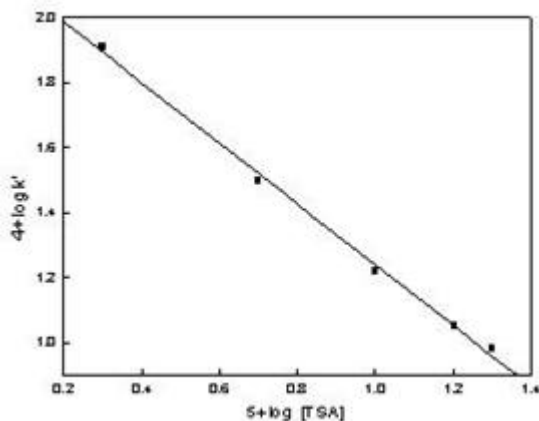
Fig.2. Plot of logk´ versus log[TSA]

[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}; $_{max}$ = 610 nm; pH = 5.8; μ = 0.1 mol dm^{-3}; T = 300K.

Effects of halide ion and ionic strength on the reaction rate

Addition of chloride ion (2.0x10^{-4} – 20.0x10^{-4} mol dm^{-3}) in the form of NaCl, to the reaction mixture had no effect on the rate. Ionic strength of the reaction medium varied by adding NaClO$_4$ (0.05 to 0.1 moldm^{-3}) did not affect the rate.

Effect of Dielectric Constant (D) on the reaction rate

The effect of dielectric constant (D) on the reaction rate was studied by varying MeOH content (0-20% v/v) in pH 5.8 buffer medium. The rate decreased with an increase in MeOH content of the medium, furthermore, a plot of log k versus 1/D gave a straight line (Figure 3, r = 0.9959) with a negative slope. This effect is in conformity with the Amis concept for dipole-dipole or dipole-ion interactions Amis (1970).
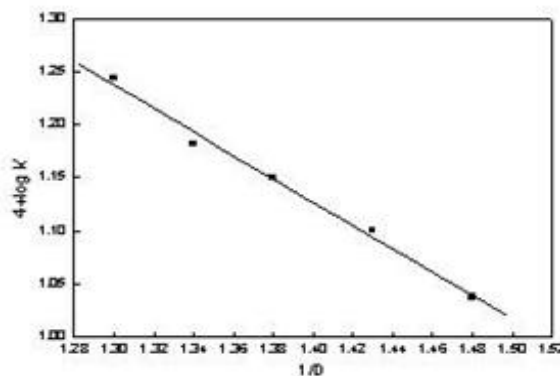
Fig.3. Plot of logk´ versus 1/D

[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}; $_{max}$ = 610 nm; pH = 5.8; μ = 0.1 mol dm^{-3}; T = 300K

Table 4. Temperature dependence of the reaction rate and activation parameters for the indigocarmine oxidation by CAT in presence of nitrite ion catalyst

[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}; $_{max}$ = 610 nm; pH = 5.8; μ = 0.1 mol dm^{-3};

Temperature(K)	k´ × 10^4 (sec^{-1})	Activation parameters
295	12.5	Ea = 57.47 (kJ mol^{-1})
300	17.5	H = 54.95 (kJ mol^{-1})
303	19.4	S = - 115.09 (JK^{-1} mol^{-1})
308	28.1	G = 89.90 (kJ mol^{-1})
313	46.7	

Effect of temperature on the reaction rate

Kinetic runs were performed at various temperatures (295 K to 313 K) while keeping the other experimental conditions the same. An Arrhenius plot of log k versus 1/T

(Table 4, r = 0.9971) used to calculate the activation parameters, namely, energy of activation (Ea), entropy of activation (ΔS), enthalpy of activation (ΔH), free energy of activation (ΔG). these results are summarized in Table 4.
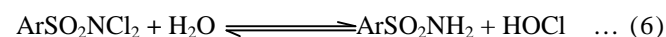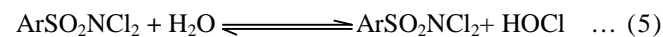
Detection of free radicals

The negative polymerization test with monomers for the detection of free radicals generated in *situ in the* reaction mixture showed the absence of free radicals. The blank experiments showed that no reaction is taking place between

(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

Mechanism

Pryde and Sopper (1926) Morries *et al.* (1958) and Bishop and Jennings (1958) have shown the existence of similar equilibria in acid medium. Chloramine-T ($ArSO_2NClNa$) or (p-$CH_3C_6H_4SO_2NClNa$. $3H_2O$) behaves as a strong electrolyte in aqueous solution forming different species as shown in equation 2 to 6.

$$ArSO_2NClNa \rightleftharpoons ArSO_2NCl^- + Na^+ \quad \dots (2)$$

$$ArSO_2NCl^- + H^+ \rightleftharpoons ArSO_2NHCl \quad \dots (3)$$

$$2ArSO_2NHCl \rightleftharpoons ArSO_2NCl_2 + ArSO_2NH_2 \dots (4)$$

$$ArSO_2NCl_2 + H_2O \rightleftharpoons ArSO_2NCl_2 + HOCl \quad \dots (5)$$

$$ArSO_2NCl_2 + H_2O \rightleftharpoons ArSO_2NH_2 + HOCl \quad \dots (6)$$

The free acid of CAT ($ArSO_2NHCl$), dichloramine-T ($ArSO_2NCl_2$), HOCl are the probable oxidizing species in acid medium. The reaction shows a second order in [CAT] and a retardation by the added p-toluenesulphonamide ($ArSO_2NH_2$) i.e., an inverse first order on $[TSA]_0$ indicating the involvement of $ArSO_2NCl_2$ as the kinetically active species in a fast preequilibrium. Additionally, the reaction rate shows dependences of a first order on [IC], a fractional order on $[H^+]$ and first order on catalyst $[NO_2^-]$. On the basis of the above discussion, a simple mechanism (Scheme 1) has been proposed for the reaction in acidic solutions**.**

$$ArSO_2NCl^- + H^+ \overset{K_1}{\underset{K_2}{\rightleftharpoons}} ArSO_2NHCl \quad \dots(fast) \quad (i)$$

$$2ArSO_2NHCl \rightleftharpoons \underset{(DCT)}{ArSO_2NCl_2} + \underset{(TSA)}{ArSO_2NH_2} \dots(fast) \quad (ii)$$

$$IC + \underset{(Sub)}{\quad} \underset{(Catalyst)}{C} \overset{K_3}{\rightleftharpoons} \underset{(complex)}{X} \quad \dots(fast) \quad (iii)$$

$$ArSO_2NCl_2 + X \overset{k_4}{\longrightarrow} X' \quad \dots(slow) \quad (iv)$$

$$X' + ArSO_2NCl_2 \overset{k_5}{\longrightarrow} Products \quad \dots(fast) \quad (v)$$
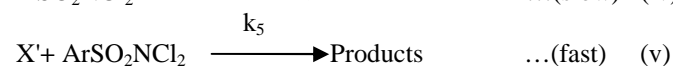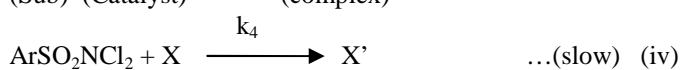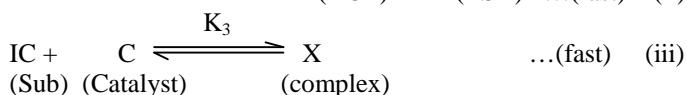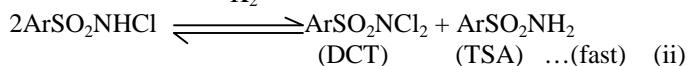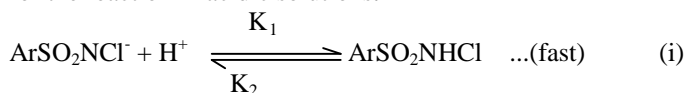
Scheme 1

The following equilibrium (equation 8) exists for $NaNO_2$ in acidic solution.

$$NaNO_2 \overset{H^+}{\longrightarrow} Na^+ + HNO_2 \quad \dots (7)$$

$$2HNO_2 \overset{H^+}{\rightleftharpoons} O = N - O - N = O + H_2O \dots (8)$$
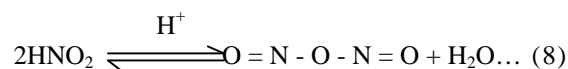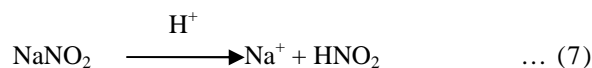
Molecular structures of complexes X and X', and other intermediate species formed are as shown in   scheme-2. This scheme shows a detailed interpretation of electronic mechanism for the oxidation of IC, Catalyst and $ArSO_2NCl_2$ (Active oxidising species of CAT). An electrophilic attack Cl^+ of $ArSO_2NCl_2$ across carbon-carbon double bond of X leads to the formation of the complex X (5-isatin sulphonate) with regeneration of the catalyst. The isatin sulphonate intermediate under goes further oxidation with $ArSO_2NCl_2$ followed by nucleophilic attacks by water and intramolecular rearrangements to form the product sulphonated anthranilic acid (SAA)

Scheme 1 leads to the rate law as follows

$$Rate = = k_4 [DCT] [X] \quad \dots (9)$$

The total effective concentration of CAT is given by

$$[CAT]_0 = [ArSO_2NCl^-] + [\overset{\frown}{ArSO_2NHCl}] + [DCT] \quad \dots (10)$$

From equalibria (i) and (ii) in scheme 1

$$[ArSO_2NCl^-] = \frac{[ArSO_2NHCl]}{K_1[H^+]} \quad \dots (6) \quad \dots (11)$$

$$[ArSO_2NHCl] = \frac{[[DCT][TSA]]^{1/2}}{K_2^{1/2}} \quad \dots (12)$$

Substitution for [$ArSO_2NHCl$] from equation (12) in equation (11) gives,

$$[ArSO_2NHCl] = \frac{[[DCT][TSA]]^{1/2}}{K_2^{1/2}K_1[H^+]} \quad \dots (13)$$

Substitute equations (12) and (13) in equation (10) one obtains,

$$[CAT]_t = \frac{[DCT]\{[TSA]^{1/2} + K_1[H^+][TSA]^{1/2} + K_2K_2^{3/2}[H^+][DCT]^{1/2}}{K_1K_2^{1/2}[H^+][DCT]^{1/2}}$$

Or

$$DCT = \frac{K_1K_2^{1/2}[H^+][DCT]^{1/2}[CAT]_t}{[TSA]^{1/2} + K_1[H^+][TSA]^{1/2} + K_2K_2^{1/2}[H^+][DCT]^{1/2}} \quad \dots (14)$$

Since in acid medium chloramine-T exists, predominantly as $ArSO_2NCl$, [$ArSO_2NHCl$] $[CAT]_t$, therefore equation (12)

takes the form.

$$[DCT]^{1/2} = \frac{K_2^{1/2}[CAT]_t}{[TSA]^{1/2}}$$

The above $[DCT]^{1/2}$ in equation (14) one gets,

$$DCT = \frac{K_1 K_2 [CAT]^2 [H^+]}{[TSA]\{1+K_1[H^+]\}+K_1 K_2 [CAT]_t [H^+]} \qquad \ldots (15)$$

From equalibria (iii) of Scheme 1

$$K_3 = \frac{X}{[IC][Catalyst]}$$

$$[X] = K_3 [IC][Catalyst] \qquad \ldots (16)$$

$$\therefore Rate = k_4 [DCT][X] \qquad \ldots (17)$$

Substituting equation (17) in equation (15)

$$\therefore Rate = \frac{k_4 K_1 K_2 [CAT]^2 [H^+] K_3 [IC][Catalyst]}{[TSA]\{1+K_2[H^+]\}+K_1 K_2 [CAT]_t [H^+]} \qquad \ldots (18)$$

Assuming third term in denominator is very small and neglecting.

$$Rate = \frac{k_4 K_1 K_2 K_3 [CAT]^2 [H^+][IC][Catalyst]}{[TSA]\{1+K_1[H^+]\}} \qquad \ldots (19)$$

The rate laws (19) are in agreement with the experimental results i.e. first order for [substrate], [catalyst], second order for [oxidant], fractional order for $[H^+]$ and inverse first order for [TSA]. If one assumes that values of protonation constant K_1 and disproportion constant K_2 of chloramine-T are nearly equal and close to $K_1[CAT]$ $K_2[CAT]$ 0.154 at pH 5.8 at 303 K Puttaswamy etal (1991). Using these approximate equilibrium constant values of CAT, it can be shown that the third term tends to be the smallest of the three terms in equation (18) justifying its omission. Amis (1970) has shown that for a limiting case of zero angle of approach between two dipoles or between an ion and dipole, a plot of log k versus 1/D (where D=dielectric constant of the solvent medium) has a negative slope for dipole-dipole or anion-dipole interactions and a positive slope for cation-dipole interactions in the rate determining step.
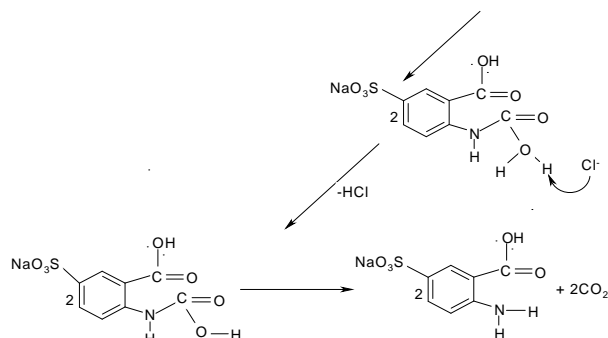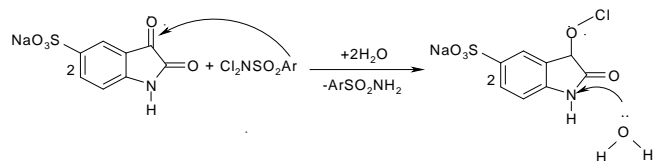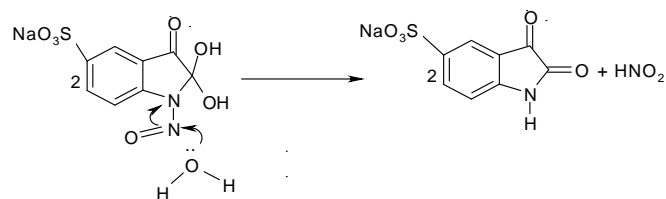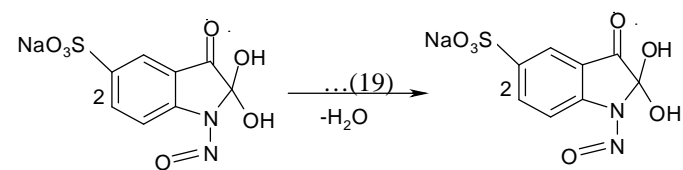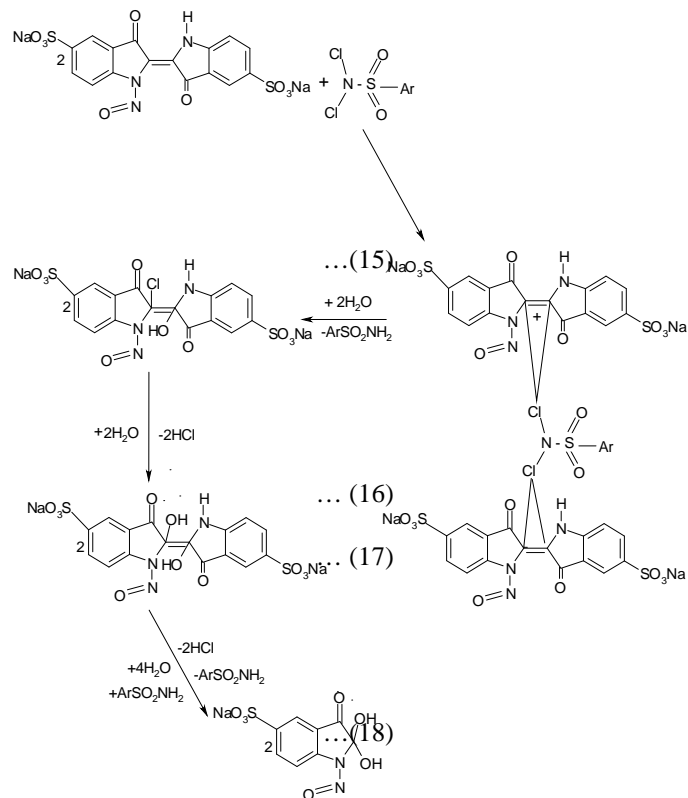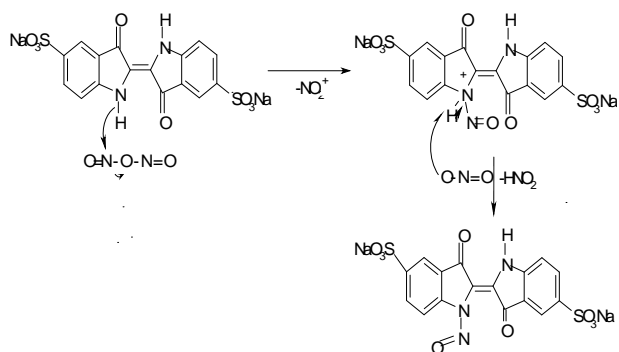
Scheme-2 Oxidation of indigocarmine by CAT in buffer medium

In the present study the observed negative effect of dielectric constant supports the proposed dipole-dipole interactions in the rate determining step in Scheme 1 of the mechanism. The value of enthalpy of activation (ΔH) is supportive of the proposed mechanism in Scheme-1 and 2. The highly negative entropy of activation (ΔS) indicates the formation of a transition state by an associative process.

Conclusion

Today, advanced oxidation processes for treatment of industrial effluents and toxic organics have become a focus of attention among environmental scientists. Several compounds have been reported as potential candidates to resolve environmental issues. Herein we report soft solution routes for decolorisation of indigocarmine dye by oxidation process using chloramine-T as oxidants and Nitrite ion as catalyst. Further more, this work indicates that spectrophotometric kinetic study enables estimation of the amount of nitrites present in water and some other samples.

Acknowledgement

REFERENCES

Amis E.S., *Solvent effects on reaction rates and mechanism.* Van Nostrand Reinhold New York , 257 (1970)

Ananda S., Jagadeesha M.B., Venkatesha B.M. and Made Gowda N. M. Kinetics of oxidation of indigocaramine by bromamine-T in acidic buffer medium. *Int. J. Chem. Kinet,* 29, 453-459 (1997).

Ananda S., Venkatesha B.M. and Mahadevappa D.S. Kinetics of oxidation of IC by chloramine-B and HOCl buffer medium. *Ind J. Chem*, 34B, 508-513 (1995).

Bishop E. and Jennings. Titrimetric analysis with chloramine-T-1: The status of chloramine-T as a titremetric reagent. *Talanta, 1,*197 (1958)

Campbell. M.M and Johnson.G. Chloramine-T and related N-halogeno-N-metallo reagents. Chem, Rev., 78, 65-85, (1978)

Feigl F., Spot tests in organic analysis, Elsevier, Amsterdam (1975). D.R. Lide, *CRC Handbook of Chemistry and Physics,*CRC Press, Boca Raton, 71st Edition, (1990)

Hardy, F.E. and Johnston, J.P.,The interactions of N-bromo-N-Sodiobenzenesulphonamide (bromamine-B) with p-nitrophenoxide ion. *J. Chem.Soc, Perkin Trans*, 2,742 (1973)

Murthy P.S.N., Subbaiah K.V. and Rao, P.V.S. Kinetics of oxidation of IC by potassium peroxydisulphate in presence of acid medium. *React. Kinet. Catal.* Lett, 11, 79 (1979).

Pryde B.G. and Soper F.G., The interaction of anilides and hypochlorous acid. *J. Chem.Soc*, 1582 (1926).

Puttaswamy, Mahadevappa D.S. and Gowda N.M.M. Kinetics of oxidation of IC by sodium hypohalites (NaOX) in alkaline buffer of pH= 9-11 spectrophotometrically. *Int. J. Chem Kinet,* 23, (1991).

Rao P.V.S., Subbaiah K.V. and Murthy P.S.N. Kinetics of EDTA catalysed oxidation of IC by Vanadium (V) spectrophotometrically in presence of acid medium. *React. Kinet. Catal. Lett,* 10, 287 (1979).

Rodd E.H., *Chemistry of Carbon Compounds, Elsevier,* Amsterdam, Volume IVB, (1960).

Saldanha RJD, Ananda S., Venkatesha B.M. and Made Gowda N. M. Oxidation of psychotropic drugs by chloramine-T in acid medium : a kinetic study using spectrophotometry. *J.mol. structure.* 606, 147-154 (2002)

Sreekantha Jonnalagadda B., Reaben H., Simarji and Gerald, K. Muthakia,. Oxidation of kinetics of IC with potassium bromate in aqueous sulphuric acid. *J. Chem. Soc. Perkin Trans II,* 1111 (1988).

Srinivasa K., Vijayashree M. and Subba Rao P.V. Kinetics and mechanism of oxidation of IC by V(v) in presence of salicylic acid and substituted salicylic acids. *Ind. J. Chem.,* 21 A,773 (1982).

Summary of colour additives for use in united states in foods, *drugs,cosmetics and medical device*s, united states food and drug administration, 1, 5 (1984).

Venkatesha B.M., Ananda S., Mahadevappa D.S. Kinetics of Oxidation of chloroacetic acid by sodium-N-bromo-p-toluene suphonamide in HCl medium and catalyzed by Ru(III)ion. *Ind.J.Chem* 33A, 128-135 (1994)

Venkatesha B.M., Ananda S., Mahadevappa D.S. and Gowda N.M.M. Oxidation of indigocaramine by chloramine-T and aqueous chlorine in acidic buffer medium. *Int. J. Chem Kinet*., 27, 663-674 (1995).

Venkatesha B.M., Ananda S., Mahadevappa D.S. Oxidation of Indole by N-sodio-N-Chlorobenzene Sulphonamide (Chloramine-B)in alkaline medium catalyzed by Os (VIII): A kinetic and mechanistic Study. *Jour.Phy.Org.Chem.* 5, 373-381 (1992)

Venkatesha B.M., Radhika R.T., Ananda S. and Byrappa K. Oxidative decolourisation of indigocaramine dye with chloramine-T catalysed by cobalt(II). *Res Chem Intermed* 37; 195-199 (2011).

Vogel A.I., *Text book of Quantitative Inorganic Analysis*, 4th Edn., ELBS. London. 427 (1978)

****