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Research Article

OXIDATIVE DECOLORISATION OF INDIGO CARMINE WITH 1-CHLOROBENZOTRIAZOLE IN ALKALINE BUFFER MEDIUM: KINETIC, MECHANISTIC AND SPECTROPHOTOMETRIC APPROACHES

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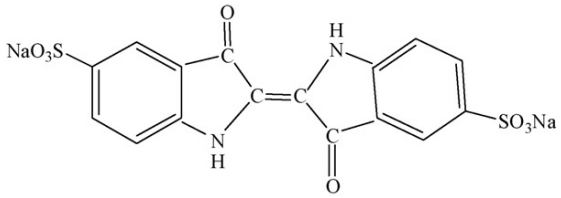
ABSTRACT

The kinetics and mechanism of oxidative decolorisation of Indigo carmine with 1-CBT in alkaline buffer medium have been spectrophotometrically investigated at λ_{max} 610 nm and at the temperature of 301 K. The reaction exhibited a first order dependence of the rate on [IC] and [CBT] and fractional order dependence on [OH^-]. Inverse fractional order dependence on [BTA]. The variation of ionic strength of the medium did not affect the rate indicating that non ionic species involved in the rate determining step. The dielectric effect is negative. The reaction was studied at deferent temperatures and the activation parameters were 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

Indigo carmine [3,3_-dioxo-1,3,1_,3_-tetrahydro-[2,2_]- bi-indolylidene-5,5_-disulfonic acid disodium salt] is one of the oldest dye and still one of the most important used. Its major industrial application is the dyeing of clothes (blue jeans) and other blue denim [1]. Indigo carmine is also used for medical diagnostic purposes, in conjunction with acetic acid the dye facilitate diagnosis of Barrett's esophagus [2]. It can also help to target biopsies even better, since in homogeneously stained or unstained areas seem to correlate with intraepithelial neoplasia [3]. Indigo carmine, however, is not readily metabolized but is rather freely filterable by the kidneys, giving intravenous injection of indigo carmine for intra-operative cystoscopy is a safe technique that can detect otherwise undetected intra-operative compromise of the urinary tract [4].

Indigo carmine dye [3,3_-dioxo-1,3,1_,3_-tetrahydro-[2,2_]-bi-indolylidene-5,5_-disulfonic acid disodium salt]



MF: $C_{16}H_8N_2Na_2O_8S_2$, MW 466.35 g/L. The peak intensity is at 608 nm; molar absorbtivity is 6309 mol ^{1} cm ^{1}[5].

Indigo carmine or IC (5,5-indigodisulfonic acid, disodium salt) finds applications as a redox indicator in analytical chemistry and as a microscopic stain in biology [6]. The chemistry of IC and its derivatives has been reviewed by Rodd [7]. Although there are several analytical methods available for IC [8,9], only a few studies of the kinetics of IC oxidation are reported in the literature. Several studies on the mechanistic aspects of oxidation of diverse organic substrates including IC by aromatic haloamines have been reported by others [10–17].

1-Chlorobenzotriazole (CBT) is a versatile oxidizing agent and its solution chemistry is reasonably well understood [18]. Kinetics of oxidation of IC by 1-CBT in acidic medium has

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been studied in our laboratory and the reaction is found to be slow. However, no such report is available in alkaline media. The kinetic aspects of oxidation of IC by BAT and CAT are also reported.[16,17].There are a few reports on the kinetics of oxidation of organic compounds by CBT.[21-25]. But there are no reports on the kinetics of oxidation of IC by 1-CBT. With this background, we report here results pertaining to the kinetics and mechanism of oxidative decolorisation of IC by 1-CBT.

1-CBT is an N-halogen compound that contains cyclic three nitrogen chain, has the capacity to undergo certain chemical reactions, which prove its usefulness in organic syntheses. It is soluble in water, chloroform, dichloromethane, ethyle acetate. 1-CBT can be used as a reagent for oxidation and chlorination reactions. Recently, 1 - CBT, has attracted the attention of organic chemists as a novel organic reagent in organic syntheses because of its reactivity towards a number of functional groups[10]. 1-CBT has considerable potential as an oxidant; it oxidizes alcohols to carbonyl compounds, hydrazo- to azo-compounds and 1,1-disubstituted hydrazine, all in high yield under very mild conditions.

MATERIAL AND METHODS

Experimental

1-CBT Solution

1-CBT is prepared by the method of Johnson *et al*[11]. An aqueous solution of 1-CBT was prepared, standardized periodically by the iodometric method and preserved in an amber colored bottle until further use[12].

Indigo Carmine Solution

As the substrate, IC, is prone to aerial oxidation and light, aqueous solutions of IC (E. Merck) were freshly prepared and used.

Buffer System

A pH 8 to 10 buffer solution was prepared by adding required amount of sodium borate and 0.2 M sodium hydroxide and its pH value checked with a pH meter.

All chemicals used were of analytical grade. A constant ionic strength in the reaction mixture was maintained by adding required amount of 0.2 M $NaClO_4$ solution. Double distilled water was used for preparing aqueous solutions.

Kinetic Procedure

Kinetic runs were prepared under pseudo-first order conditions of [IC]<[CBT] at 301 K. For each run requisite amounts of solutions of IC and buffer of known pH were taken in a stoppered pyrex glass tube whose outer surface were coated black to eliminate photochemical effects. A required amount of distilled water was added to maintain a constant volume in all runs. The tube was thermally equilibrated at a given temperature. The reaction was initiated by adding a measured amount of prequilibrated CBT solution and shaken periodically for uniform concentration. The progress of the reaction was monitored using UV-VIS. Spectrophotometer LMSP-UV1200 by measuring the absorbance of IC at its λ_{max} of 610 nm at regular intervals of three half-lives. The pseudo-first-order rate constants k, calculated. Regression analysis of the experimental data were carried out on a WINDOWS 2007 intel core i5 computer to obtain the regression coefficient, R^2.

RESULTS

Effect of CBT and IC concentration on the reaction rate

Under pseudo -first order conditions of $[CBT]_0>[IC]_0$ at constant temperature and pH, the plots of log $[OD]_0/[OD]_t$ versus time were linear indicating a first order dependence of the reaction rate of [IC],(table 6, Figure 6), $[OD]_t$ is the absorbance of the reaction mixture at time interval 't'. The pseudo -first order rate constant k obtained at 301 K are independent of $[IC]_0$. At constant pH, temperature, $[IC]_0$ and ionic strength the rate increased with increasing $[CBT]_0$ (Table 1). Furthermore a plot of log k versus log $[CBT]_0$ was straight line with a slope 1.17 showing first order dependence on [CBT] (Table 1, Figure 1, R^2=0.999).

Table 1 Effect of Varying CBT Concentrations on the Reaction Rate λ_{max} = 610 nm; pH 9.0; and temp 301 K

[CBT] x 10^4 (M)	[IC] x 10^5 (M)	k x 10^4 (s^{-1})
0.5	6.0	8.52
0.5	8.0	8.58
0.5	10.0	8.66
0.5	12.0	8.70
0.5	14.0	8.72
1.0	10.0	20.04
1.5	10.0	31.38
2.0	10.0	44.46
2.5	10.0	57.97
3.0	10.0	71.62

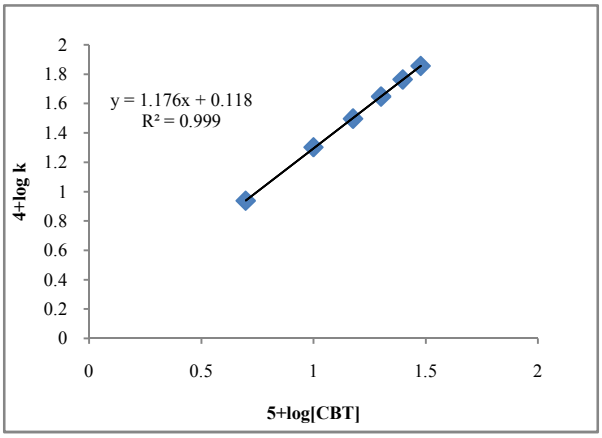


Figure 1

The complete decoloration of IC with CBT at constant [IC], [CBT], pH and temperature requires 60 minutes, the values of absorbance with regular intervals of time as shown in the table 6.

Effect of pH on the reaction rate

The reaction rate increased with increasing pH of the medium (Table 2, figure 2, R^2=0.975). A plot of log k versus log [$[OH^-]$ was straight line with a slope of 0.70 showing fractional order dependence on $[OH^-]$.

Effect of reduction product [BTA] on the reaction rate

The effect of extremely added reduction product, BTA on the rate at other constant conditions was studied in the range ($1x10^{-4}$ to $4x10^{-4}$ M) to the reaction mixture retarded the reaction rate. A plot of log k versus log [BTA] was straight line with a slope of -0.39 showing inverse fractional order.(Table 3, Figure 3, R^2=0.999).

Table 2 Effect of pH on the Reaction Rate λ_{max} = 610 nm; [CBT]o =0. 5 x 10^{-4} M; [IC]o = 10 x 10^{-5}M

pH	k x 10^4 (s^{-1})
8.0	1.06
8.5	3.39
9.0	8.66
9.5	15.77
10.0	28.55

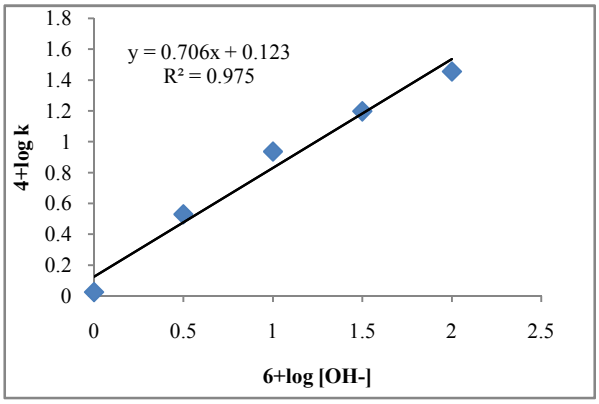


Figure 2

Table 3 Effect of varying Benzotriazole (BTA) Concentration on the Reaction Rate λ_{max} = 610 nm; [CBT]o =0. 5 x 10^{-4} M; [IC]o = 10 x 10^{-5}M pH 9.0;

[BTA] x 10^5 (M)	k x 10^4 (s^{-1})
0.0	8.66
10.0	8.365
20.0	6.38
30.0	5.43
40.0	4.48

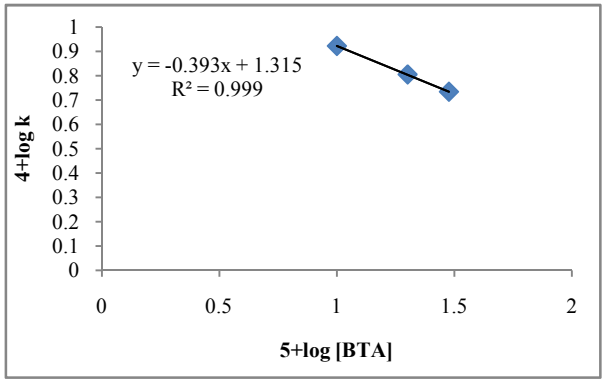


Figure 3

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 (0-30%) at pH 9 buffer medium. The rate decreased with an increase in MeOH content of the medium. The plot of log k versus 1/D gave a straight line with a negative slope. (Table 4, Figure 4, R^2=0.93).This effect is in conformity with the Amis concept of dipole-dipole interaction or dipole-ion interactions.[30]

Table 4 Effect of varying Methanol Concentration on the Reaction Rate λ_{max} = 610 nm; [CBT]o =0. 5 x 10^{-4} M; [IC]o = 10 x 10^{-5}M pH 9.0;

MeOH (%)	Dielectric Constant (D)	Kx10^4 (s^{-1})	1/D	4+log k
0	76.73	8.66	0.0130	0.937
10	72.37	8.52	0.0138	0.930
20	67.48	8.45	0.0148	0.926
30	62.71	8.38	0.0159	0.923

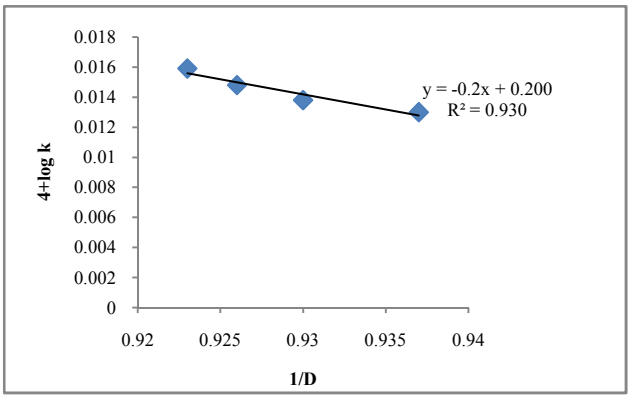


Figure 4

Effect of halide ion and ionic strength on the Reaction Rate

Addition of halide ion ($0.4x10^{-3}$ to $4x10^{-3}$ 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 $NaClO_4$ (0.001 to 0.1 mol dm-3) did not affect the rate.

Effect of temperature on the react ion rate

Kinetic runs were performed at various temperatures 297K to 313K while keeping other experimental conditions same.

Table 5 Temperature Dependence of the Reaction Rate and Activation Parameters for the Indigo Carmine Oxidation by 1-CBT. λ_{max} = 610 nm; [CBT]o = 0.5 x 10^{-4} M; [IC]o = 10 x 10^{-5}M pH 9.0;

Temperature (K)	k x 10^4 (s^{-1})	Activation Parameters
297	7.19	Ea : 39.85 kJmol^{-1}
301	8.66	$\triangle H^{\#}$: 37.34 kJmol^{-1}
305	9.59	$\triangle S^{\#}$: -179.32 JK^{-1}mol^{-1}
309	12.59	$\triangle G^{\#}$: 91.34 kJmol^{-1}
313	15.15	

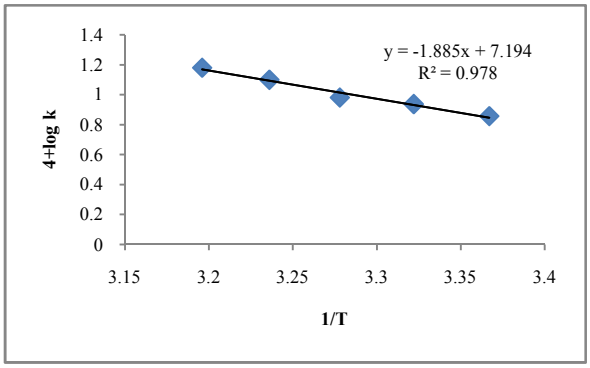


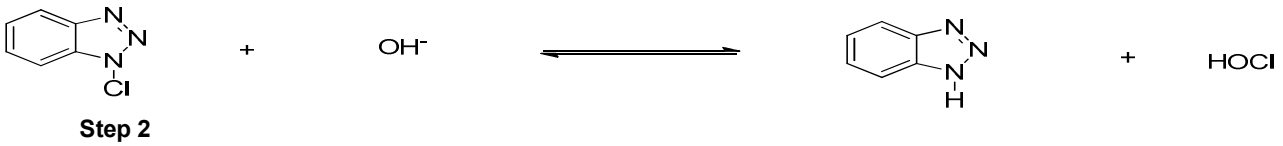
Figure 6

An Arrehenius plot of log k versus 1T (Table 5, R^2 =0.978) used to calculate the activation parameters, namely energy of activation (E_a), entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($H^{\#}$) and free energy of activation ($\Delta G^{\#}$). These results are shown in Table 5, Figure 5.

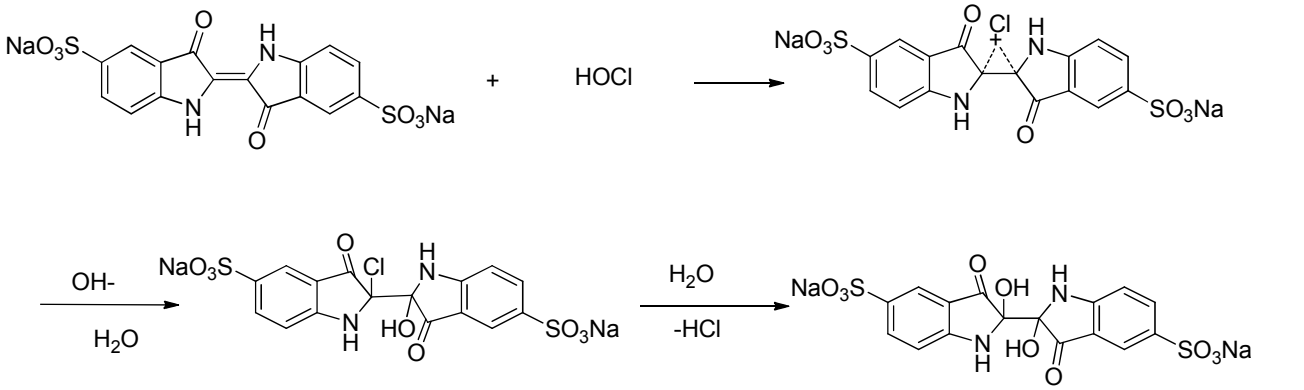
Mechanism

The proposed mechanism is give below.

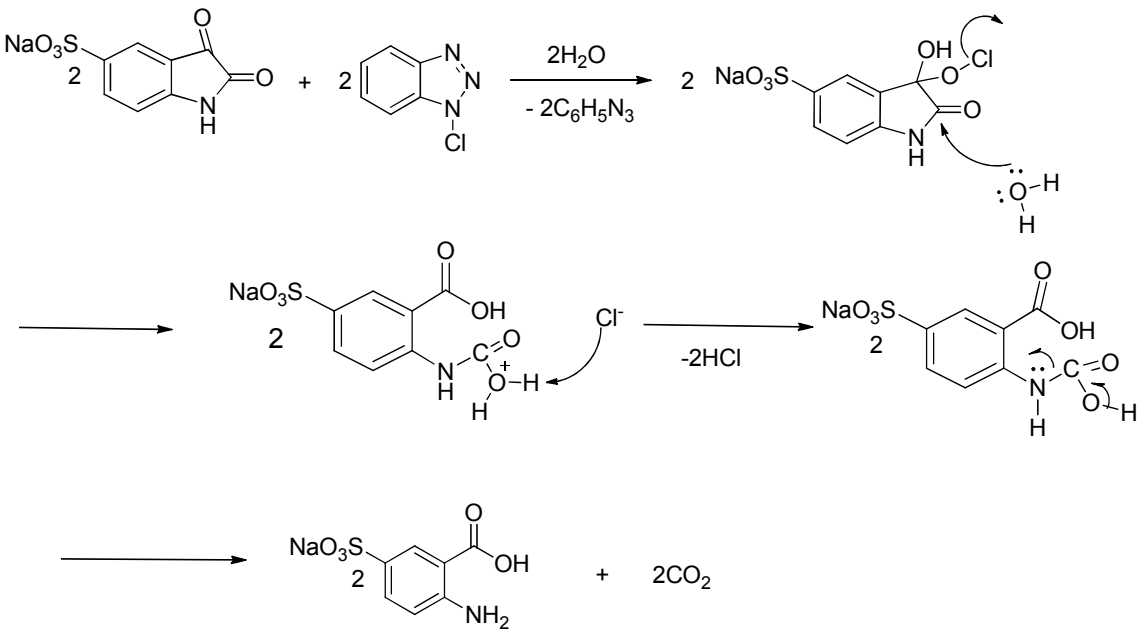
Step 1:



Step 2



Step 3:



Reaction Stoichiometry

Varying ratios of the oxidant (CBT) to IC in pH 9.0 buffer medium were equilibrated at 28^0 C for 12 hrs. Aliquots of the reaction mixture were idometrically titrated with a standard thiosulphate solution, using starch indicator, to determine the concentrations of unchanged CBT.

The mole ratio (number of moles of CBT consumed per mole of IC) was calculated. The results of IC reaction with CBT showed a definite stoichiometry of 1:4 (i.e four moles of the oxidant reacted with every mole IC) forming SAA and CO_2 as oxidation products and BTA and HCl as reduction products.

$$C_{16}H_8O_8S_2N_2Na_2 + 4C_6H_4N_3Cl + 6H_2O \longrightarrow 2C_7H_6O_5NSNa + 4C_6H_5N_3 + 2CO_2 + 4HCl$$

Table 6 IC decolorisation with time at 301 K in pH 9.0 [Reprentative Run] λ_{max} = 610 nm; [CBT]o = 0.5 x 10^{-4} M; [IC]o = 10 x 10^{-5}M and temp 301 K

Time (mins)	Absorbance	k x 10^4 (s^{-1})
0	0.543	
4	0.438	
8	0.346	
12	0.280	
16	0.229	
20	0.190	
24	0.160	
28	0.137	
32	0.121	
36	0.106	
40	0.094	**8.66**
44	0.084	
48	0.075	
52	0.068	
56	0.064	
60	0.053	

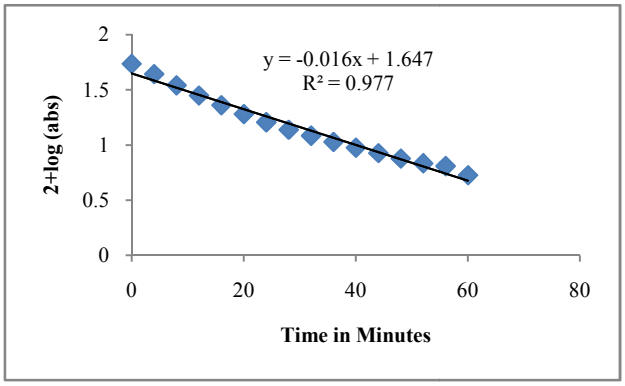
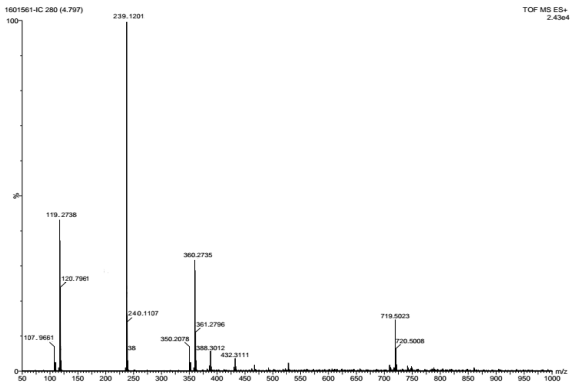


Figure 6

Product Analysis

The reduction product of CBT, benzotriazole (BTA) was isolated and identified by TLC using butanol-acetic acid-water (4:1:1) as solvent and iodine as the detecting agent (R_f=0.92).The obtained R_f value was consistent with literature value.[29]. The oxidation product of IC, sodium salt of sulphonated anthranilic acid (SAA) was analyzed.[31] Amounts of anthranilate present in the reaction mixture were quantitatively determined using a standard method involving its precipitation as zinc(II) salt $Zn(C_7H_5O_5NSNa)_2$.[31] The recovery of the anthranilate from several reaction mixtures in pH 9.0 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. The presence of oxidized product sodium salt of sulphonated anthranilic acid (SAA) and reduced product benzotriazole (BTA) were also confirmed by LC-MS.



The mass spectrum which showed a molecular ion peak 239 amu and 119 amu indicating the structure of SAA and BTA.

DISCUSSION

CBT being N-haloamine gives several oxidizing species in aqueous solution. The concentration of each species depends on the concentration of CBT, the nature (polar or non-polar) and pH of the medium. Benzotriazole (BTA), the parent compound of CBT, has pK_b 5.8 and hence it might largely exist in protonated form in an aqueous solution, [28]. The prominent species present in alkaline halomine solutions are RNCl(CBT), HOCl and OCl^- oxidizing speicies .One could expect appreciable concentrations of HOCl and OCl^- as oxidizing species .The retardation of the reaction rate by the presence of benzotriazole indirectly support the possibility of involvement of HOCl as an oxidizing species during the reaction. The following reaction mechanism appears plausible to account for the rate law.

A first order dependence on [CBT] (R^2 = 0.999) and fractional order dependence on $[OH^-]$ (R^2 = 0.975) and observed retardation of rate by BTA can be explained by the following mechanisms,

The total effective concentration of CBT can be written as
$[CBT]t = [BTA] + [HOCl] + [X]$

If only HOCl is reacting species we can wrire the following mechanism and rate law

Assuming $[CBT]t = [CBT] + [HOCl] + [X]$ …(1)

$$k_1 = \frac{[BTA][HOCl]}{[CBT][OH^-]} \quad ...(2)$$

$$[CBT] = \frac{[BTA][HOCl]]}{k_1\ [OH^-]} \quad …(3)$$

$$k_2 = \frac{[S][HOCl]}{[X]} \quad ...(4)$$

$$[HOCl] = \frac{[X]}{k_2[S]} \quad …(5)$$

Substitute [CBT] and [HOCl] in [CBT]t

$$[CBT]t = \frac{[BTA][HOCl]}{k_1[OH^-]} + \frac{[X]}{k_2[S]} + [X]$$

$$[CBT]t = \frac{[BTA][X]}{k_1[OH^-]k_2[S]} + \frac{[X]}{k_2[S]} + [X]$$

$$[CBT]t = [X]\left\{\frac{[BTA]+k1[OH^-]}{k_1[OH^-]k_2[S]} + 1\right\}$$

$$[X] = \frac{[CBT]t\, k_1[OH^-]k_2[S]}{k_1[OH^-]+[BTA]} + 1 \quad \ldots(6)$$

Substitute [X] in Rate=$k_3[X]$

$$\text{Rate} = -\frac{d[CBT]}{dt} = \frac{k_1\, k_2\, k_3\, [CBT]t[OH^-][S]}{k_1[OH^-]+[BTA]} + 1 \quad \ldots(7)$$

The rate laws (7) is in close agreement with the experimental results that is first order for [IC] and [CBT] and fractional order for $[OH^-]$ and inverse fractional order for [BTA].The addition of acrylamide to the reaction mixture had no effect on the reaction rate. This shows the absence of free radicals in the reacting system during oxidation. The change in the ionic strength of the medium during the oxidation reaction by using $NaClO_4$ did not alter the rate, indicating that non-ionic species involved in the rate determining step. A slight negative dielectric constant effect on the rate supports the fact that the dipole-dipole interaction in the rate determining step. The proposed mechanism is supported by the moderate values of energy of activation and other thermodynamic parameters. The fairly high positive values of free energy of activation and enthalpy of activation indicate that the transition state is highly solvated, while the high negative entropy of activation suggests the formation of compact activated complex with fewer degrees of freedom.

CONCLUSION

1-CBT is new oxidant. It is used as oxidizing agent for the oxidation of amino acids, carbohydrates, amines and amides.There were no reports on the oxidation of dyes with 1-CBT as oxidant. Here we reported the soft solution routes for decolorisation of indigocarmine dye with chlorobenzotriazole as oxidant in alkaline buffer medium.

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References

1. F.J. Green (Ed.), the Sigma Aldrich Handbook of Stains, Dyes and Indicators, Aldrich Chemical, Milwaukee, WI, 1990, p. 403.
2. M. Stolte, M. Vieth, Acta Endosc. 31 (2) (2001) 125.
3. C.F.I. Jabs, H.P. Drutz, R.L. Summit Jr., *Am. J. Obst. Gynecol*. 185 (6) (2001) 1368.
4. S. M oncada, R.M.J. Palmer, E.A. Higgs, Pharmacol. Rev. 43 (1991) 109.
5. Othman, R.M. Mohamed, F.M. Ibrahem. *Journal of Photochemistry and Photobiology A: Chemistry* 189 (2007) 80–85.
6. E. Curr. *Encyclopedia of Microscopic Stain,* Loenard Hall (Books) Ltd., London, 1960, p. 235.
7. E. H. Rodd, *Chemistry of Carbon Compounds,* Elsevier, Amsterdam, 1960, Volume IVB.
8. N. M. Made Gowda and D. S. Mahadevappa, *Curr. Sci.,* 44(21), 757 (1975); N. M. Made Gowda, V. M. S. Ramanujam, N. M. Trieff, G. J. Stanton, and D. S. Mahadevappa, *Microchem. J.,* 26, 95 (1981).
9. D. S. Mahadevappa, K. S. Rangappa, B. Thimme Gowda, and N. M. Made Gowda, *Microchem. J.,* 26, 132 (1981). 5. P. V. S. Rao, K. V. Subbaiah, and P. S. N. Murthy, *React. Kinet. Catal. Lett.,* 10, 79 (1979); 11, 287 (1979).
10. K. Srinivas, M. Vijayashree, and P. V. S. Rao, *Ind. J. Chem.,* 21A, 773 (1982).
11. S. P. Jonnalagadda, R. H. Simoyi, and G. K. Muthakia, *J. Chem. Soc. Perkin Trans. II,* 1111 (1988).
12. Puttaswamy, D. S. Mahadevappa, and K. S. Rangappa, *Bull. Chem. Soc. Jpn.,* 62, 3343 (1989).
13. Puttaswamy, D. S. Mahadevappa, and N. M. Made Gowda, *Int. J. Chem. Kinet.,* 23, 27 (1991).
14. S. Ananda, B. M. Venkatesha, and D. S. Mahadevappa, *Ind. J. Chem.,* 34B, 508 (1995).
15. B. M. Venkatesha, S. Ananda, D. S. Mahadevappa, and N. M. Made Gowda, *Int. J. Chem. Kinet.,* 27, 663 (1995)
16. S. Ananda, M. B. Jagadeesha, B. M. Venkatesha, N. M. Made gowda, *Int.J.Chem.Kinet,* 29-459 (1997).
17. Chandrashekar, R.T.Radhika, B.M.Venkatesh and S.Ananda, *Int.J.Cur.Res*. Vol.6,No.05,pp.6786 (2014).
18. R.C.Hiremath, S.M. Mayanna and N. Venkatasubramanian, J. Sci. Ind. Res. 49 122 (1990).
19. C.R. Johnson, C.C Bacon and W.D. Kingsbury, *Tetrahedron Lett.*, 501 (1978).
20. C. Channe Gowda and S. M. Mayanna - Tokmru, Vol. 38, No. 12, pp. 1427-1430, (1991).
21. R.C Hiremath, R V Jagadeesh, Puttaswamy and S.M Mayanna *J. Chem. Sci., Vol. 117, no. 4*, pp. 333–336 (2005).
22. Nanda, S. M Mayanna and N.M. M Gowda -, *Int. J. Chem. Kinet*, 31 153 (1990).
23. N. Nanda and S.M. Mayanna, *Oxid. Commun.* 22 107 (1990).
24. N.Nanda, B.S.Sheshadri and S.M. Mayanna, *React. Kinet. Catal.* 67 35 (1990)
25. C. Channe Gowda and S. M. Mayanna ,Tokmru Vol. 38, No. 12, pp. 1427-1430, (1991).
26. C.R. Johnson, C.C Bacon and W.D. Kingsbury, *Tetrahedron Lett.* 501 (1978).
27. V. Terry Hughes, D.Stephen. Hammond, and P. Michael Cava, *J. Org. Chem.* 63, 401-402 (1998).
28. N .S Srinivasan and Venkatasubramanian N - *Tetrahedron Lett.* 30 419 (1974)
29. R.C.Hiremath and S.M.Mayanna, *Mikrochim.Acta (Wein)* 11 175 (1984).
30. E.S.Amis-*Solvent effects on reaction rates and mechanism.* Van Nostrand reinhold New York, 257(1970)
31. A.I. Vogel., *Text book of Qualitative Inorganic Analysis,* 4th Edn, ELBS. London. 427 (1978)