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Degradation of Indigocarmine Dye by Oxidation using Chloramine-T in Acidic Buffer Medium Catalyzed by Vanadium(V) Ion: A Kinetic and Mechanistic Study

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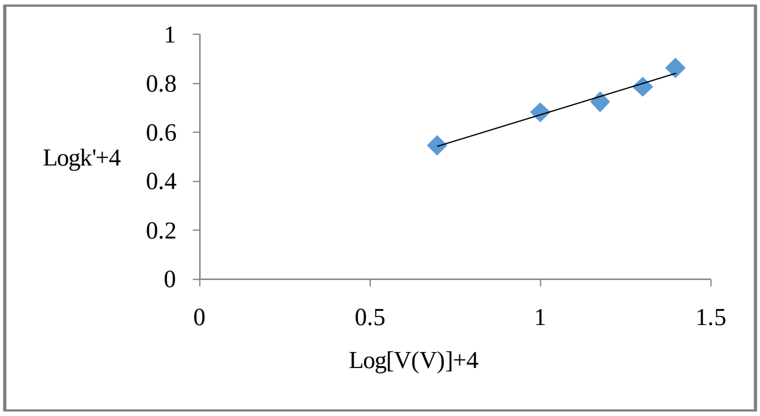
ABSTRACT

Today the advanced oxidation processes of treatment of industrial effluents and toxic organics has become a focus of attention among Material Scientists and Environmental Scientists. Several compounds have been reported as the potential candidates to resolve the environmental issues. In the present paper, the authors report the soft solution routes of advanced oxidation of dye material. Degradation of indigocarmine dye by oxidation process using chloramine-T as oxidant and V(V) as catalyst in acidic buffer media, pH 4.0 has been kinetically studied at 303K. Degradation of indigocarmine dye was followed by using spectrophotometric routes. Degradation and oxidation lead to a decrease in COD of the dye. V(V) catalyzed reaction shows first order dependence of the rate on chloramine-T and indigocaramine concentrations. It also shows fractional order dependence on [V(V)] and [H^+]. Addition of halide ions, reduction product of chloramine-T i.e. toluenesulfonamide, variation of ionic strength and dielectric constant of the medium do not have any significant effect on the reaction rate. Thermodynamic parameters have been evaluated from the Arrhenius plot. A kinetic mechanism is proposed for the reaction.

Graphical Abstract



Effect of catalyst [V(V)] on reaction rate.

Keywords: Degradation, Indigocarmine dye, Chloramine-T, Vanadium(V), Catalysis.

INTRODUCTION

Today the advanced oxidation processes of treatment of industrial effluents and toxic organics have become a focus of attention among Material scientists and Environmental scientists. Several compounds have been reported as the potential candidates to resolve the environmental issues. In the present paper, the authors report the soft solution routes of advanced oxidation of dye material. Indigocarmine (IC) is a dye which is used as a redox indicator in analytical chemistry and as a microscopic stain in Biology [1]. The chemistry of IC and its derivative has been reviewed by Rodd [2]. Although there are several analytical methods available for IC, compared to the studies on analytical aspects of IC, its kinetic investigations are less [3-5]. Several studies on the mechanistic aspects of oxidation of diverse organic substrate including IC by aromatic haloamines have been reported by us and others [6-11]. In the present article, we report the kinetics of degradation of indigocarmine dye by oxidation process using chloramine-T as oxidant and V(V) as catalyst in acidic buffer pH4.0 with a view to elucidate the mechanism of oxidation of dye in solution.

MATERIALS AND METHODS

CAT (E, Merck) was purified by the method of Morries *et al* [12]. An aqueous solution of chloramine-T was prepared and standardized by iodometric method. Indigocarmine and Vanadium(V) solution were freshly prepared using double distilled water. pH 4.0 buffer solutions were prepared by using acetic acid and sodium acetate. Ionic strength of the reaction mixture was kept at a high value using concentrated solution of $NaClO_4$.

Kinetic Procedure: Kinetic runs were performed under pseudo- first order conditions with large excess of the oxidant over IC at 303 K, using V(V) solution as catalyst. Requisite amounts of $NaClO_4$ (To maintain a constant ionic strength) and a buffer of known pH were mixed in a stoppered pyrex glass tube whose outer surfaces were coated black. The tube was thermostated in 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 reaction, degradation of IC dye was followed spectrophotometrically by measuring the absorbance at the λ_{max}= 610 nm. The pseudo-first order rate constants (k') calculated from these plots were reproducible within ±3%.

Reaction Stoichiometry: Varying ratios of oxidant to IC in presence of V(V) in pH 4.0 buffer were equilibrated at 303 K for 24 h. The unchanged chloramine-T in the reaction mixture was determined by iodometric titration. The analysis showed that one mole of IC reacted with four moles of chloramine-T, according to the following stoichiometry, forming sulphonated anthranilic acid.

$$C_{16}H_8O_8S_2N_2Na_2 + 4ArSO_2NCl^- + 6H_2O \rightarrow 2C_7H_6O_5NSNa + 2CO_2 + 4ArSO_2NH_2 + 4Cl^- + 4H^+$$

RESULTS AND DISCUSSION

The reaction was performed in the acidic buffer solution under pseudo first order condition of [CAT] >> [IC] at constant [CAT], [V(V)], pH and temperature. The plots of $\log D_0/D_t$ versus time were linear indicating a first order dependence of reaction rate on [IC]. D_t is the absorbance of the reaction mixture at time interval t. The pseudo first order rate constants k' obtained at 303 K were independent of $[IC]_o$ (Table 1), further confirming the first order dependence on$[IC]_o$. Under the same experimental conditions an increase in [CAT] increased the k' values (Table 1). Plot of log k' versus log[CAT] (Figure 1) was linear with unit slope showing first order dependence of rate on [CAT]. The reaction rate increases with the increase in concentration of Vanadium (V) (Table 2) and plot of log k' versus log [V(V)] was linear with slope~0.44 (Figure 3) showing fractional order dependence on [V(V)]. As the [H^+] increases the rate also increases, i.e. The decrease of buffer pH increases the rate of reaction (Table 2). A plot of log k' versus log [H^+] gives straight line with a fractional slope(~ 0.42) (Figure 2) indicating that the rate of oxidation of IC is of fractional order with respect to [H^+] .Addition of reaction product toluene sulphonamide has no effect on the reaction rate. Addition of Cl^- ion, variation of ionic strength of the medium and variation of dielectric constant have no effect on the rate of reaction. Addition of reaction mixture to aqueous acryl amide did not initiate polymerization showing the absence of free radical species. The reaction was studied at varying temperature 298 K to 313 K. From the linear plot of log k' versus 1/T, activation parameter were computed (Table 3).

Table 1. Effect of varying the reactants concentration on the reaction rate:
[V(V)] = $1.5x10^{-3}$mol dm^{-3}, µ = 0.2 M, Temp.= 300K and pH=4.0

[CAT] x 10^4 mol dm^{-3}	[IC] x 10^5 mol dm^{-3}	k' x 10^4 S^{-1}
2.0	5.0	5.12
2.0	10.0	5.30
2.0	15.0	5.06
2.0	20.0	5.18
2.0	25.0	5.16
1.0	10.0	2.69
1.5	10.0	3.61
2.5	10.0	6.39
3.0	10.0	8.00
3.5	10.0	10.19

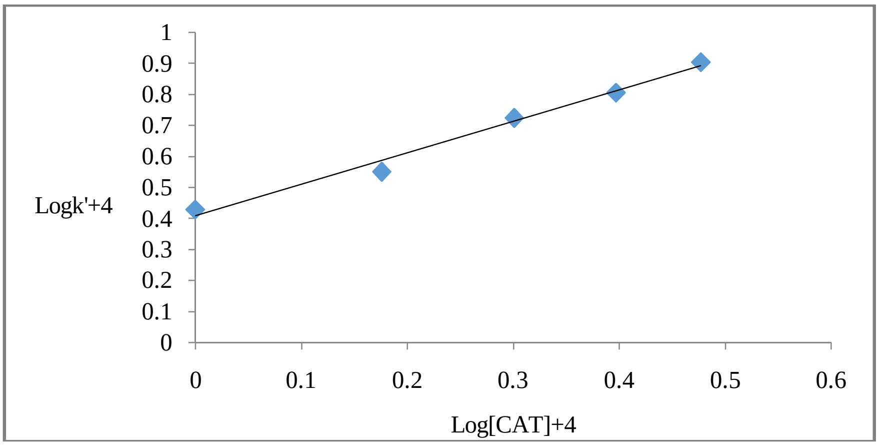


Figure 1. A plot of logk' vs log[CAT] :[IC] = 10.0 x 10^{-5} mol dm^{-3}[V(V)] = $1.5x10^{-3}$mol dm^{-3}, µ = 0.2 M, Temp.= 300K and pH=4.0

Table 2. Effect of varying the concentration of Vanadium(V) ion and pH on the rate of reaction:
[CAT]= 2.0 x 10^{-4} mol dm^{-3}, [IC] = 10.0 x 10^{-5} mol dm^{-3}, µ = 0.2 M, Temp.= 300K

pH	V(V) x 10^4 mol dm^{-3}	k' x 10^4 s^{-1}
3.7	15	7.1
3.8	15	6.2
4.0	15	5.3
4.2	15	4.5
4.4	15	3.8
4.0	5	3.5
4.0	10	4.8
4.0	20	5.3
4.0	25	6.1

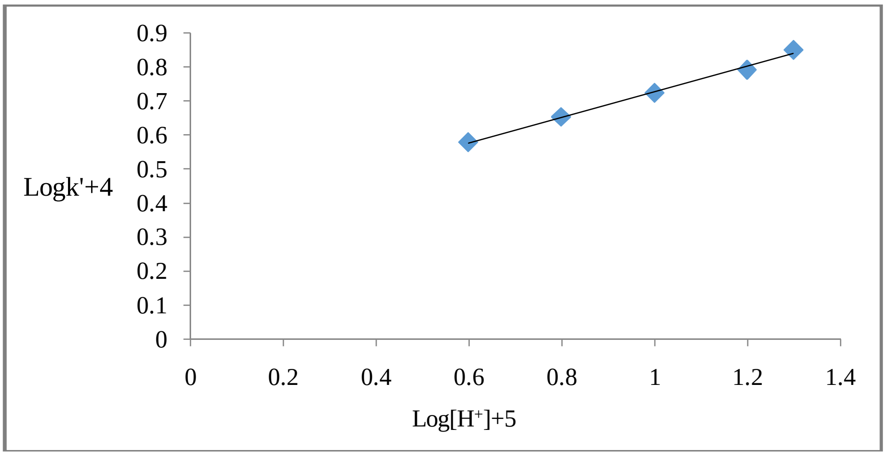


Figure 2. A plot of logk' vs log[H^+] : [CAT]= 2.0 x 10^{-4} [IC] = 10.0 x 10^{-5} mol dm^{-3} [V(V)] = 1.5x10^{-3}mol dm^{-3}, µ = 0.2 M, Temp.= 300K and pH=4.0

Chloramine-T which behaves as a strong electrolyte [13, 14] dissociates in aqueous solutions to furnish an anion $ArSO_2NCl^-$ this anion undergoes protonation in acid medium to form free acid $ArSO_2NHCl$.Although the free acid has not been isolated , the conductometric studies of CAT have provided ample evidence of its formation[15]. In acid medium free acid undergoes a reaction to form dichloramie-T ($ArSO_2NCl_2$) and p-toluenesulfonamide ($ArSO2NH_2$). $ArSO_2NHCl$ hydrolyses to HOBr as one of the product. Several equilibria exist in acidic conditions.

$$ArSO_2NClNa \rightleftharpoons ArSO_2NCl^- + Na^+ \quad ...(1)$$

$$ArSO_2NCl^- + H^+ \rightleftharpoons ArSO_2NHCl \quad ...(2)$$

$$2ArSO_2NHCl \rightleftharpoons ArSO_2NCl_2 + ArSO_2NH_2 \quad ...(3)$$

$$ArSO_2NCl_2 + H_2O \rightleftharpoons ArSO_2NHCl + HOCl \quad ...(4)$$

$$ArSO_2NHCl + H_2O \rightleftharpoons ArSO_2NH_2 + HOCl \quad ...(5)$$

The possible reactive species in the acidified CAT solution are therefore $ArSO_2NHCl$, $ArSO_2NCl_2$ and HOCl. The involvement of $ArSO_2NCl_2$ in the mechanism leads to a second order rate law, which is contrary to the experimental observations, as equation (3) indicates.

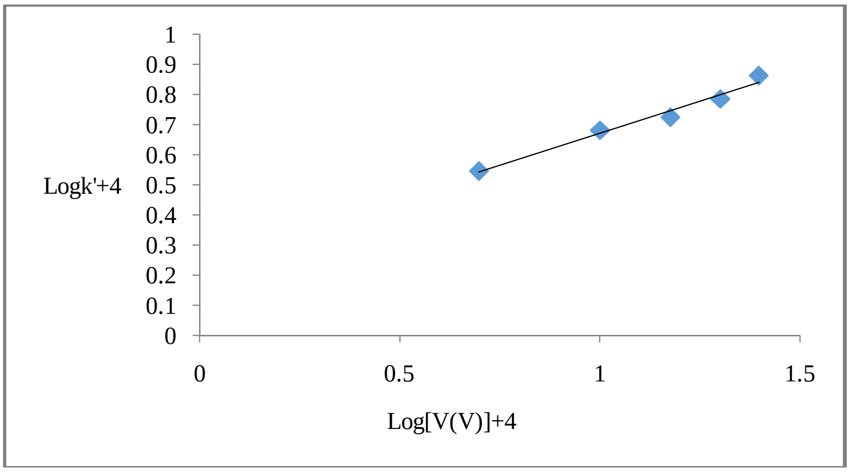


Figure 3. Effect of catalyst [V(V)] on reaction rate.

If a slow hydrolysis of $ArSO_2NHCl$ occured as in equation (4) leading to HOBr as the primary oxidising species, a first order retardation of the rate by the added $ArSO_2NH_2$ would be expected. This is contrary to the experimental results. In the present study of IC oxidation, the reaction shows first order on [CAT] and reaction rate shows dependence of the first order on [IC]. It is observed that a fractional order (~ 0.42) on $[H^+]$. Further fractional order (~ 0.44) on catalyst [V(V)] is observed which shows that $ArSO_2NHCl$ is the likely oxidizing species. Based on the preceding discussion and from the results, the following kinetic scheme is proposed to account for the experimental observations.

$$ArSO_2NCl^- + H^+ \overset{K_1}{\rightleftharpoons} ArSO_2NHCl \qquad \text{… i}$$

$$ArSO_2NHCl + V(V) \overset{K_2}{\rightleftharpoons} X \qquad \text{... ii}$$

$$X + IC \xrightarrow{k_3} X' \qquad \text{Slow Step} \qquad \text{…ii}$$

$$X' \xrightarrow{k_4} \text{Products} \qquad \text{... iv}$$

Kinetic Scheme

From the slow step of the kinetic scheme Rate= $k_3[IC][X]$ … 6

As proposed kinetic scheme $[CAT]_t = [ArSO_2NCl^-]+[ArSO_2NHCl]+[X]$ …7

$$\text{From step i } K_1 = \frac{[ArSO_2NHCl]}{[ArSO_2NCl^-][H^+]} \qquad \text{… 8}$$

$$\text{From step ii } [ArSO_2NHCl] = \frac{[X]}{K_2[V(V)]} \qquad \text{… 9}$$

From equation 8, we get

$$[ArSO_2NCl^-] = \frac{[ArSO_2NHCl]}{K_1[H^+]} \qquad \text{...10}$$

Therefore,

$$[ArSO_2NCl^-] = \frac{1}{K_1[H^+]}\frac{[X]}{K_2[V(V)]}. \qquad \text{…11}$$

Substituting equations 9 & 11 in equation 7

$$[CAT]_t = \frac{[X]}{K_1K_2[H^+][V(V)]} + \frac{[X]}{K_2[V(V)]} + [X] \qquad \text{…12}$$

Therefore,

$$[X] = \frac{K_1K_2[H^+][V(V)][CAT]t}{1+K_1[H^+]+K_1K_2[H^+][V(V)]} \qquad \text{…13}$$

Substituting [X] in rate equation 6 leads to Rate law,

$$\text{Rate} = \frac{K_1K_2k_3[IC][H^+][V(V)][CAT]t}{1+K_1[H^+]+K_1K_2[H^+][V(V)]} \qquad \text{…14}$$

The rate law equation is in very good agreement with the experimental results, which includes first order in [IC], first order in [CAT] , fractional order on [H^+] and fractional order on V(V) catalyst. The thermodynamic parameters are obtained and energy of activation (Ea) for the V(V) catalyzed reaction is slightly less than that of the energy of activation in absence of catalyst in the previous work carried out in our laboratory. The moderate value of enthalpy of activation ($\Delta H^{\#}$) is supportive of the proposed mechanism in kinetic scheme. The highly negative entropy of activation ($\Delta S^{\#}$) indicates the formation of rigid transition state by an associative process.

Table 3. Temperature dependence and activation parameters for the Oxidation of IC by CAT in presence of V(V) at pH = 4.0

Temp. (K)	$k^1 \times 10^3$	Thermodynamic Parameters
298	4.76	Ea = 46.69KJ mol^{-1}
303	5.34	$\Delta H^{\#}$ = 44.14 KJ mol^{-1}
308	6.37	$\Delta S^{\#}$ = -85.30 JK^{-1} mol^{-1}
313	10.63	$\Delta G^{\#}$ =70.76 KJ mol^{-1}

APPLICATION

This method advanced catalyzed oxidation process can be used for waste water treatment and purification of industrial effluents and toxic organics.

CONCLUSION

In recent days, 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 reports soft solution routes for degradation of indigocarmine dye by oxidation process using chloramine-T as oxidant and Co(II) as catalyst. The oxidation or degradation of indigocarmine is fast compared with without catalyst. The results of this paper suggest the possibility of degradation of dyes by oxidation process using the eco friendly oxidizing agent chloramine-T in industry.

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