

KINETIC STUDY OF OXIDATIVE DEGRADATION OF A XANTHENE DYE ERYTHROSINE B BY CHLORAMINE-T IN ACID MEDIUM : A SPECTROPHOTOMETRIC APPROACH

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Abstract : Kinetic investigation of oxidative degradation of Erythrosine B (EB) a xanthene dye by chloramine - T (CAT) in acid medium was studied spectrophotometrically. The effect of variation of concentrations of the dye EB, oxidant CAT and HCl was studied at 298K. The reaction shows first order dependence on the both dye EB and the oxidant CAT. At the same time the reaction shows fractional order dependence on $[H^+]$. Halide ions, $NaClO_4$ and PTS shown negligible effect on rate of the reaction. The impact of variation of temperature on the rate of reaction was studied and various activation parameters were computed accordingly. The effect of dielectric constant on the rate was also investigated. A rate equation was derived and a plausible mechanism for the oxidation of EB dye by CAT was deduced.

Key Words- Erythrosine B, Xanthene dye, CAT, HCl, Oxidative degradation.

I. INTRODUCTION

Erythrosine B (EB) is an important and well known xanthene dye. It is the disodium salt of 2, 4, 5, 7-tetraiodofluorescein. EB is extensively used as a coloring variety of foods like sweets creams, dragees coatings, ice cream, cake-decorating gels, sausages, meat etc. EB is also used in cosmetic and pharmaceutical industry pills coverage, syrups, toothpaste, lipstick, make up products, bath and shower products, hair-care products and conditioners, shampoos, deodorants etc. It is used in most of the countries of the world despite its toxic and carcinogenic effects against animals and humans. Few studies indicated that high doses of EB can cause cancer in rats, in particular thyroid tumor formation. Other effects are associated with bronchoconstriction, sequential vascular response, elevation of protein-bound iodide, and chromosomal damage. Due to its hazardous nature, it is partially banned in USA.

Various efforts have been made to remove EB from waste water considering its health hazards. Mainly adsorption and photocatalytic degradation methods [1-11] have been reported for the removal of EB from waste water. Literature survey revealed that no efforts were made to degrade or decolourise EB through oxidation by Chloramine - T. Therefore, in the present study, we are reporting an oxidative degradation of EB by CAT in acid medium.

The chemistry of aromatic sulfonyl haloamines, commonly known as N-haloamines, is a topic of huge interest. This is because to their capability to act as sources of both halonium cations and N - anions they can act as both bases and nucleophiles. These N - haloamines behave as mild oxidants and they interact with a variety of functional groups in an aqueous, partially aqueous and non- aqueous media in the presence of either an acid or an alkali[12-18]. Sodium N-chloro-p-toluenesulfonamide, commonly known as Chloramine - T (CAT), is the most important member of this group of N- haloamines. Chloramine - T has been used as an oxidant for number of substrates in both acidic and alkaline medium as it acts as a source of positive halogen. Usually, Chloramine -T shows two electron change in its reactions forming the products P- toluenesulfonamide and sodium chloride[19]. The redox potential of Chloramine - T is pH dependent and it decreases with increase in pH of the medium[20-21]. The kind and property of the active oxidising species of Chloramine -T is dependent on the reaction conditions and also on the pH of the medium[22]. In addition to above facts, Chloramine - T is easily available, non-toxic, water soluble and easy to handle.

II. MATERIALS AND METHODS

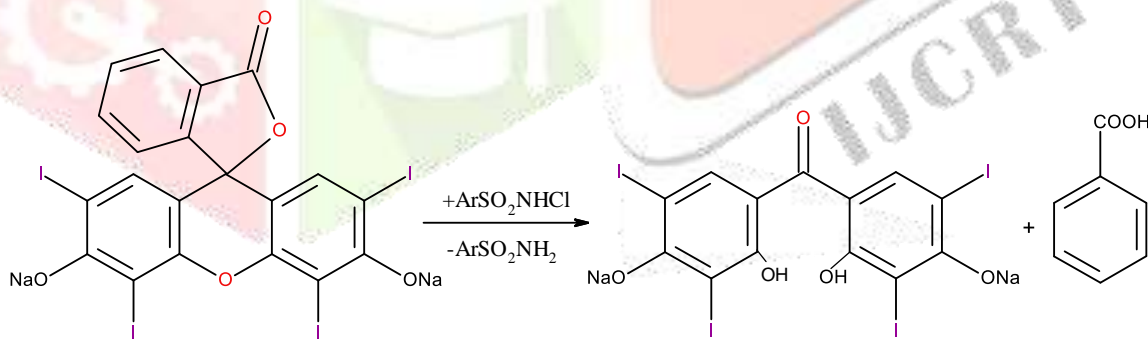
CAT (Merck) was purified using the method given by Morris et al [21]. The stock solution of CAT with required concentration was freshly prepared by dissolving in water, standardized iodometrically and kept in brown bottles to prevent any photochemical degradation. EB (TCI chemicals) was used as received. Aqueous solution of EB was freshly prepared before the mechanistic investigation process. All other chemicals used were of analytical grade and procured from sd fine chemicals. All other chemical solutions were prepared by using doubly distilled water.

III. KINETIC PROCEDURE

Kinetic reactions of oxidation of EB dye by CAT in HCl medium was studied under pseudo first-order conditions by taking excess of $[\text{oxidant}]_0$ over $[\text{EB}]_0$ at a fixed concentration of HCl at 298K. Kinetic reactions were conducted using a UV-visible spectrophotometer (Chemito UV - 2100 Spectrophotometer). Kinetic runs were conducted in the temperature range of 300K to 316K in this present study. For all the kinetic runs, a constant temperature with an accuracy of $\pm 0.1\text{K}$ was maintained using Raaga Ultra Cold chamber with digital temperature control. Glass stoppered Pyrex boiling tubes (these are coated with black colour on outer surface to rule out any photochemical effect) were used to carry out the kinetic reactions. The accurately calculated amounts of CAT, EB dye, HCl solutions and water (it is to maintain the constant total volume of the reaction mixture for all the runs) were filled in separate tubes and thermostated at 298K for 30 minutes. By rapidly pipetting out a required amount of CAT into the reaction mixture containing the substrate(EB) in the HCl medium, the oxidation process of the substrate (EB) was commenced. 3ml of the above reaction mixture was immediately pipetted out into a cuvette placed in spectrophotometer. The kinetic procedure was observed and followed upto two half lives. The absorbance values at $t = 0$ (D_0) and $t = t$ (D_t) were recorded to obtain plots of $\log(D_0/D_t)$ versus time. Pseudo-first-order rate constants(k) were evaluated from the above plots which were proven to be reproducible within $\pm 5\%$. Regression analysis of the experimental data was done using a $f_x - 100\text{W}$ calculator which is used to evaluate the regression coefficient, r .

1. Reaction Stoichiometry

Various ratios of CAT to EB dye were taken in the presence of 2×10^{-4} mol dm⁻³ of HCl and were equilibrated at 300K for 48 hours. The CAT which left unreacted was determined by iodometric titration. This clearly showed that, CAT and EB reacted with each in the ratio 1:1. The below scheme shows the observed reaction stoichiometry of the reaction.



Scheme 1 : Reaction scheme of Oxidation of EB Dye by Chloramine-T

2. Product Analysis

The calculated amounts of EB, CAT and HCl were mixed in the stoichiometric ratio and kept for 48 hours at 300K to undergo complete reaction. Once the reaction was completed, the products were neutralized and extracted with NaOH and ether respectively. Thin layer chromatography was used to monitor the completion of reaction. The formation of oxidation products was also revealed by thin layer chromatography. The products were identified as disodium salt of 6,6'-dihydroxy-3,3,5,5'-tetraiodobenzophenone and benzoic acid. LC-MS analysis confirmed the oxidation products. It was also noted that, there was no reaction between products of oxidation and CAT under the given experimental conditions.

P-toluenesulfonamide (PTS), the reduction product of chloramine-T was detected and confirmed by paper chromatography and LC-MS analysis respectively.

3. Results and discussion

A UV-visible spectra of the reaction mixture (mixture of EB, CAT and HCl at required stoichiometric ratio) were recorded at different time intervals. The spectra in the figure 1 clearly shows the oxidative decolourization of the dye EB. It is clear from the spectra that 60% decolourization of the dye is over in 60 minutes and 100% decolourization of the dye is noticed in 24 hours.

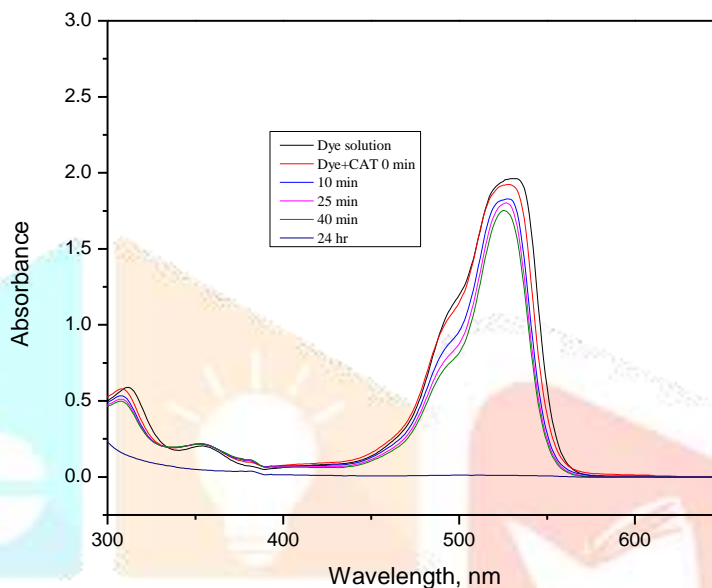


Figure 1. UV-visible spectra of oxidative decolourisation of EB by CAT

3.1 Effect of Variation of Concentration of EB Dye on the Reaction Rate

The oxidation of EB by CAT (hereafter abridged as oxidant) was kinetically studied at various concentrations of reactant (EB) under pseudo first-order conditions of $[\text{oxidant}]_0 \gg [\text{EB}]_0$, in HCl medium at 298K. Under the conditions of $[\text{oxidant}]_0 \gg [\text{MY}]_0$, at constant $[\text{CAT}]_0$, HCl and temperature, linear ($r > 0.9965$) plots of $\log(\text{Abs})$ vs time were indicating first-order dependence of rate on $[\text{EB}]_0$. The values of pseudo first-order rate constants ($k^1 \text{ s}^{-1}$) are shown in Table I which reveals that they are independent of $[\text{EB}]_0$, indicating the first-order dependence on $[\text{EB}]_0$.

Table 1. Effect of varying concentration of dye on the rate of oxidation at 300K

$[\text{CAT}] = 1.6 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{HCl}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$

| $10^5 [\text{EB}]$ mol dm^{-3} | $10^4 k^1 (\text{s}^{-1})$ |
|--|----------------------------|
| 2 | 5.01 |
| 3 | 4.92 |
| 4 | 5.13 |
| 5 | 5.29 |
| 6 | 4.98 |

3.2 Effect of Variation of Concentration of Oxidant on the Reaction Rate.

It was seen that, there was an increase in the rate of reaction with increase in [oxidant]. A straight line ($r > 0.9986$) with a slope of unity on plotting of $\log k^1$ versus $\log[\text{oxidant}]$ indicating a first-order reaction with respect to [oxidant]. A linear plot of k^1 versus $\log[\text{oxidant}]$ was linear passing through the origin ($r > 0.9817$) further substantiates the first-order dependence of rate with respect to [oxidant].

Table 2. Effect of varying [CAT]₀ on the rate of oxidation at 300K
[EB] = 4×10^{-5} mol dm⁻³ and [HCl] = 2×10^{-4} mol dm⁻³

| $10^3[\text{CAT}]$ mol dm ⁻³ | $10^4 k^1$ (s ⁻¹) | 4+logk' |
|--|-------------------------------|---------|
| 0.8 | 2.66 | 0.424 |
| 1.2 | 3.97 | 0.599 |
| 1.6 | 5.13 | 0.710 |
| 2.0 | 6.92 | 0.84 |
| 2.5 | 8.79 | 0.944 |
| 3.5 | 12.35 | 1.091 |

$$\text{Order} = 1.05 \quad R^2 = 0.9972$$

3.3 Effect of Variation of HCl Concentration on the Reaction Rate

An increase in the rate with increase in [HCl] was observed as shown in **Table 1**. A linear ($r > 0.9976$) plot of $\log k^1$ versus $\log [\text{HCl}]$ with a slope equal to 0.6 unity clearly reveals a fractional-order dependence on [HCl].

Table 3. Effect of varying concentration of HCl on the rate of oxidation at 300K
[CAT] = 1.6×10^{-3} mol dm⁻³ and [EB] = 4×10^{-5} mol dm⁻³

| $10^4[\text{HCl}]$ mol dm ⁻³ | $10^4 k^1$ (s ⁻¹) | 4+logk' |
|--|-------------------------------|---------|
| 1.0 | 3.52 | 0.546 |
| 1.5 | 4.21 | 0.624 |
| 2.0 | 5.13 | 0.710 |
| 3.0 | 6.68 | 0.825 |
| 4.0 | 7.91 | 0.898 |

$$\text{Order} = 0.6 \quad R^2 = 0.993$$

3.4 Effect of Variation of Halide ion Concentration on reaction rate

Chloride and Bromide ions (from 1.0×10^{-3} to 5.0×10^{-3} mol dm⁻³) in the form of their sodium salt solutions were added to the reaction mixture. Effect of the halide ions on the reaction rate was studied by increasing in concentration of halide ions during the kinetic runs by keeping other parameters constant. There was no impact observed on the reaction rate ruling by increase in concentrations of halide ions which rules out any of their role in the rate-determining step.

3.5 Effect of Ionic Strength on the Reaction Rate

Concentration of NaClO_4 was varied from 0.1 to 0.4 mol dm^{-3} while keeping other experimental conditions constant to investigate the impact of variation of ionic strength of the medium on the rate of reaction. But no change in the reaction rate was observed on changing the concentration of NaClO_4 indicating the negligible effect of variation of ionic strength on the reaction rate. This reveals that the non-ionic species are involved in the rate-determining step of the reaction. Hence, there was no need to maintain a constant ionic strength of the medium during the kinetic runs.

3.6 Effect of Variation of PTS Concentration on the Reaction Rate

Reduction product PTS (P-toluenesulphonamide) was added to the reaction mixture in the range of 1.0×10^{-4} to 6.0×10^{-4} by keeping other parameters constant. But the addition of PTS did not show any significant effect on the reaction rate as shown in table II. Therefore it is cleared that, PTS was not involved in the rate-limiting step of the reaction.

3.7 Effect of Variation of Dielectric Constant of the Medium on the Reaction Rate

MeOH was added to the reaction mixture in the range of (0-40 % v/v) to vary dielectric constant (D) of the medium while keeping other experimental conditions constant at 298K. Reaction rate was found to be decreased on increasing the value of dielectric constant of the medium as shown in the table 2. The values of dielectric constant of MeOH- H_2O mixtures were taken from the literature[23].

Table 4. Effect of varying dielectric constant on the reaction rate at 300K.

[CAT] = 1.6×10^{-3} mol dm^{-3} , [EB] = 4×10^{-5} mol dm^{-3} and [HCl] = 2×10^{-4} mol dm^{-3}

| Methanol (%) | Dielectric constant (D) | 1/D | $10^4 k^1 (\text{s}^{-1})$ | 5+logk' |
|--------------|-------------------------|--------|----------------------------|---------|
| 0 | 76.73 | 0.0130 | 5.13 | 1.71 |
| 10 | 72.37 | 0.0138 | 3.46 | 1.539 |
| 20 | 67.48 | 0.0148 | 2.51 | 1.399 |
| 30 | 62.71 | 0.0159 | 1.62 | 1.209 |
| 40 | 58.06 | 0.0172 | 0.91 | 0.959 |

$$R^2 = 0.996$$

3.8 Effect of Variation of Temperature on the Reaction Rate

Temperature was varied from 300K to 316K by keeping other parameters constant for the kinetic runs to study the impact of temperature variation on reaction rate. Arrhenius plots of $\log k^1$ versus $1/T$ ($r > 0.9988$) are shown in figure 2. From these plots, the values of composite activation parameters (E_a , ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger and $\log A$) were obtained for the oxidation of EB by CAT. The obtained data are summarized in Table 6

Table 5. Effect of Temperature on the Reaction Rate.

[CAT] = 1.6×10^{-3} mol dm^{-3} , [EB] = 4×10^{-5} mol dm^{-3} and [HCl] = 2×10^{-4} mol dm^{-3}

| Temperature (K) | $10^3(1/T)$ | $10^4 k^1(\text{s}^{-1})$ | 4+logk ¹ |
|-----------------|-------------|---------------------------|---------------------|
|-----------------|-------------|---------------------------|---------------------|

| | | | |
|-----|------|-------|-------|
| 300 | 3.33 | 5.13 | 0.710 |
| 304 | 3.29 | 6.47 | 0.811 |
| 308 | 3.25 | 8.01 | 0.904 |
| 312 | 3.21 | 9.92 | 0.997 |
| 316 | 3.16 | 12.56 | 1.098 |

$$R^2 = 0.9976$$

$$\text{Slope} = -2286.2$$

Table 6. Activation parameters for the oxidation of EB by Chloramine-T

| Ea (kJ mol ⁻¹) | ΔH^\ddagger (kJ mol ⁻¹) | ΔG^\ddagger (kJ mol ⁻¹) | ΔS^\ddagger (J K ⁻¹ mol ⁻¹) | Log A |
|----------------------------|---|---|--|---------------|
| 54.859 | 52.267±(0.05) | 96.066±(0.6) | -140.75±(0.3) | 44.28±(0.015) |

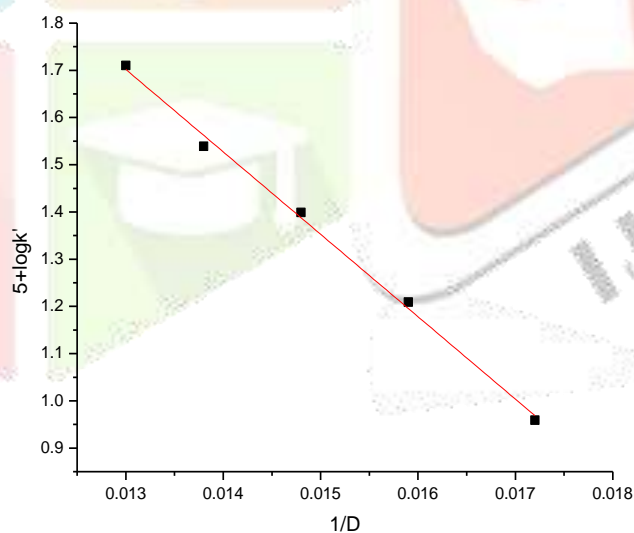


Fig 2. Plot of logk' vs 1/D

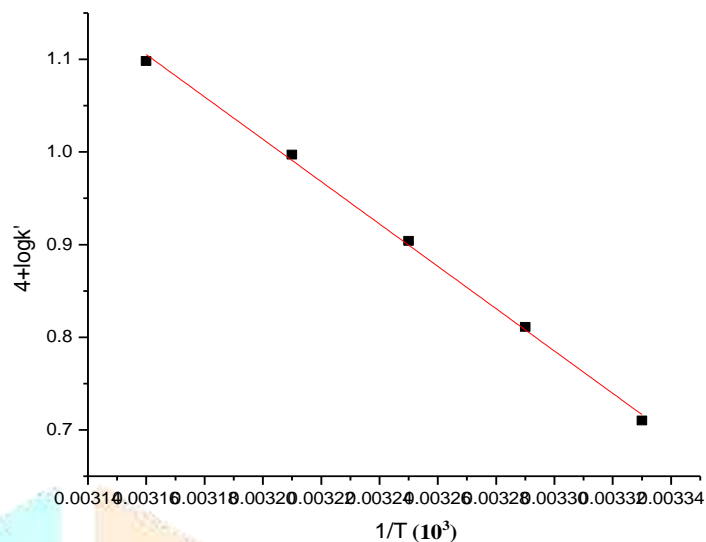
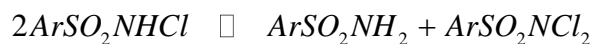
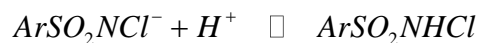


Fig 3. Plot of $\log k'$ vs $1/T$

3.9 Discussion

Reactive Species of Chloramine-T

Chloramine-T shows its oxidising behaviour in both acidic and alkaline media[22]. It usually undergoes two electron change producing the reduction product PTS (TsNH_2) and sodium chloride[23]. pH of the medium controls the potential of CAT-PTS redox couple. The potential is 1.138 V, 1.778 V, 0.614 V and 0.5 V at pH 0.65, pH7.0, pH9.7 and pH 12 respectively[27]. Chloramine-T shows a strong electrolytic nature and produces variety of reactive species in the solution depending on pH of the medium[27]. Depending on pH of the medium, Chloramine-T produces various reactive species as shown in the reaction scheme 2. ($\text{ArSO}_2 - \text{CH}_3\text{C}_6\text{H}_5\text{SO}_2$)

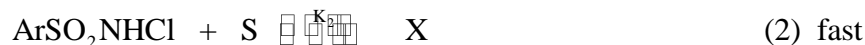


Scheme 2: Reactive Species of Chloramine-T.

The pH of the medium in a reaction decides the particular species responsible for oxidizing property of chloramine-T. In acidic condition, the species accountable for oxidation of substrate are the conjugate free acid (ArSO_2NHCl), dichloramine-T ($\text{ArSO}_2\text{NCl}_2$), hypochlorous acid (HOCl) and possibly H_2OCl^+ . Further, formation of the species like $\text{ArSO}_2\text{NH}_2\text{Cl}^+$ has been reported.

If $\text{ArSO}_2\text{NCl}_2$ and HOCl were to be the reactive species, then the reaction rate would follow second-order dependence on $[\text{oxidant}]_0$ and first-order retardation on adding $[\text{ArSO}_2\text{NH}_2]$. But, the experimental observations are against to these expectations.

Bishop and Jennings[24] in their studies on aqueous solutions of CAT shown that, at $\text{pH} > 3$, the concentration of $\text{ArSO}_2\text{N}^-\text{Cl}$ is more than that of free acid. Thus, one can assume the protonation equilibrium including the anion in aqueous acidic solution. In the present investigation, increase in rate of reaction by H^+ hints at ArSO_2NHCl as the most probable reactive species.



Scheme 3: The Reaction Scheme for Oxidation of EB by Chloramine-T in HCl Medium.

In the first step, the anion $\text{ArSO}_2\text{N}^-\text{Cl}$ picks up a proton to give the free acid as shown in equation (2.1). The resulting free acid attacks the substrate (EB) producing an intermediate complex (X) as shown in equation (2.2). This is the slow and the rate determining step. In the last step, the intermediate complex (X) undergoes hydrolysis forming the products.

From the rate limiting step of scheme 3, if $[\text{CAT}]_t$ is the total effective concentration of CAT, then

$$[\text{CAT}]_t = [\text{ArSO}_2\text{N}^-\text{Cl}] + [\text{ArSO}_2\text{NHCl}] \quad (4)$$

From equation (2.1),

$$[\text{ArSO}_2\text{N}^-\text{Cl}] = \frac{[\text{ArSO}_2\text{NHCl}]}{K_1[\text{H}^+]} \quad (5)$$

From equation (2.1) and (2.2) of scheme 3 ,

$$K_1 = \frac{[\text{ArSO}_2\text{NHCl}]}{[\text{ArSO}_2\text{N}^-\text{Cl}][\text{H}^+]} \quad (6)$$

$$K_2 = \frac{[\text{X}]}{[\text{ArSO}_2\text{NHCl}][\text{S}]} \quad (7)$$

Rearranging equation (2.6) and substituting for $[\text{ArSO}_2\text{N}^-\text{Cl}]$ from equation (2.7), we get

$$[\text{ArSO}_2\text{N}^-\text{Cl}] = \frac{[\text{X}]}{K_1 K_2 [\text{S}][\text{H}^+]} \quad (8)$$

Substituting for $[\text{ArSO}_2\text{NHCl}]$ and $[\text{ArSO}_2\text{N}^-\text{Cl}]$ from equation (2.7) and (2.8) in equation (2.4) ,

$$[\text{CAT}]_t = \frac{[\text{X}]}{K_1 K_2 [\text{S}][\text{H}^+]} + \frac{[\text{X}]}{K_2 [\text{S}]} \quad (9)$$

Rearranging equation (8),

$$[\text{X}] = \frac{K_1 K_2 [\text{S}][\text{H}^+][\text{CAT}]_t}{1 + K_1[\text{H}^+]} \quad (10)$$

Also from equation (2.3) of scheme 3,

$$\text{Rate} = k_3[\text{S}][\text{H}_2\text{O}] \quad (11)$$

Finally substituting equation (2.10) in (2.11),

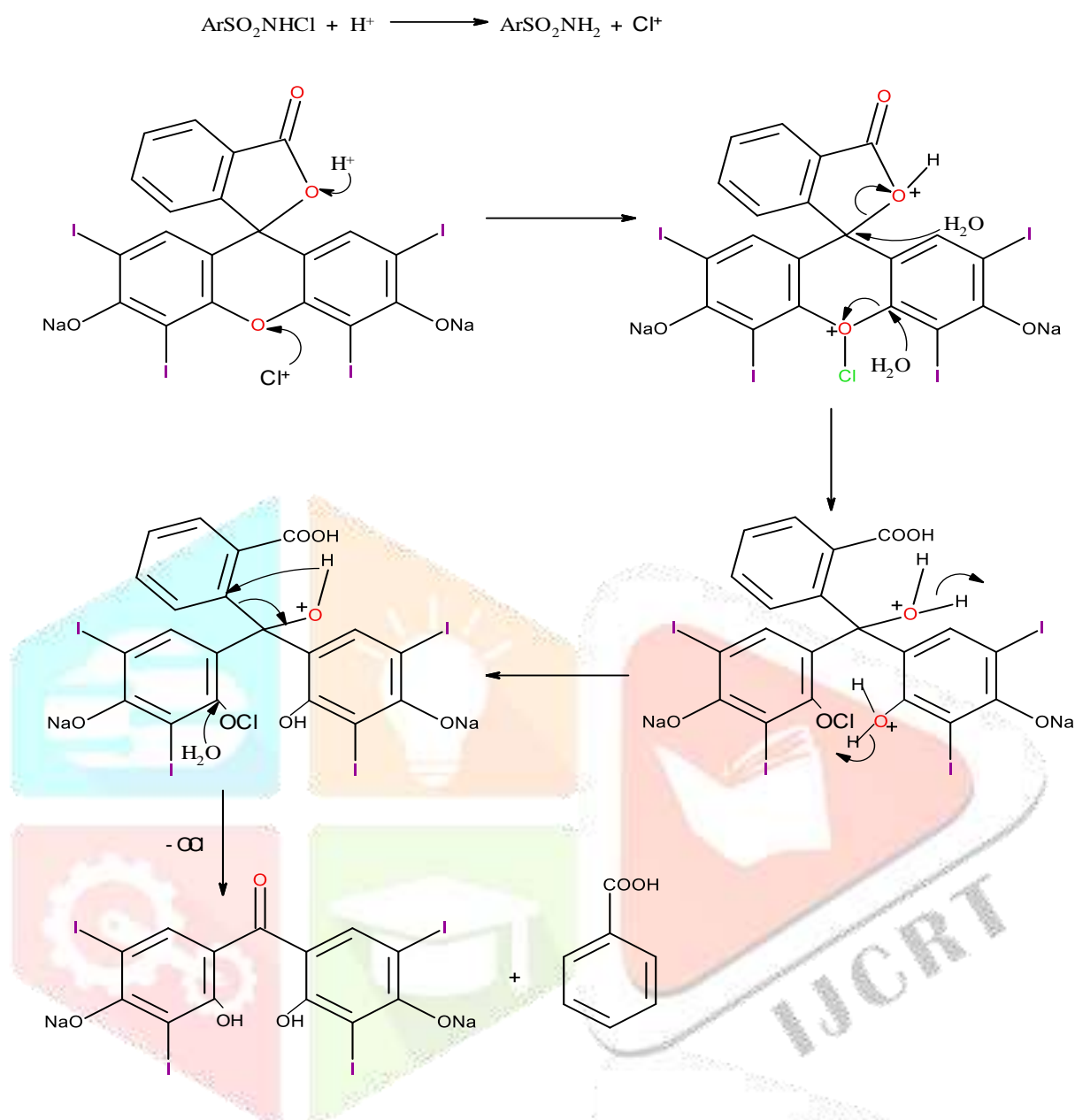
$$\text{Rate} = \frac{K_1 K_2 k_3 [\text{S}][\text{H}^+][\text{CAT}]_t [\text{H}_2\text{O}]}{1 + K_1[\text{H}^+]} \quad (12)$$

Rate law (12) satisfactorily explains the observed kinetic data which shows a first order dependence of rate on $[\text{EB}]$ and $[\text{CAT}]$ and fractional order dependence on $[\text{H}^+]$.

3.10 Reaction Mechanism:

In the first step, formed from dissociation of Chloramine-T takes up a proton from acid solution to give the free acid monochloramine-T (ArSO_2NHCl) as shown in equation (1). The resulting free acid, monochloramine-T reacts with substrate EB forming an intermediate complex (X). In the next step, the complex (X) undergoes hydrolysis to give the oxidized product.

A plausible reaction mechanism for oxidative degradation of RhB dye by CAT in HCl medium is given in reaction scheme 4:



Reaction Scheme 4: A plausible reaction mechanism for oxidative degradation of EB dye by CAT in HCl medium.

Conclusion

Investigation of kinetics of oxidation of Erythrosine B by CAT in HCl medium was done. The experimental rate law was determined to be $-\frac{d[\text{CAT}]}{dt} = k[\text{EB}][\text{CAT}]^1[\text{H}^+]^y$ where y is less than unity. The oxidation products were identified as disodium salt of 6,6'-dihydroxy-3,3',5,5'-tetraiodobenzophenone and benzoic acid. ArSO_2NHCl is expected to be the reactive species, which reacts with the dye EB to give a complex which on further hydrolysis to give the final products. An appropriate rate law was derived which suits the proposed mechanism.

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