EXPLORATION OF OXIDATIVE DEGRADATION OF ACID RED 18 DYE USING CHLORAMINE-T AND CHLORAMINE-B IN ACID MEDIUM

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Abstract—Spectrophotometric investigation of oxidative degradation of an azo-dye Acid Red 18 (AR18) by Chloramine-T (CAT) and Chloramine-B (CAB) as oxidizing agents in HCl medium has been reported. Effect of dye, oxidant and HCl concentration on rate was investigated under pseudo first order conditions. The addition of $NaClO_4$, chloride ions showed no effect on the rate of oxidation.Addition of the reduction product p-toluenesulphonamide retarded the rate of reaction. The dielectric effect studied by adding different volume of methanol indicated decreased rate with increase in dielectric constant. Kinetic studies revealed first-order dependence of rate on each oxidant, dye and a fractional order dependence on HCl with both the oxidants. However, rate of oxidation of dye by CAB was found to be faster compared to CAT. The stoichiometry of the reaction and the oxidation products were found to be same with both the oxidants. The reaction was studied at different temperatures and the activation parameters were estimated. Based on experimental results, the rate law was deduced and a plausible mechanism is put forward.

IndexTerms—Acid Red 18, Chloramine-T, Chloramine-B, Kinetics.

I. INTRODUCTION

Azo dyes are the most important class of synthetic organic dyes used in many industries [1]. Effluents from these industries are highly coloured, very stable in the environment and resistant to oxidation and biodegradation. Many of azo dyes are toxic, carcinogenic or mutagenic to aquatic life [2]. Acid red 18 (AR18) is a synthetic, organic, water soluble azo dye which is widely used in textile industries for colouring wool, silk, polyamide fiber and blended fabrics. It is also used for dyeing of leather, paper, plastic, and wood materials. It is also commonly used as food dye with code E-124, C.I. 16255 and routinely found in many common food products such as beverages, sweets, dairy produce, bakery products, medicine and cosmetics [3]. Due to their complex aromatic structure, azo dyes are difficult to be treated by conventional aerobic oxidation method. Hence, several physical, chemical and biological methods have been devoted to the study of degradation and discoloration of AR18 in aqueous medium as evidenced from literature [4]. Photocatalytic degradation of AR18 is reported to be temperature sensitive and depends on catalyst quantity [5,6]. There are many studies in which removal of AR18 from wastewaters by electrochemical methods have been investigated [7-9]. Iron based catalysts were found to be active for oxidation of AR18 by hydrogen peroxide [10,11]. An integrated anaerobic/aerobic method in polyethylene medium is reported to be highly effective in decolorization and biodegradation of AR18 [12]. Li wang has reported a microwave assisted method for effective adsorption of AR18 dye [13]. But, to the best of our knowledge there are no reports in literature about the kinetic studies of degradation and discoloration of AR18 in aqueous medium by mild oxidizing agents and mechanistic aspects of the reaction.

Aromatic sulfonylhaloamines, generally known as N-haloamines, are well known mild oxidizing agents which can act as source of both hypohalite species, haloniumcations and N-anions. They contain a strongly polarized halogen in +1 oxidation state bonded to nitrogen. Sodium N-chloro-p-toluenesulfonamide (chloramine-T; CAT) and (chloramine-B; CAB) are two principal members of this category of compounds [14]. These reagents have been explored for oxidation of wide range of organic substrates in aqueous, partially aqueous, and non-aqueous media in the presence of an acid or alkali, sometimes with the aid of a catalyst [15-20]. Even though the reactive species furnished by these reagents and the kinetic and mechanistic features of many of its reactions are well authenticated in the literature, only sporadic references are existing on the kinetic aspects of oxidation of azo dyes [21-23]. In this context, the present investigation was taken up with the main objective of studying the oxidation of an azo-dye, AR18 using CAT and CAB as oxidizing agents. Further objectives of the study were to: i) identify the reaction products ii) estimate the activation parameters iii) deduce an appropriate rate law, and iv) elucidate a feasible mechanism.

II. EXPERIMENTAL WORK

Materials and Methods

CAT, CAB and AR18 dye were purchased from Sigma Aldrich and were used without further purification. Stock solutions of CAT and CAB were freshly prepared and stored in brown bottles to prevent photochemical disintegration. Concentration of CAT and CAB solutions was monitored intermittently by iodometric titration. Aqueous solution of AR18 dye of desired strength was freshly prepared before its use. Analytical grades of p-toluenesulphonamide (PTS), $NaClO_4$, HCl, CH_3OH and NaCl were procured from s .d. fine chemicals and were used as such. All the solutions used in kinetic studies were prepared using triple distilled water.

Kinetic Measurements

The kinetic runs of oxidation of AR18 dye by CAT or CAB in HCl medium was investigated under pseudo first-order conditions with a known excess of [oxidant]o over $[AR18]_0$ using a UV–visible spectrophotometer (Chemito UV - 2100 spectrophotometer). In the present study, the kinetic experiments were carried out between 303 and 323 K. A constant temperature with an accuracy of ± 0.1 K was maintained using a Raaga Ultra Cold Chamber with digital temperature control (India). Reactions were carried out in glass stoppered Pyrex boiling tubes whose outer surfaces were coated black to eliminate any photochemical effects. In a typical experimental procedure, a known concentration of CAT, CAB and AR18 dye solution in HCl medium were maintained at the desired temperature for 30 minutes. Oxidation of substrate was initiated by pipetting a requisite amount of CAT or CAB into the reaction mixture containing substrate in acidic medium. The discoloration of dye was measured spectrophotometrically by taking about 3mL of the reaction mixture in a cuvette, made of quartz with path length of 1cm. The absorbance or optical density (OD) was measured choosing radiation of wavelength 507 nm which corresponds to the maximum absorbance of AR18 dye. The kinetics of oxidation was followed up to two half-lives. The absorbance readings at t = 0 (D_0) and t = t (D_t) were used to obtain plots log (D_0/D_t) versus time from which pseudo-first-order rate constants (k) were evaluated. Regression analysis of the experimental data was carried out on an fx −100W scientific calculator to evaluate the regression coefficient, r.

Product analysis

Oxidant and substrate were taken in stoichiometric proportion in HCl medium and were allowed to react for 24 h at 298 K. Completion of the reaction was monitored by thin layer chromatography. After completion the reaction products were neutralized with sodium hydroxide and the products were extracted with ether. The reduction product of the reaction p-toluenesulfonamide was detected by paper chromatography. Benzyl alcohol saturated with water was used as the solvent system with vanillin (0.5 %) inHCl solution (1 %) in ethanol as spray reagent (R_f= 0.904). Reaction mixture was further analysed by LC-MS studies which revealed the formation of naphthol and 1,2-diketo-naphthalene-3,6-disulfonic sodium salt as products of oxidation and p-toluenesulfonamide as the reduction product.

Reaction Stoichiometry

Different known ratios of AR18 dye and CAT in presence of 3.0 x 10^{-4}mol dm^{-3}HCl were equilibrated at 298 K for 24 h. The unreacted oxidant in the reaction mixture was estimated by iodometric titration. This analysis showed that in both the cases one mole of AR18 consumed one mole of oxidant and the observed reaction stoichiometry is represented in reaction scheme 1.
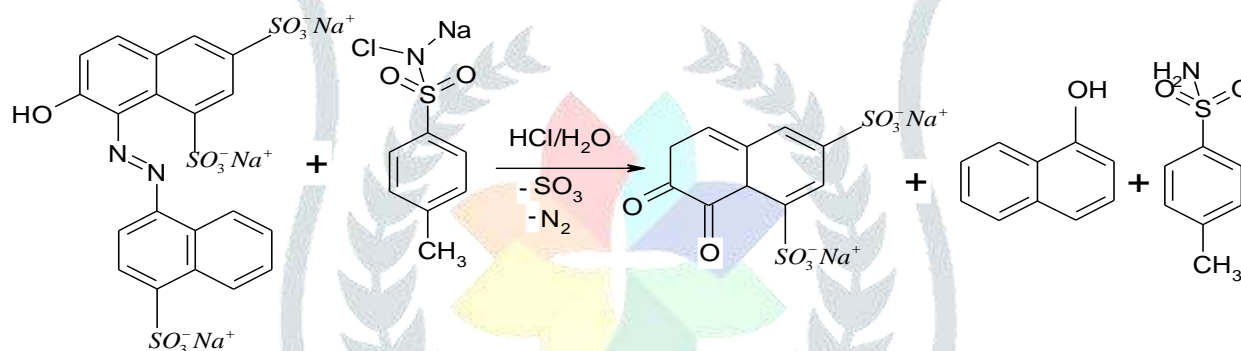
Reaction scheme 1: Stoichiometric oxidation of AR 18 dye by CAT

III. RESULTS AND DISCUSSIONS

The repetitive UV-visible spectra were taken at different time intervals for a typical reaction with a known concentration of dye, oxidant and HCl. The oxidative discolouration of AR18 Dye by CAT was clearly apparent in the spectra shown in fig. 1. It is evident from the spectra that more than 75 % of dye was disintegrated in just 45 minutes and complete discolouration was observed in 24 hr.
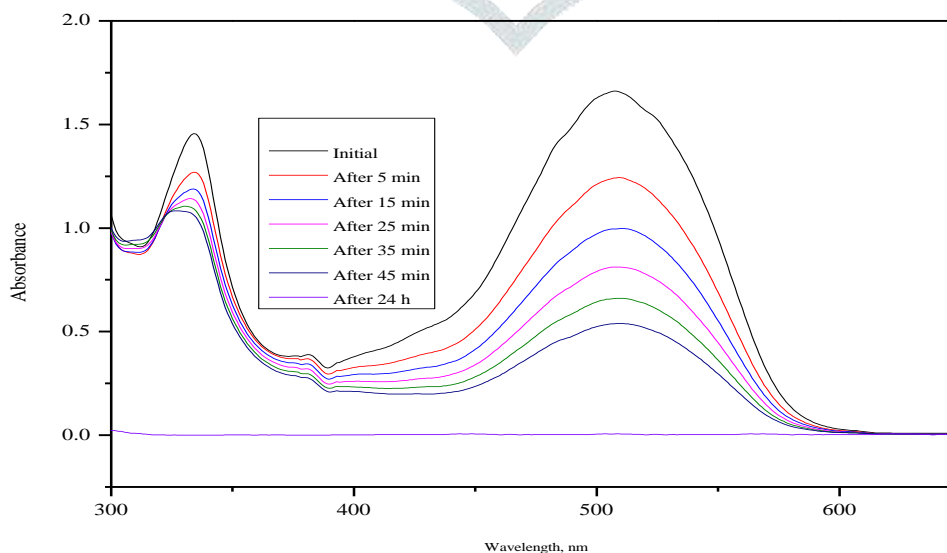

Figure 1: Evolution of the AR18 spectra in presence of an excess of CAT as a function of time at 298 K. AR18 - 4.0 x10^{-5}mol dm^{-3}, CAT-4.0x10^{-4}mol dm^{-3}, HCl 3.0x10^{-4}mol dm^{-3}.

Effect of reactant concentration on the rate

The kinetics of oxidation of AR18 dye by CAT and CAB (hereafter abridged as oxidant) have been investigated at several initial concentrations of the reactants, under pseudo first-order conditions of $[oxidant]_0 >> [AR\ 18]_0$, in presence of HCl at 298 K in both the cases. The kinetics of oxidation of AR18 with the closely related oxidants CAT and CAB in HCl medium are same under identical experimental conditions but the comparative rates of oxidation of AR18 by CAB was found to be faster than by CAT. Under the conditions $[oxidant]_0 >> [AR\ 18]_0$ at constant $[AR\ 18]_0$, [HCl], temperature, plots of log (Absorbance) versus time were linear (r>0.9952) indicating a first-order dependence of rate on $[AR\ 18]_0$ in both the cases. The linearity of these plots in both cases, together with the constancy of the slopes obtained at different $[AR\ 18]_0$, substantiates the first-order dependence of rate on $[AR\ 18]_0$. The pseudo first-order rate constants (k^l) obtained are recorded in Table 1. Under the same experimental conditions the rate of reaction increased with increase in $[oxidant]_0$ (Table 1) and plots of log k^l versus log $[oxidant]_0$ were linear with r>0.9839 and 0.9951 for CAB and CAT respectively with unit slopes in both the cases. This establishes that the order of the reaction is first-order with respect to $[oxidant]_0$. Further, plots of k^l versus $[oxidant]_0$ were linear with r>0.9847 and 0.9896 for CAB and CAT respectively passing through the origin further substantiating the first-order dependence of rate on $[oxidant]_0$. The rate of reaction augmented with increase in [HCl] (Table 1) and plots of log k^l versus log [HCl] were linear with r > 0.9958 and 0.9875 with slopes of 0.25 and 0.29 for CAB and CAT respectively, showing a fractional-order dependence on [HCl].

Table 1. Effect of varying concentrations of oxidant, substrate and medium on the reaction rate at 298 K

$10^4 \times [oxidant]_0$ mol dm^{-3}	$10^5 \times [AR\ 18]_0$ mol dm^{-3}	10^4[HCl] mol dm^{-3}	$10^5\ k^1$ (s^{-1})	
			CAT	CAB
1.0	4.0	3.0	1.64	3.75
2.0	4.0	3.0	6.14	9.98
3.0	4.0	3.0	8.86	15.5
4.0	4.0	3.0	15.3	28.0
5.0	4.0	3.0	18.3	35.2
6.0	4.0	3.0	22.6	44.6
4.0	1.0	3.0	15.7	27.6
4.0	2.0	3.0	15.2	27.5
4.0	3.0	3.0	14.7	28.1
4.0	4.0	3.0	15.3	28.0
4.0	5.0	3.0	15.0	28.7
4.0	4.0	1.0	7.06	21.9
4.0	4.0	2.0	11.8	26.5
4.0	4.0	3.0	15.3	28.0
4.0	4.0	4.0	15.5	30.5
4.0	4.0	5.0	17.1	32.8
4.0	4.0	6.0	19.9	35.6

Effects of halide ions and p-toluenesulfonamide concentration on the rate

In order to verify the effect of p-toluenesulfonamide (PTS) which is the reduced product of CAT on the reaction rate, concentration of PTS was varied from 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3} at constant oxidant, substrate and HCl concentration at 298 K. Rate constants evaluated at different concentration are tabulated in Table 2. With increase in concentration of PTS reaction rate decreased considerably. This clearly indicates that PTS is involved in the rate determining step or any step prior to it.

Under otherwise similar experimental conditions, rate of reaction was investigated by varying concentration of halide ions, Cl-, in the form of its sodium salt from 1.0×10^{-3} to 6.0×10^{-3} mol dm^{-3}. Increase in concentration of halide ions did not show pronounced effect on the rate clearly ruling out their role in the reaction.

The ionic strength of the reaction medium was varied from 0.1 to 0.3 mol dm^{-3} with NaClO$_4$ solution keeping other experimental conditions constant. It was found that addition of NaClO$_4$ showed negligible effect on the reaction rate, representing the participation of non-ionic species in the rate-determining step. Hence no attempts were made to maintain the ionic strength of the medium stable for kinetic runs.

Table 2. Effect of varying concentration of PTS and methanol on the reaction rate at 301K.

$10^4 \times$ [PTS] mol dm^{-3}	$10^5\ k^1$ (s^{-1})	Methanol (%)	Dielectric constant (D)	$10^5\ k^1$ (s^{-1})
1.0	9.84	0	76.73	9.21
2.0	7.38	10	72.37	7.52
3.0	6.00	20	67.48	6.00
4.0	5.23	30	62.71	3.99
5.0	4.16	40	58.06	1.92

Effect of dielectric constant of the medium on the rate

The effect of dielectric constant (D) of the medium on rate was investigated by adding MeOH (0-40 wt %) to the reaction mixture keeping all other experimental conditions constant at 298 K. The rate constant decreased with decrease in dielectric constant as shown in table 2 clearly indicating the retarding effect of methanol on the oxidation of AR 18 by CAT. The dielectric constant values of MeOH–H$_2$O mixtures were taken from the literature [24]. A plot of log k^l vs 1/D as shown in fig. 3 is linear ($R^2 = 0.989$) with a negative slope.
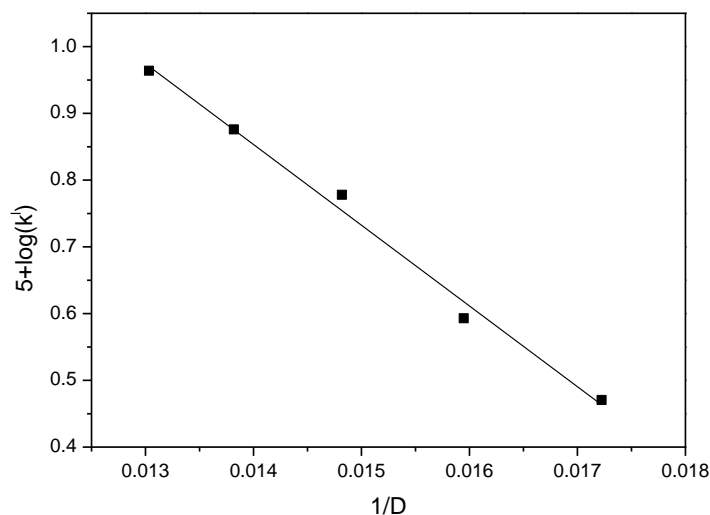
**Figure 2:** A plot oflog k^lvs 1/D at 0 - 40 wt % of MeOH.

Effect of temperature on the rate

The effect of temperature on the rate of reaction was studied by varying temperature from 303 to 323 K, under otherwise similar conditions. From the linear Arrhenius plots of log k^l vs. 1/T (r > 0.9955) shown in fig. 3, the values of composite activation parameters (Ea, $\Delta H\neq$, $\Delta S\neq$, $\Delta G\neq$ and log A) were computed for the oxidation of AR18 by CAT and CAB. These data are summarized in Table 3.

Table 3.Effect of temperature on the reaction rate.

Temperature (K)	CAT	CAB	Activation parameters	CAT	CAB
	$10^4 k^1 (s^{-1})$	$10^4 k^1 (s^{-1})$			
303	1.15	3.19	Ea (kJ mol^{-1})	71.11	56.72
308	2.00	4.43	Log A	44.28	33.25
313	3.36	6.39	#ΔH(kJ mol^{-1})	68.51	54.11
318	4.87	8.88	#ΔS(J K^{-1}mol^{-1})	-93.69	-133.6
323	6.52	12.88	#ΔG(kJ mol^{-1})	97.8	95.84

AR18 - 4.0 x10^{-5}mol dm^{-3}, CAT- 4.0x10^{-4}mol dm^{-3}, HCl 3.0x10^{-4}mol dm^{-3}.
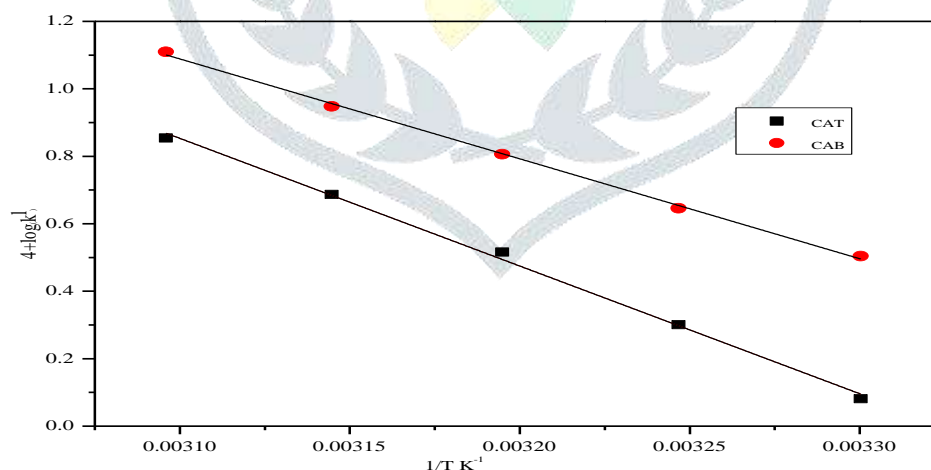
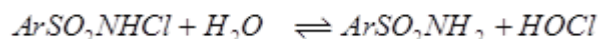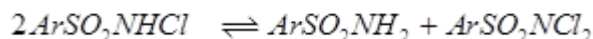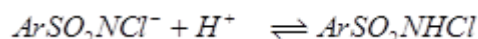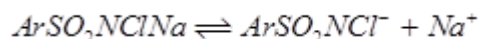**Figure 3:** A plot of log k^lvs 1/T for CAT and CAB.

Reactive species of sodium N-halo-p-toluenesulfonamides

Both Chloramine-T and Chloramine-B (represented as ArSO$_2$NClNa) are strong electrolytes in aqueous solutions and act as very good oxidizing agents in acidic media [25]. In general, they undergo a two electron change in their reactions forming the reduction product (ArSO$_2$NH$_2$) and sodium chloride [26]. The potential of Chloramine-T –sulphonamide redox couple decreases with increase in pH of the medium. Potential of couple is 1.138 V, 1.778 V, 0.614 V and 0.5 V at pH 0.65, 7.0, 9.7 and 12, respectively [27]. In view of the homogeneity in properties of N-haloamines, similar redox potential behaviour can be expected for CAB also. Depending upon the pH of the medium, they furnish different types of reactive species in solutions [28, 29] as shown in reaction scheme 2.

The species accountable for oxidizing ability of CAT and CAB may be different depending on the pH of the medium. In acidic medium, the species responsible for oxidation of substrate are the conjugate free acid (ArSO$_2$NHCl), dichloramine-T (ArSO$_2$NCl$_2$), hypochlorous acid (HOCl) and possibly H$_2$OCl$^+$.If ArSO$_2$NCl$_2$ was to be the reactive species, then the rate law predicts a second-order dependence of rate on
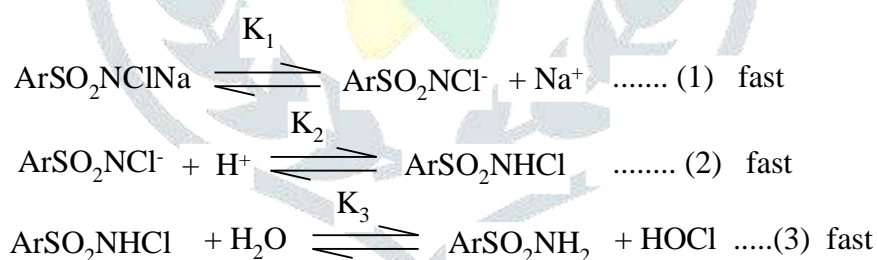
[CAT]$_0$, which is contrary to the experimental observations. V.J. Jennings, and E. Bishophave studied the pH dependent relative concentrations of the species present in acidified CAT solutions of comparable molarities and shown that $ArSO_2NHCl$ is the likely oxidizing species in acid medium [26]. However, in the present study a first-order retardation of rate was clearly observed on addition of p-toluenesulfonamide in the oxidation of substrate by CAT. This clearly shows that HOCl is the most probable reactive oxidizing species for the oxidation of dye.

$$ArSO_2NClNa \rightleftharpoons ArSO_2NCl^- + Na^+$$

$$ArSO_2NCl^- + H^+ \rightleftharpoons ArSO_2NHCl$$

$$2\,ArSO_2NHCl \rightleftharpoons ArSO_2NH_2 + ArSO_2NCl_2$$

$$ArSO_2NHCl + H_2O \rightleftharpoons ArSO_2NH_2 + HOCl$$

$$ArSO_2NCl_2 + H_2O \rightleftharpoons ArSO_2NHCl + HOCl$$

$$HOCl \rightleftharpoons H^+ + OCl^-$$

$$HOCl + H^+ \rightleftharpoons H_2OCl^+$$

$$ArSO_2NHCl + H^+ \rightleftharpoons ArSO_2NH_2Cl^+$$
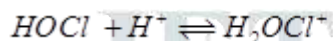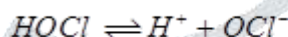
Reaction Scheme 2: Reactive species of N-halo-p-toluenesulfonamides.

Reaction scheme

The first-order dependence of rate on [oxidant]$_0$ and a clear retardation of rate with increase in [ArSO$_2$NH$_2$] clearly shows that HOCl is the most probable reactive species. Since organic haloamines have similar chemical properties, the same equilibrium can be expected for CAB also. From the above discussion and experimental facts, a general reaction scheme is proposed to explain the oxidation of AR18 by CAT in HCl medium

$$ArSO_2NClNa \xrightleftharpoons{K_1} ArSO_2NCl^- + Na^+ \quad \text{....... (1) fast}$$

$$ArSO_2NCl^- + H^+ \xrightleftharpoons{K_2} ArSO_2NHCl \quad \text{........ (2) fast}$$

$$ArSO_2NHCl + H_2O \xrightleftharpoons{K_3} ArSO_2NH_2 + HOCl \quad \text{.....(3) fast}$$

$$HOCl + Substrate \xrightarrow{k_4} X \qquad \text{(4) slow and rate limiting}$$

$$X + H_2O \xrightarrow{k_5} Products \qquad \text{(5) } fast$$

Reaction Scheme 3: A general reaction scheme for the oxidation of AR 18 dye by CAT in acid medium.

In the first step, Chloramine-T dissociates according to equation (1). The resulting anion picks up a proton from acid solution to give the free acid monochloramine-T, which on hydrolysis gives ArSO$_2$NH$_2$ and HOCl. The HOCl thus formed reacts with the substrate in the slow rate limiting step to form an intermediate complex (X). In the last step, the complex undergoes hydrolysis to give the oxidized product. From equation (1),

$$K_1 = \frac{\left[ArSO_2NCl^-\right]\left[Na^+\right]}{\left[ArSO_2NClNa\right]} \qquad (6)$$

From equation (2) and (3),

$$K_2 = \frac{[ArSO_2NHCl]}{[ArSO_2NCl^-][H^+]} \qquad (7)$$

$$K_3 = \frac{[ArSO_2NH_2][HOCl]}{[ArSO_2NHCl][H_2O]} \qquad (8)$$

Rearranging equation (7) and (8), we get

$$\left[ArSO_2NCl^-\right] = \frac{[ArSO_2NH_2][HOCl]}{K_2 K_3 [H^+][H_2O]} \qquad (9)$$

$$\left[ArSO_2NHCl\right] = \frac{[ArSO_2NH_2][HOCl]}{K_3 [H_2O]} \qquad (10)$$

If $[CAT]_t$ is the total effective concentration of CAT, then

$$[CAT]_t = \left[ArSO_2NCl^-\right] + \left[ArSO_2NHCl\right] + \left[HOCl\right] \qquad (11)$$

Substituting equation (9) and (10) in (11), and solving for [HOCl]

$$[HOCl] = \frac{K_2 K_3 [H^+][CAT]_t [H_2O]}{K_2 [ArSO_2NH_2][H^+] + [ArSO_2NH_2] + K_2 K_3 [H^+][H_2O]} \qquad (12)$$

Also from equation (4),

$$Rate = k_4 [HOCl][AR18] \qquad (13)$$

Finally Substituting equation (12) in (13),

$$[Rate] = \frac{K_2 K_3 k_4 [H^+][CAT]_t [H_2O][AR18]}{K_2 [ArSO_2NH_2][H^+] + [ArSO_2NH_2] + K_2 K_3 [H^+][H_2O]} \qquad (14)$$

The derived rate law fits well to the observed kinetic data which reveals a first order dependence of rate on [AR18] and [CAT] and fractional order dependence of rate on [H$^+$] and inverse fractional order dependance on [PTS].

Reaction mechanism

Most probable mechanism for oxidation of AR 18 dye by CAT or CAB in acid medium is given in reaction scheme 4. AR18 dyeloses a proton in solution, resulting in a negatively charged ion, which is attacked by HOCl, to form an intermediate complex (X). The intermediate complex in acid medium undergoes protodesulphonation with cleavage of azo bond followed by hydrolysis to yield the eventual products naphthol and 1,2-diketo-naphthalene-3,6-disulfonic sodium salt.
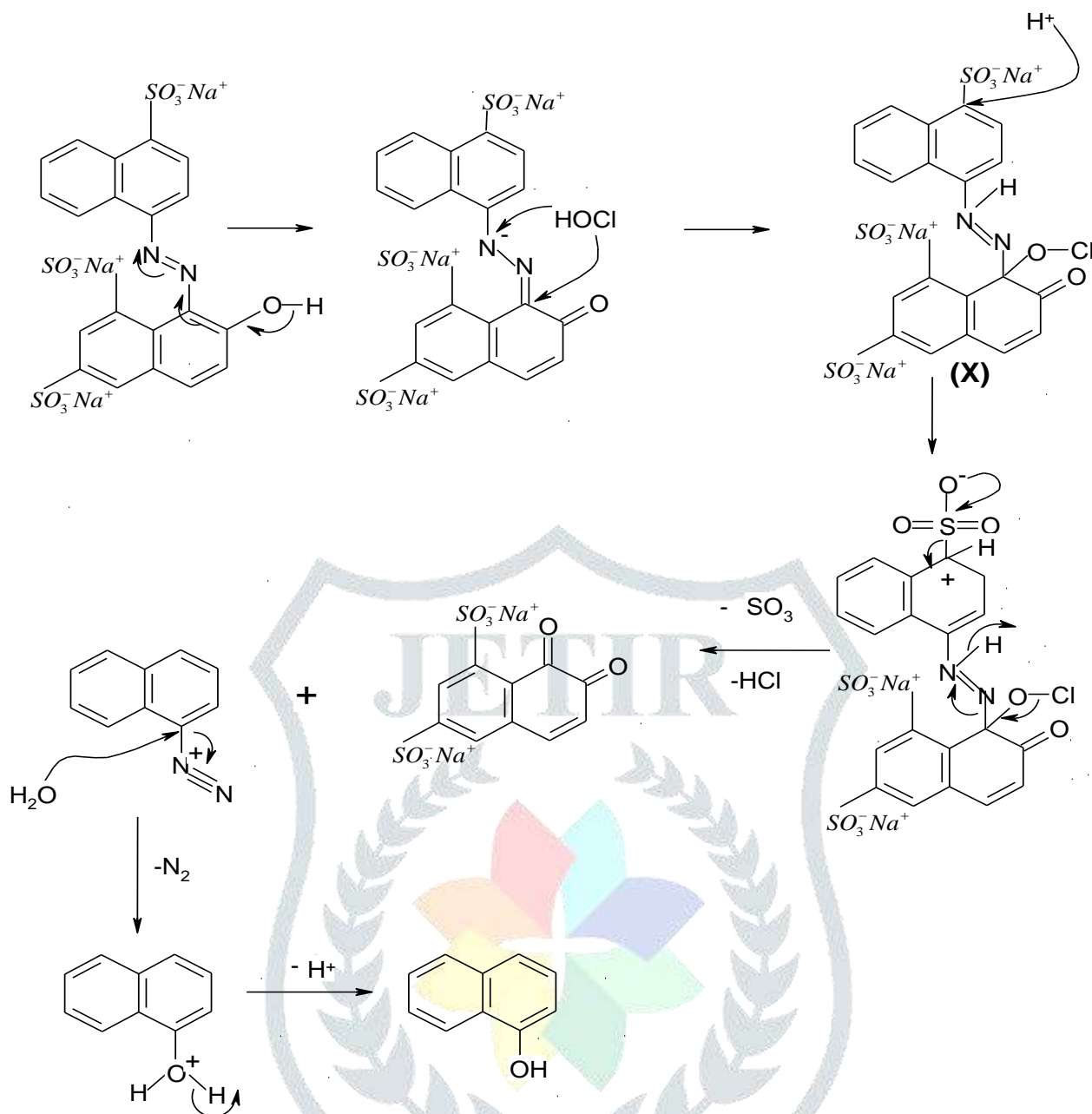
IV. CONCLUSIONS

Chloramine-T and Chloramine-B have been proven effective oxidants for chemical degradation of AR 18 dye in acid medium. Rate of oxidation was faster with CAB compared to CAT. Kinetic studies revealed a pseudo first order dependence of rate on oxidant, dye and fractional order dependence on HCl. Decrease in rate of reaction was observed with decrease in dielectric constant brought about by increasing wt % of methanol in reaction medium. Kinetic rate law in agreement with experimental observations has been deduced and probable reaction mechanism is put forward. The present method developed for the oxidative decolorization of AR 18 with CAT and CAB is advantageous and could be used for treating industrial effluents containing AR 18 dye to eliminate its toxicity.

V. ACKNOWLEDGMENT

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