Kinetic and Mechanistic Study of Chloramine-T Assisted Color Removal of Triphenyl Methylene Dyes Containing Waste Water: A Spectrophotometric Approach

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ABSTRACT

The removal of color in water which contains Tiphenylmethylene dyes by Chloramine-T (oxidizing agent) was studied in acid medium at 301 K. The mechanism of color removal was investigated. The experimental results show that the efficiency of color removal by CAT depends upon the concentration of CAT and pH of the medium. It was observed that the oxidation of AG50 and PB5 followed similar order with both the dyes. The experimental rate law is found to be $-d[CAT]/dt = k[AG50][CAT]^2[H^+]^{-X}[PTS]^{-Y}$, $-d[CAT]/dt = k[PB5][CAT]^2[H^+]^{-X}[PTS]^{-Y}$. Other factors like ionic strength of the medium, dielectric effect, the addition of halide ions and reduction product (PTS) were also studied. The Stoichiometry was same in each case. The reaction was studied at different temperatures and the activation parameters were computed. Finally the observed results have been explained by plausible mechanism and the rate laws have also been deduced. Finally, CAT assisted color removal is found to be a very good alternative to some of the more conventional forms of chemical treatment, especially for treating actual textile waste with low natural pH.

Keywords: Food dyes, Chloramine-T, kinetics, Reaction mechanism, Oxidative decolorization.

INTRODUCTION

Even with its large abundance on earth surface, water is the most precious commodity, and only a small portion of it (approximately 0.03%) is found to be fit for human activities. Due to rapid increase in the population as well as industries there is a huge demand for water in proportion to the supply available, which remains constant. Hence, there is an urgent need to minimize its consumption and also it is necessary to return it back to the environment with the minimum amount of contamination because of the limited capacity of self-purification. Hence wastewater treatment process plays an important role [1]. Food, drug and cosmetic industries use many kinds of artificial dyes and discharge large amounts of highly

colored wastewater. These wastes must be treated before its discharge so that it will be less hazardous to the environment. Biological treatment processes is one of the common process used in the waste water treatment. These processes are found to be efficient for biochemical oxygen demand (BOD) and suspended solids (SS) removal, but they are ineffective for the removal of color from the waste water [2]. Hence, the treated waste water may contain appreciable amounts of color when discharged. The technologies suggested for the treatment of water effluent in order to remove color are physico-chemical treatment operations, like adsorption, chemical precipitation and ozone treatment. Many researchers have summarized a number of studies on physicochemical method for the removal of dyes from wastewater such as advanced oxidation [3-4], bioadsorbent [5] activated carbon [6], coagulation and flocculation [7], ozonation and photo catalysis [8]. The methods suggested above have their own merits and demerits in application [9].Therefore, most of the researchers have focused their studies on finding other alternative approaches for the removal of color from dye wastewater. In the present studies we have selected dyes, Acid Green 50 (AG50) and Patent blue 5 (PB5). Treatment of dyes used in food, drug and cosmetic products with mild oxidizing agents like Chloramine-T is relatively cheap and simple to use, have been the focus of recent studies on dye decolorization. Aromatic N-halo sulphonamides are mild oxidizing agents in both acidic as well as alkaline medium. It contains nitrogen which is linked to Halogen present in +1 oxidation state. The diverse nature of their chemistry is due to their ability to act as, hypohalite species, halonium cations and N-anions, which act both as nucleophiles and bases [10]. The prominent member of this class of compounds is Chloramine-T (p-Me-C_6H_4-SO_2NClNa.3H_2O, CAT). Since they interact with a wide range of functional groups, affecting a variety of molecular changes, they are used as reagents for analytical and kinetic investigations [11-15]. Although the mechanistic aspects of many reactions using CAT are well documented, very limited information is available in the literature about the oxidative behavior of CAT towards food dyes. Number of studies is published on oxidation of sunset yellow different oxidizing agents [16-18]. Recently, the kinetics and mechanistic investigation of oxidation of Sun Set Yellow by peroxydisulphate has been reported by Gemeay et al [19]. Vinod and Puttaswamy have studied the kinetics of oxidation of sun set yellow by CAT in the presence of both acidic and alkaline medium [20]. As per our knowledge there are no reports in the literature on the oxidation of AG50 and PB5 from its kinetic and mechanistic point of view. Therefore, the objective of this study was to evaluate the ability of the Chloramine-T for waste water treatment to remove dyes from industrial effluents. Also, the objectives were to: i) derive an appropriate rate law ii) elucidate a plausible mechanism, iii) identify the reaction products, iv) evaluate activation parameter.

MATERIALS AND METHODS

In order to find out the stoichiometry of the oxidation reaction the reaction mixture which contained different ratios of PB5 to CAT in the presence of 4.0 x10^{-3} mol dm^{-3} HCl were allowed to react for 24 h at 301 K. The unreacted CAT was determined by Iodometric method.

It was observed that the stoichiometry of subs: oxi was 1:2 i.e 1 mole of the substrate consumed for 2 moles of CAT. The stoichiometry remains same for the oxidation of AG50 by CAT. The observed stoichiometry can be represented by equation **(1)**. The oxidized products of Acid Green 50 (1) are found to be bis-(4-diethylamino-phenyl)-methanone **(2)** and 6-hydroxy naphthalene-2-sulphonic acid **(3).** Also the oxidized products of Acid Green 50 **(4)** are (4-diethylamino-phenyl)–[(4-ethylmethylamino)-phenyl]-methanone **(5)** and 2-hydroxybenzenesulphonic acid **(6).**
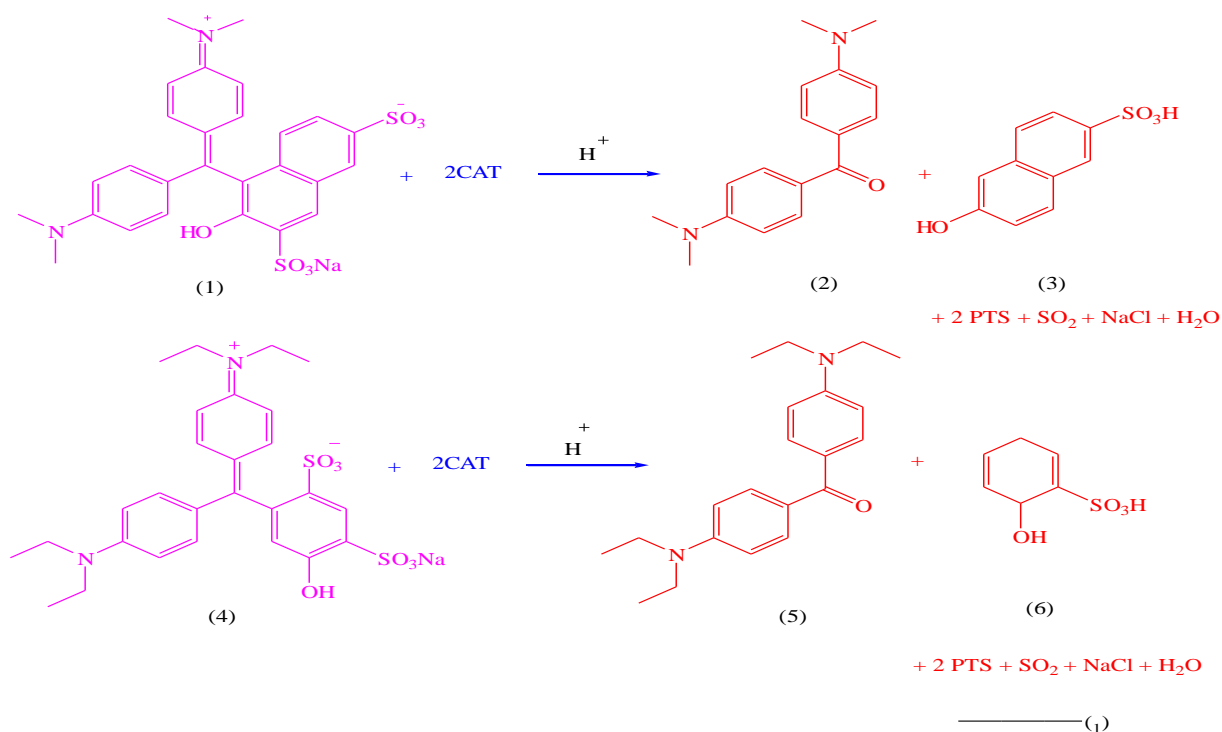
The dyes (AG50 and PB5) were purchased from Sigma Aldrich in order to study the kinetics. The name, molecular structure and their corresponding wavelength of maximum absorbance selected for this study are shown in table 1.

Table 1: Structure, molecular weight and λ_{max} of AG50 and PB5

Dye	Acid Green 50 (AG50)	Patent Blue 5 (PB5)
structure		
Mol. Wt. (g/ mol)	576	582
λ_{max}	631nm	639nm

CAT was also purchased from sigma Aldrich and was purified if necessary by the method of Morris et.al. An aqueous solution of CAT was prepared and used whenever it was required. The solution was stored in brown bottles in order to avoid any photochemical deterioration. The concentration of CAT was determined periodically with the help of Iodometric titration. Other reagents like $NaClO_4$, PTS and D_2O also purchased from Sigma and were used as such. All the other chemicals used were of analytical grade and Triple distilled water was used in order to prepare the solution and for kinetic runs.

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The kinetics measurements were carried out spectrophotometrically under pseudo-order conditions i.e $[CAT]_0 >> [Dye]_0$ using Shimadzu-1800 UV-Vis spectrophotometer at 301 K. The characteristic wavelength for each dye was determined by running a scan of the dye on a spectrophotometer (Shimadzu UV-1800). The maximum absorbance wavelength (λ_{max} = 631nm and 639 nm (Fig 1) for AG50 and PB5 dyes respectively) was used for all absorbance readings. CAT along with suitable amount of substrate; HCl and water (in order to maintain constant volume) were thermostated separately at 301 K. After attaining constant temperature required amount of the CAT was pipetted out in to the mixture containing substrate in order to initiate decolorization of the dye. Immediately the absorbance of the reaction mixture was measured by pipetting out around 3ml of the aliquot in to a cuvette, which is made up of quartz and whose path length is 1cm. The kinetics of oxidation was followed up to two half-lives. Regression coefficient (R^2) was calculated with the help of fx-991ms.
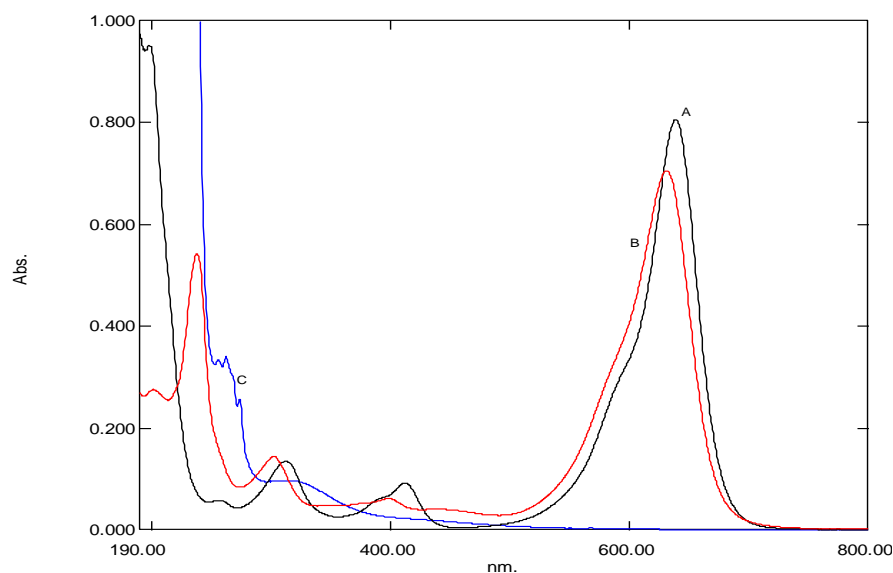

Fig. 1: (a) and (b) represents the electronic spectra of water containing AG50 and PB5 dye respectively whereas (c) represents the spectra of treated dye solution
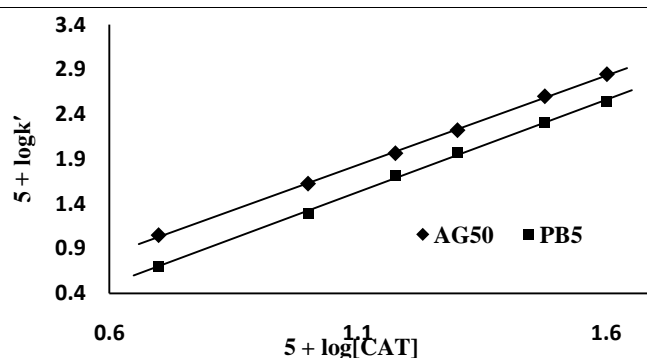
RESULTS AND DISCUSSION

The kinetic studies were performed under pseudo first order conditions such that [CAT] >> [Dye]. The kinetics of both the substrates i.e. AG50 and PB5 has been investigated with several initial concentrations of the reactants in the presence of HCl at 301 K. We observed similar oxidation process in both the dyes under similar conditions.

Effect of concentrations of Dye and CAT on the rate: With the concentration of CAT in excess, at constant [CAT], [HCl] and temperature, plot of log (abs) Vs time was found to be linear with an intercept on y-axis which indicates a first order dependence of the rate on $[Dye]_0$. The values of pseudo first order rate constants (k') are listed in table 2. The units of concentration and rate constant are expressed in mol dm^{-3} and s^{-1} respectively. An increase in [CAT] resulted in the increase in the value of k' for the both the oxidation reactions and the order w.r.t CAT was obtained by the plot of log [CAT] vs log k'. The nature of the graph was linear with the slope value of 1.99 and 2.05 with R^2 equal to 0.99 and 0.99 for AG50 and PB5 respectively (Fig 2). This clearly indicated the second order dependence of rate on the concentration of $[CAT]_o$.

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Table 2 Effect of varying concentrations of oxidant, substrate and medium on the rate at 299k

$10^4 \times$[CAT] mol dm-3	$10^5 \times$[Dye] mol dm-3	$10^3 \times$ [HCl] mol dm-3	10^4 k′ (s⁻¹)	
			Acid Green 50	Patent Blue 5
0.5	2.0	4.0	1.12	0.50
1.0	2.0	4.0	4.20	1.96
1.5	2.0	4.0	9.22	5.21
2.0	2.0	4.0	16.66	9.36
3.0	2.0	4.0	40.00	20.03
4.0	2.0	4.0	70.23	35.15
1.0	0.5	4.0	3.73	2.14
1.0	1.0	4.0	4.37	2.22
1.0	1.5	4.0	3.93	2.28
1.0	2.0	4.0	4.20	1.96
1.0	2.5	4.0	4.00	2.18
1.0	2.0	1.0	20.37	13.92
1.0	2.0	2.0	9.09	5.29
1.0	2.0	3.0	5.51	2.95
1.0	2.0	4.0	4.20	1.96
1.0	2.0	5.0	3.24	1.45
1.0	2.0	6.0	2.68	1.10

Fig.2: Plot of logk′ Vs log [CAT]

Effect of acid concentration (pH) on the rate: The rate of the reaction was studied at different concentrations of HCl, by keeping other conditions constant. It was found that the rate of oxidation decreased with an increase in the concentration of HCl. The order w.r.t HCl was obtained by the plot of log [HCl] Vs log k′. The nature of the graph was linear and the order w.r.t to HCl was found to be -1.14 and -1.42 with R^2 equal to 0.99 and 0.99 for AG50 and PB5 respectively (Fig 3).This clearly indicated an inverse fractional order dependence of rate on [H⁺].
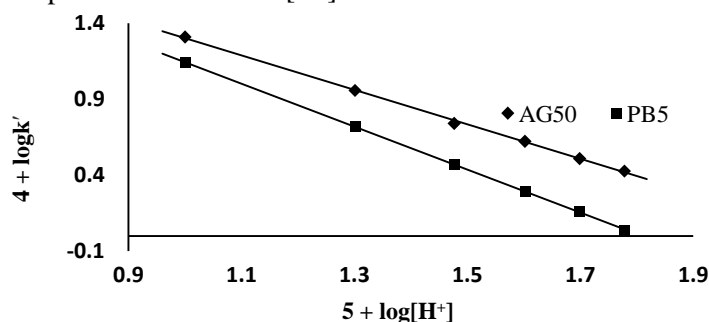
Fig.3: Plot of log k′ Vs log [H⁺]

Effect of varying ionic strength and halide ion concentration on the rate: The ionic strength (μ) of the reaction medium was varied in the range 0.1-0.4 mol dm⁻³ by the addition of NaClO₄ solution by keeping

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other experimental conditions constant. It was found that there was no significant effect in the rate of oxidation of both the dyes even with the increase in the concentration of $NaClO_4$. This clearly indicates an ion-dipolar or dipolar-dipolar interaction in the rate limiting step according to the Bronsted and Bjerrum concept of primary salt effects. Hence no attempt was made to keep the ionic strength constant for kinetic runs. Further the addition of halide ions in the form of NaCl (0.001-0.005M) had no pronounced effect on the rate of oxidation of both AG50 and PB5. This implies the dependence of the rate on [HCl] reflected the effect of [H^+] only and also no free chlorine is formed in the reaction.

Effect of reduction product, PTS on the rate of the reaction: The rate of the reaction decreased with the addition of *p*-toluene sulfonamide (reduction product of CAT) which indicates that reduction product is formed in a fast pre-equilibrium to the rate limiting step. Further the plot of log k' Vs log [PTS] gave a straight line (Fig 4) with a slope of -0.73 and -0.78 for AG50 and PB5 respectively.

Table 3: Effect of PTS on the rate of the reaction with [Dye] $=2.0 \times 10^{-5}$ mol dm^{-3} [CAT] $=1.0 \times 10^{-4}$ mol dm^{-3} [HCl] $=4.0 \times 10^{-3}$ mol dm^{-3}

10^4 [Reduction product] mol dm^{-3}	10^4 k$'$ (s^{-1})	
	Acid Green 50	Patent Blue 5
1.0	4.11	1.82
1.5	3.27	1.49
2.0	2.44	1.06
3.0	2.05	0.8
4.0	1.49	0.61

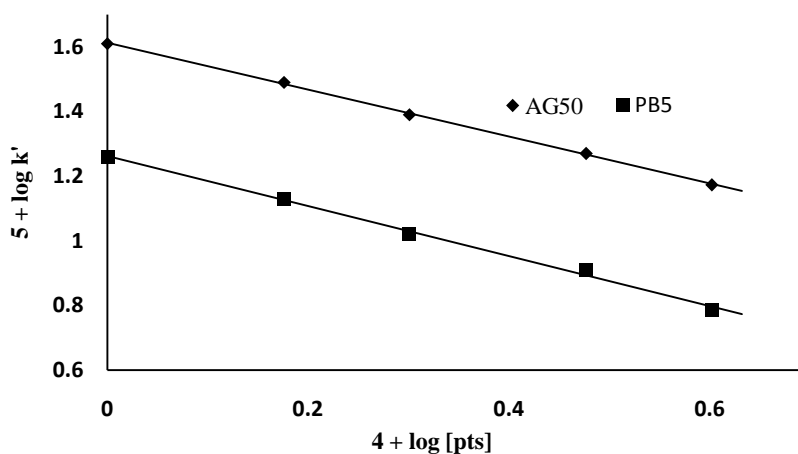**Fig 4: log k' Vs log [PTS]**

Effect of varying dielectric constant of the medium on the rate: Methanol at different compositions (0-20% v/v) was used in order to study the effect of dielectric constant of the medium. It was noticed that the rate decreased with the increase in the methanol content for the oxidation of both the dyes. The plot of log k$'$ vs 1/D was linear (R^2=0.98 and 0.99, Fig 5) with negative slope in both the cases which indicates an ion dipolar interaction in the rate limiting step. The values of dielectric constants for various methanol-water mixtures were employed with the help of literature [21-23]. Meanwhile the blank experiments were performed and were observed that MeOH was not oxidized significantly by CAT under the standard conditions (without substrate).

Table 4. Effect of dielectric constant on the rate of the reaction with [Dye] =2.0×10^{-5} mol dm^{-3} [CAT] =1.0×10^{-4} mol dm^{-3} [HCl] =4.0×10^{-3} mol dm^{-3}

% MeOH (v/v)	D	10^4 k$'$ (mol dm^{-3} s^{-1})	
		Acid Green 50	Patent Blue 5
0	76.73	4.20	1.96
5	74.50	3.02	1.83
10	72.37	2.27	1.67
20	67.48	1.42	1.35
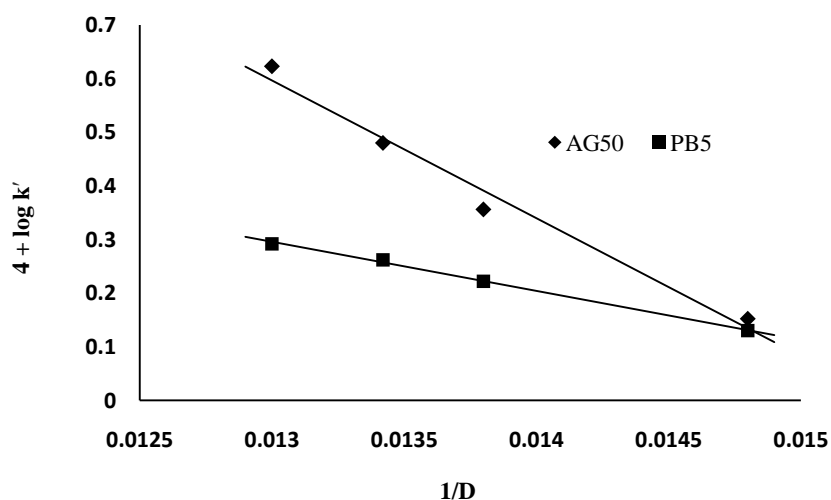
Fig.5: Plot of log k′ Vs 1/D

Proton inventory studies: The proposed mechanism is also supported by the decrease in the rate in D_2O medium. Since D_3O^+ is stronger than H_3O^+ by ~ 2-3 times, the solvent isotopic effect i.e k $(H_2O)/k(D_2O) <$ 1. But in the present case since the rate is retarded by the H^+ ion, this ratio should be greater than 1, as observed in the present case. The proton inventory technique provides information about the number of protons undergoing a significant change in bonding in the transition state (TS) with respect to the ground state. Equation (2) which is also referred as Gross-Butler equation, indicates the relationship between the observed rate constant in the mixtures of H_2O and D_2O with known isotopic composition and the fractionation factors (ϕ) for the exchangeable protons and n is the atom fraction of D in the medium.

$$K_o/k_n = \Pi^{TS} (1-n + n\phi_i)/\Pi^{RS} (1- n + n\phi_j) \qquad \text{------ (2)}$$

In the above equation ϕ_i and ϕ_i represents the isotopic fractionation factors for isotropically exchangeable hydrogenic sites in the transition and reactant sites, respectively. If we assume that the reaction proceeds through a single transition state equation (2) can be transformed into equation (3)

$$(K_o/k_n)^{1/2} = 1+ n(\phi_j-1) \qquad \text{-------(3)}$$

The above equation indicates a linear relationship between $(K_o/k_n)^{1/2}$ and n which is shown in fig 6 (R^2=0.99). The slope $(\phi_i-1) = 0.49$ and 0.47, from which the fractionation factor ϕ_j is found to be 1.49 and 1.47 for AG50 and PB5 respectively.

Table 5. Effect of varying D_2O-H_2O composition on the rate at 301 K with [Dye] $=2.0\times10^{-5}$ mol dm^{-3} [CAT] $=1.0\times10^{-4}$ mol dm^{-3} [HCl] $=4.0\times10^{-3}$mol dm^{-3}

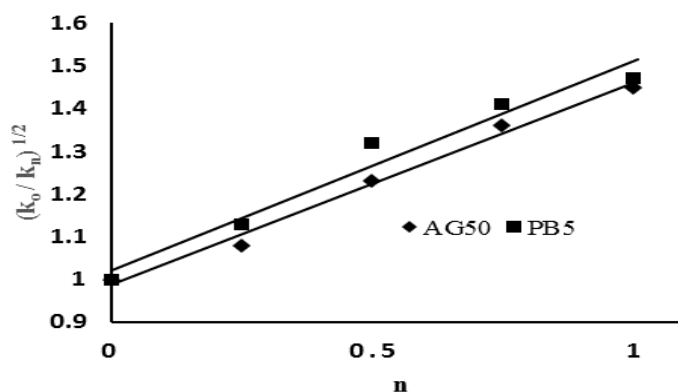| D_2O-H_2O mixture	Atom fraction of deuterium(n)	$10^4\ k_n$ (mol dm^{-3}s^{-1})		$(k_o/k_n)^{1/2}$	
		Acid Green 50	Patent Blue 5	Acid Green 50	Patent Blue
0	0.000	4.20	1.96	1.00	1.00
25	0.248	3.60	1.53	1.08	1.13
50	0.497	2.77	1.12	1.23	1.32
75	0.745	2.25	0.98	1.36	1.41
96	0.954	2.00	0.90	1.45	1.47

Fig.6: Plot of log $(k_o/k_n)^{1/2}$ Vs n

Effect of temperature and calculation of activation parameters: The effect of temperature on the rate was studied by performing the kinetic measurements at 5 different temperatures (301,305,309,313 and 317) keeping all other experimental conditions constant. The Arrhenius plot of log k$^{'}$ Vs1/T was found to be linear (Fig 7). The activation parameter (Ea), Enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), free energy of activation ($\Delta G^{\#}$) and frequency factor (A) were obtained with the help of Arrhenius plot. The activation parameters are tabulated in the table 6.
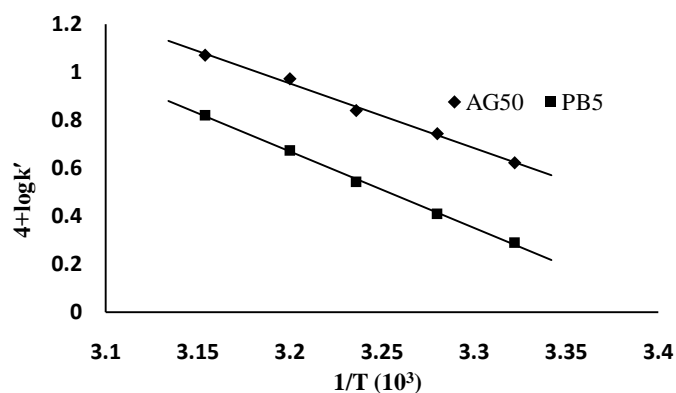

Fig.7: Plot of log k$'$ vs 1/T

Table 6. Effect of temperature on the rate of the reaction and corresponding values of activation parameters for the oxidation of AG50 and PB5 by CAT in acid medium with [Dye] =2.0x10^{-5} mol dm^{-3} [CAT] = 1.0x10^{-4} mol dm^{-3} [HCl] = 4.0x10^{-3} mol dm^{-3}

Temperature(K)	10^4 k$'$(mol dm^{-3} s^{-1})		Activation parameters		
	AG50	PB5		AG50	PB5
301	4.20	1.96	Ea(KJ mol^{-1})	51.30	66.93
305	5.55	2.59	△H$^{\#}$(KJ mol^{-1})	48.75 ± (0.04)	64.37 ± (0.03)
309	6.92	3.49	△G$^{\#}$(KJ mol^{-1})	93.88 ± (0.06)	95.64 ±(0.05)
313	9.39	4.73	△S$^{\#}$(JK^{-1} mol^{-1})	-147.03± (0.1)	-101.83±(0.08)
317	11.74	6.62	log A	5.56 ± (0.05)	7.92 ± (0.04)

Spectral analysis of the color removal mechanism by CAT
Spectral analysis of treated and untreated wastes: The spectral analysis was made under standard conditions on untreated dye solution and treated dye solution. The results are shown as curves a, b and c in fig. 1. It was found that the waster after treatment did not show any characteristic dye peaks in the wavelength range from 300 to 800 nm. This clearly indicated that the dye in the solution was oxidized into colorless organic products.

Analysis of the oxidized products formed after decolorization
Product analysis: The reaction mixture under standard concentrations was allowed to progress for 24 h at 301k. After the completion of the reaction (Which was monitored by TLC) the reaction products was neutralized by the addition of NaOH and was extracted with ethyl acetate. The reaction products were characterized with the help of LC-MS. The mass spectrum was obtained using electron impact ionization technique. The mass spectra showed a molecular ion peak at 238 amu and 324 amu (Fig. 8) indicating the structure of benzene-1, 3-disulphonic acid and (4-diethylamino-phenyl)-methanone.

Test for free radicals: Addition of reaction mixture to an aqueous solution of acrylamide did not initiate polymerization, which indicates that no free radical is involved or generated in the mechanism.
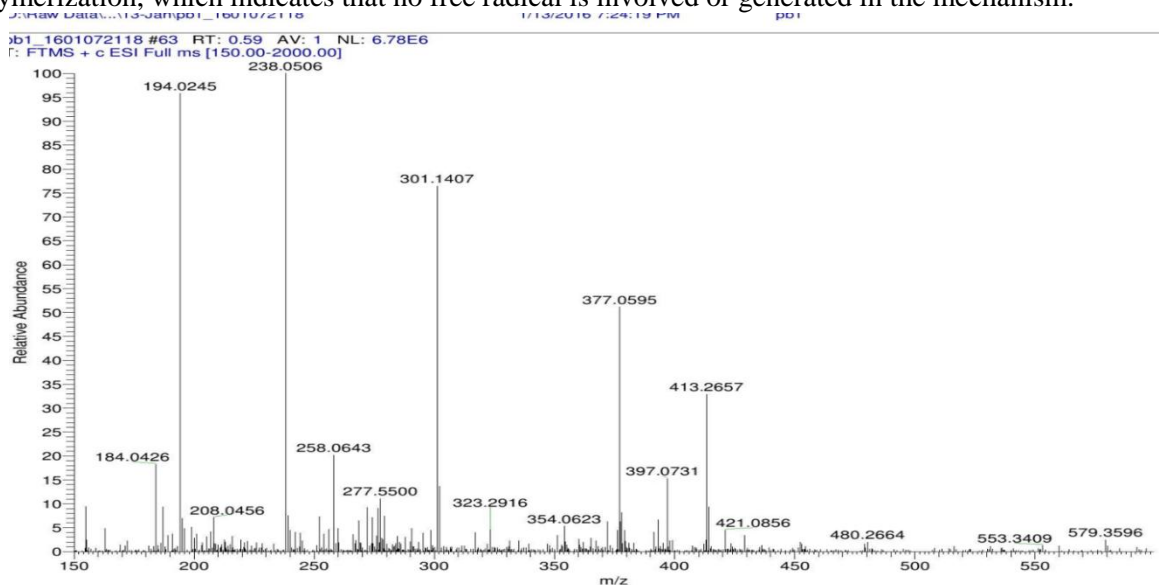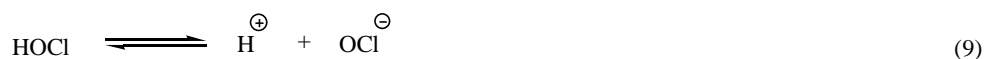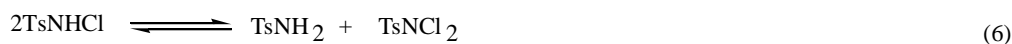

Fig 8: The mass spectra which showed a molecular ion peak at 238 amu and 324 amu indicating the structure of benzene-1, 3-disulphonic acid and (4-diethylamino-phenyl)-methanone

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Chloramine-T is known to be the oxidizing agent in both acidic and basic medium. These two oxidants generally undergoes two electron change in their reactions [23]. The solution of CAT act as strong electrolyte and it generates different types of reactive species, based on the pH of the solution. From the investigations of pryde and soper [24], Bishop and Jennings [23], and Hardy and Johnton [25], on organic N-haloamines have shown that similar equilibria exist in both acidic as well as in basic solutions. The possible equilibria that exist in aqueous solutions of CAT are as shown below.
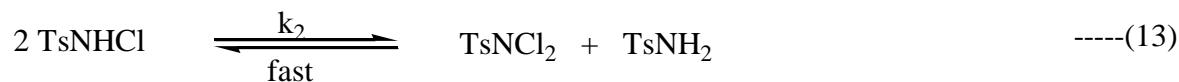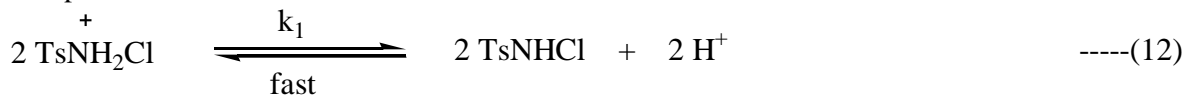
$$TsNClNa \rightleftharpoons TsNCl^{\ominus} + Na^{\oplus} \tag{4}$$

$$TsNCl^{\ominus} + H^{\oplus} \rightleftharpoons TsNHCl \tag{5}$$

$$2TsNHCl \rightleftharpoons TsNH_2 + TsNCl_2 \tag{6}$$

$$TsNHCl + H_2O \rightleftharpoons TsNH_2 + HOCl \tag{7}$$

$$TsNCl_2 + H_2O \rightleftharpoons TsNHCl + HOCl \tag{8}$$

$$HOCl \rightleftharpoons H^{\oplus} + OCl^{\ominus} \tag{9}$$

$$HOCl + H^{\oplus} \rightleftharpoons H_2OCl^{\oplus} \tag{10}$$

Further, formation of species of the type $TsNH_2Cl^+$ has been reported [26-27] with CAT and the protonation constant for the reaction, is found to be 1.02×10^2 at 25^0C.

$$TsNHCl + H^+ \rightleftharpoons TsNH_2Cl^+ \tag{11}$$

If HOCl is the reactive species then the rate law predicts a first order dependence of rate on $[CAT]_o$, and the rate is affected with the addition of PTS and if TsNHCl were to be the reactive species, then the rate law predicts a first order dependence of rate on $[CAT]_o$. Both the above cases are not observed in the present kinetics. Since the rate law predicts a second order dependence of rate on $[CAT]_o$, and $[H^+]$ and decreases with the addition of PTS, we can conclude $TsNCl_2$ is the most probable oxidizing reactive species for the oxidation of AG50 and PB5 by CAT. From the above discussion and experimental facts, scheme-1 is proposed to explain the reaction mechanism for the oxidation of AG50 and PB5 by CAT in HCl medium.

In the first step, the protonated oxidant (TsN^+H_2Cl) generates the free conjugate acid (TsNHCl), which undergoes disproportionation to give the active species $TsNCl_2$ The active species formed reacts with the substrate to form the complex (X). Later the complex (X) undergoes series of changes to give the final oxidized products.

$$2\,TsNH_2Cl^+ \underset{\text{fast}}{\overset{k_1}{\rightleftharpoons}} 2\,TsNHCl + 2\,H^+ \qquad \text{-----(12)}$$

$$2\,TsNHCl \underset{\text{fast}}{\overset{k_2}{\rightleftharpoons}} TsNCl_2 + TsNH_2 \qquad \text{-----(13)}$$

$$TsNCl_2 + S \underset{\text{slow}}{\overset{k_3}{\longrightarrow}} X \qquad \text{-----(14)}$$

$$X + H_2O \longrightarrow \text{products} \qquad \text{----(15)}$$

Scheme 1: A reaction scheme for the oxidative removal of color of AG50 and PB5 by CAT in acid medium

From equation (12) and (13) of scheme-1

$$k_1 = \frac{[TsNHCl]^2 [H^+]^2}{[TsNH_2Cl^+]^2} \qquad \text{-----(16)}$$

$$k_2 = \frac{[TsNCl_2] [TsNH_2]}{[TsNHCl]^2} \qquad \text{----(17)}$$

Substituting equation (17) in (16) and rearranging, we get

$$[TsNH_2Cl^+]^2 = \frac{[TsNCl_2][TsNH_2][H^+]^2}{k_1 k_2} \qquad \text{----(18)}$$

Rearranging equation (17),

$$[TsNHCl]^2 = \frac{[TsNCl_2] [TsNH_2]}{k_2} \qquad \text{----(19)}$$

If $[CAT]_t$ is the total effective concentration, then
$$[CAT]_t = [TsNH_2Cl^+] + [TsNHCl] + [TsNCl_2] \qquad \text{----(20)}$$

By substituting for $[TsNH_2Cl^+]$, $[TsNHCl]$ from equation (18) and (19) into equation (20) and solving for $[TsNCl_2]$, we get

$$[TsNCl_2] = \frac{k_1 k_2 [CAT]^2}{[TsNH_2][H^+]^2 + k_1[TsNH_2] + k_1 k_2[TsNCl_2]} \qquad \text{----(21)}$$

Since $[TsNCl_2] \ll [TsNHCl]$ equation (21) becomes

$$[TsNCl_2] = \frac{k_1 k_2 [CAT]^2}{[TsNH_2][H^+]^2 + k_1[TsNH_2] + k_1 k_2} \qquad \text{----(22)}$$

From equation (14),
Rate$= k_3 [TsNCl_2] [S]$ ---- (23)
Finally substituting equation (22) in equation (23), we get

$$\text{Rate} = \frac{k_1 k_2 k_3 [CAT]^2 [S]}{[TsNH_2][H^+]^2 + k_1[TsNH_2] + k_1 k_2} \qquad \text{----(24)}$$

Rate law (24) satisfactorily fits well to the observed kinetic data i. e second order dependence of rate on [CAT], first order dependence on [S] and inverse fractional order on [H$^+$] and [PTS].

The mechanism is also supported by the solvent isotope effects which gives an idea about the number of protons transferred prior to the rate determining step in both the medium. Since D_3O^+ and OD^- are strong acid and base than H_3O^+ and OH^- the rate increases in D_2O medium for a fast equilibrium H$^+$ or OH$^-$ transfer. In the present case we observe that the value of k (D_2O) / k (H_2O) <1 thus confirming the above theory. Dielectric constant of the medium gives an idea about the nature of the reactive species in the rate determining step. According to Amis

$\ln k = \ln k_o - (NZ_A Z_B e^2 / DRTr_{\#})$ where k_o = rate constant in a medium of infinite dielectric constant
Z_A and Z_B = charges on the ions
$r_{\#}$ = radius of the activated complex

For an interaction between two dipoles or an ion - dipole system a plot of log k′ v/s 1/D gives a straight line, with a negative slope for a reaction between a negative ion and a dipole or between two dipoles-dipole, while a positive slope for a positive ion-dipole interaction.

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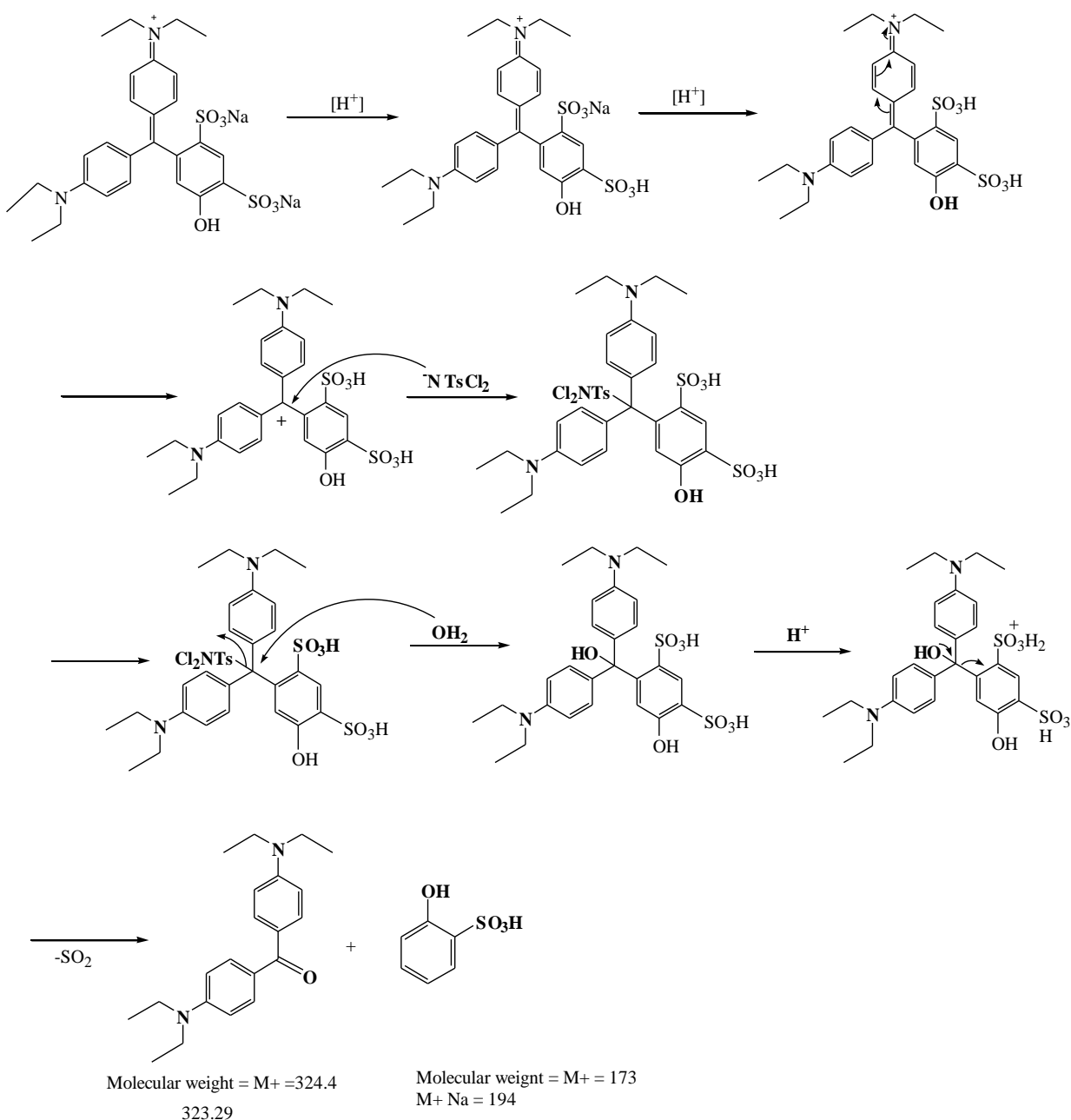
Scheme 2: A detailed mechanism for the oxidative decolorization of Patent blue 5 by CAT in HCl medium

The former concept agrees with the present observations, i.e. a negative ion and a dipole interaction involved in the rate determining step. The rate of the ionic reactions is also influenced by the charges carried by the ions and the ionic strength of the medium. According to equation, $\log k / k_o = 1.02\ Z_A\ Z_B\ (I)^{1/2}$ a plot of $\log k$ Vs $(I)^{1/2}$ will give a straight line of slope $1.02\ Z_A Z_B$ and intercept is $\log k_0$. If one of the reactants is a neutral molecule, $Z_A Z_B$ is zero and the rate constant is expected to be independent of the ionic strength which holds good in the present case. The constancy of rate constant on addition of PTS, Chloride ions also supports the proposed mechanism and derived rate law. The proposed mechanism is also supported by observed activation parameters for both the substrates.

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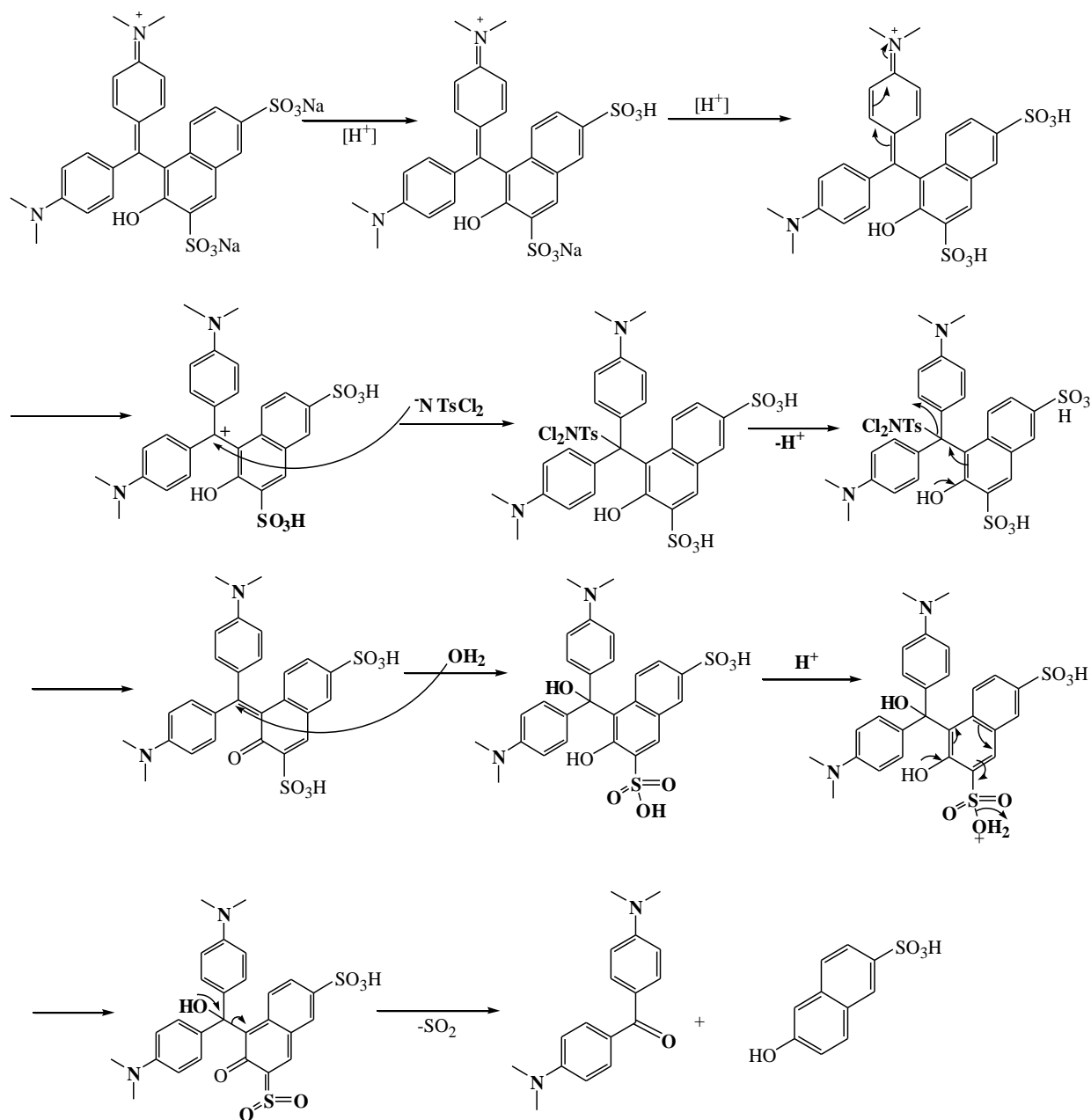
Scheme 3: A detailed mechanism for the oxidative decolorization of Acid Green 50
by CAT in HCl medium

The activation parameters like energy of activation and other thermodynamic parameters are moderate. The energy of activation is less for the fast reaction and vice-versa, which indicates that the reaction is enthalpy controlled. The negative values of $\Delta S^{\#}$ indicates that the transition state is highly ordered compared to that of initial ground state which is due to greater degree of solvation during the formation of activated complex.

APPLICATIONS

Triphenyl methylene dyes is one of the most used synthetic colorants in the food industry and other applications. If such industrial wastewaters are not conveniently treated before discharge, their impact on the surrounding ecosystems may be dramatic. Some few studies have focused on the fate of these dyes

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upon application of non-electrochemical advanced oxidation processes. But as far as we are concerned its removal by mild oxidizing agents has not been reported yet. The latter process is of great interest for the removal of food azo dyes. Hence the main objective of this research was to elucidate the mechanism of oxidative decolorization of TPM dyes and to obtain the rate law consistent with the experimental results. Also the present work will be a foundation for those researchers who are working on colours used in food additives and to know the mechanism behind the harmful effects caused by them.

CONCLUSIONS

Chloramine-T assisted oxidation has been proven a promising technology for the removal of food colors like AG50 and PB5 present in water effluents. The kinetics of Oxidation of both the dyes was studied by CAT as an oxidant in acid medium at 301 K. The experimental rate law was $-d[CAT]/dt = k[AG50]^{1}[CAT]^{1.99}[H^+]^{1.42}[PTS]^{-0.73}$ and $-d[CAT]/dt = k\ [PB5]^{1}[CAT]^{2.05}[H^+]^{1.13}[PTS]^{-0.78}$. The oxidation kinetics was also studied by varying the ionic strength, dielectric constant of the medium. Finally the reaction was studied at different temperatures and the products were isolated. Based on the observations made an appropriate rate law was derived and a possible mechanism was suggested.

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