



## RESEARCH ARTICLE

### KINETIC AND MECHANISTIC INVESTIGATION OF ALLURA RED AC BY CHLORAMINE-T IN HCL MEDIUM: A SPECTROPHOTOMETRIC APPROACH

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#### ARTICLE INFO

##### Article History:

Received 16<sup>th</sup> May, 2016

Received in revised form

10<sup>th</sup> June, 2016

Accepted 27<sup>th</sup> July, 2016

Published online 31<sup>st</sup> August, 2016

##### Key words:

ARED, CAT, kinetics,  
Reaction mechanism, HCl.

#### ABSTRACT

Allura Red AC (ARED) is an azo dye allowed as a food additive in the European Union and other developed countries. The kinetics of oxidation of ARED with Chloramine-T in HCl medium has been studied spectrophotometrically at 302K. The reaction exhibited first-order dependence of rate on both [ARED] and [CAT], inverse fractional order dependence of rate on [HCl]. Solvent composition shows negative effect indicating the involvement of negative ion-dipolar molecule in the rate determining step. Variation of ionic strength of the medium and addition of halide ions showed negligible effect. Addition of *p*-toluenesulphonamide, the reduction product retards the rate. Oxidation products were isolated and characterized and were identified as 1, 2-naphthaquinone and 4-methyl anisole which are often allergic to human beings. The effect of temperature is studied at different temperatures and Activation parameters have been evaluated. Plausible mechanism and related rate law have been deduced for the observed kinetics.

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Citation: Muddegowda Harsha, Muddegowda Umashankar, Kitappa Malavalli Mahadevan, Sannaiah Ananda and Manikyanahalli Narasigowda Kumara, 2016. "Kinetic and mechanistic investigation of Allura red ac by Chloramine-t in HCL medium: A Spectrophotometric approach", *International Journal of Current Research*, 8, (08), 36931-36938.

## INTRODUCTION

Allura Red AC (ARED) is an azo dye allowed as a food additive in the European Union and other developed countries. Allura Red AC consists essentially of disodium 2-hydroxy-1-(2-methoxy-5-methyl-4-sulphonatophenylazo) naphthalene-6-sulphonate and subsidiary coloring matters, together with sodium chloride and/or sodium sulphate as the principal uncolored components. It is found in soft drinks, candy, children's medications, cereal, beverages, snacks, gelatin desserts, baked goods, and ice cream. It was originally introduced in the United States as a replacement for the use of amaranth as a food coloring. It is approved by the food and drug administration for use in cosmetics, drugs and food by the United States. It is the most commonly used dye replacing other dyes like amaranth and erythrosine. Currently, Allura

Red AC is an allowed synthetic food coloring substance in the European Union with a maximal allowed use level of 25 to 500 mg/kg food for various foodstuffs. Allura Red AC is also allowed in alcoholic beverages at levels up to 200 mg/L and non-alcoholic beverages up to 100 mg/L. The safety of this colorant is highly controversial. The Delhi High Court has banned import of food additive Allura Red AC, as a coloring agent, after the country's food safety authority admitted it was a prohibited chemical. The literature reveals that while some sensitivity reactions after Allura Red AC intake (urticaria, rhinitis and asthma) have been reported, mostly when Allura red AC is taken within mixtures of other synthetic colors. To the best of our knowledge, the oxidation of Allura red AC by any oxidant has not been reported from its mechanistic point of view. Hence the oxidation-kinetic studies is of much benefit in understanding the mechanistic profile of Allura red AC in acidic media. Sodium *N*-chloro-*p*-toluenesulfonamide (Chloramine-T) is the most important member of organic haloamine family and behaves as a mild oxidizing agent in both acidic and basic medium (Cambell and Johnson, 1978;

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Manjunatha et al., 2015; Armesto et al., 1998; Gupta et al., 1998; Mahadevappa et al., 1981; Ramachandra et al., 1996; Puttaswamy et al., 2005; Prashanth et al., 2014). A 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 amaranth by various oxidizing agents (Nadupalli et al., 2011; Chung-Hsin Wuet al., 2005; Dachipally and Jonnalagadda, 2011). Recently, the kinetics and mechanistic investigation of oxidative decolourisation of Sun Set Yellow by peroxydisulphate has been reported by Gemeay et al. (2007). Vinod and Puttaswamy have studied the kinetics of oxidation of sun set yellow by CAT in the presence of both acidic and alkaline medium (Vinoda et al., 2009). In view of the above, the present communication reports for the first time on the kinetic and mechanistic aspects of oxidative decolourisation of ALLURA RED AC with CAT in acid medium.

## MATERIALS AND METHODS

2.1 CAT (Sigma Aldrich) was purified by the method of Morris et al. (1948). An aqueous solution of CAT was prepared, standardized iodometrically and stored in amber colored stoppered bottles until further use to prevent its photochemical deterioration. The concentrations of stock solutions were periodically determined. Allura red AC (food additive) was purchased from Aldrich and was used as received without any further purification. An aqueous solution of Allura red AC was freshly prepared whenever required. All other chemicals used were of analytical grade. Triple distilled water was used for preparing solutions.

### Kinetic measurement

The kinetic runs were performed under pseudo-first-order conditions by ensuring an excess of CAT over Allura red AC in hydrochloric acid at 302 K using UV-Vis spectrophotometry (Shimadzu-1800). A constant temperature was maintained with an accuracy of  $\pm 0.1^\circ\text{C}$ . Reactions were carried out in glass stoppered Pyrex boiling tubes whose outer surface were coated black to eliminate any photochemical effects. The oxidant as well as requisite amounts of ARED, HCl solutions and water (to keep the total volume constant for all runs) were taken in separate tubes. The absorbance reading were thermo stated for nearly 30 minutes at 302 K. The reaction was initiated by the rapid addition of a measured amount of oxidant to the stirred reaction mixture. 3 ml of aliquot of the solution was pipetted into a cuvette placed in the spectrophotometer. Absorbance measurements were made at  $\lambda_{\text{max}} = 502 \text{ nm}$  (ARED dye, Figure 1) for more than 75% of completion of the reaction. Plots  $\log(\text{abs})$  Vs time were made to evaluate the pseudo-first-order rate constants  $k$  ( $\text{s}^{-1}$ ). Regression analysis of the experimental data was carried out on fx-991MS scientific calculator to evaluate the regression coefficient. Figure 2 shows the UV-Vis spectrum of the oxidized products.

### Reaction stoichiometry

Reaction mixtures containing different ratios of CAT and ARED in  $4 \times 10^{-3} \text{ mol dm}^{-3} \text{ HCl}$  were allowed to react for 24hrs at 302k. The determination of unreacted CAT in the reaction

mixture showed that one mole of the dye consumed two moles of CAT, leading to products like 1,2Naphthoquinone and 4-methyl anisole. The overall reaction can be represented as

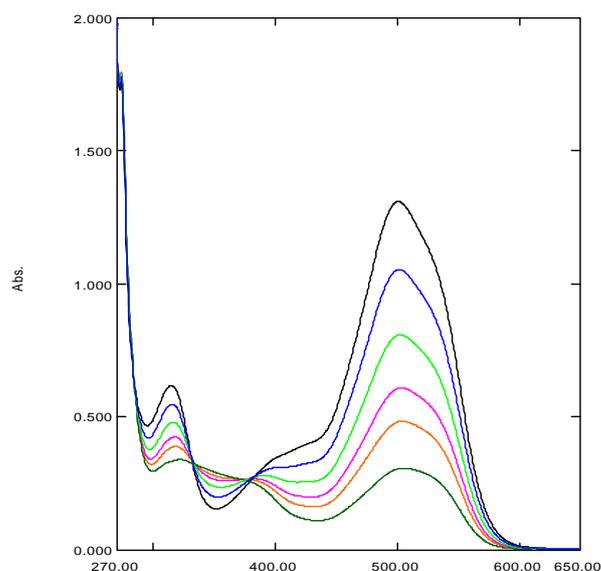


Fig. 1. UV-Vis spectra of Allura Red AC at different initial concentration

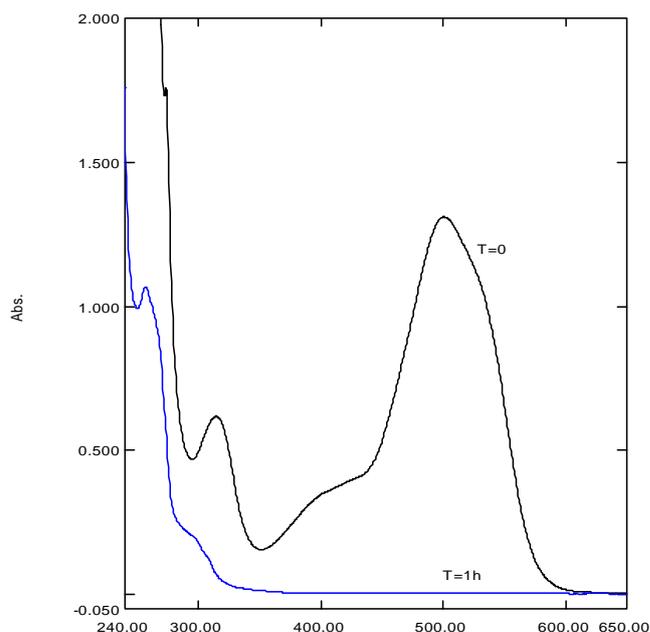
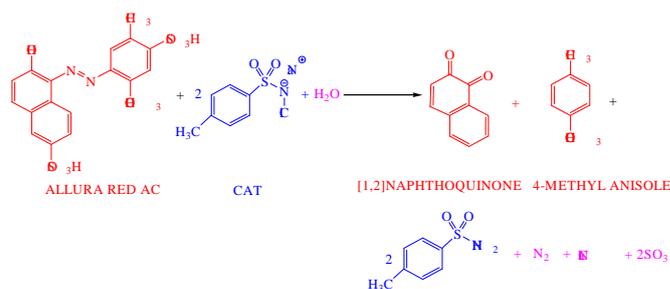


Fig. 2. The disappearance of peak at 502nm indicates the formation of product



### Product analysis

The reaction mixture in the stoichiometric ratio in the presence of HCl media was allowed to progress for 24 hrs at 302 K under stirred condition. After completion of the reaction (monitored by TLC and also by the disappearance of peak at 502nm and appearance of new peak at 257 nm), the reaction products were extracted with ether. Evaporation of ether layer was followed by column chromatography on silica gel (60-120 mesh). The organic products were identified as 1, 2-naphthaquinone and 4-methyl anisole which was confirmed by LC-MS analysis. The mass spectra showed a molecular ion peak at 159 amu (Figure 3) and 122amu (Figure 4) indicating the structures for 1,2naphthoquinone and 4-methyl anisole respectively. The oxidized products were also further characterized by  $H^1$ -NMR analysis (Figure 5 and 6 respectively)

The reduction product of CAT, *p*-toluenesulphonamide (PTS) was detected by TLC. It was further confirmed by its melting point of 138° C. It was also observed that there was no further oxidation of the products formed under the given kinetic conditions

## RESULTS AND DISCUSSION

### Effect of varying reactant concentration on the rate

With the oxidant in excess and keeping  $[CAT]_0$ ,  $[HCl]$  and temperature constant, plot of  $\log(\text{abs})$  Vs time was found to be linear ( $R^2=0.9988$ ) indicating a first order dependence on  $[ARED]_0$ . The values of Pseudo-First order rate constants ( $k \text{ s}^{-1}$ ) are listed in Table 1.

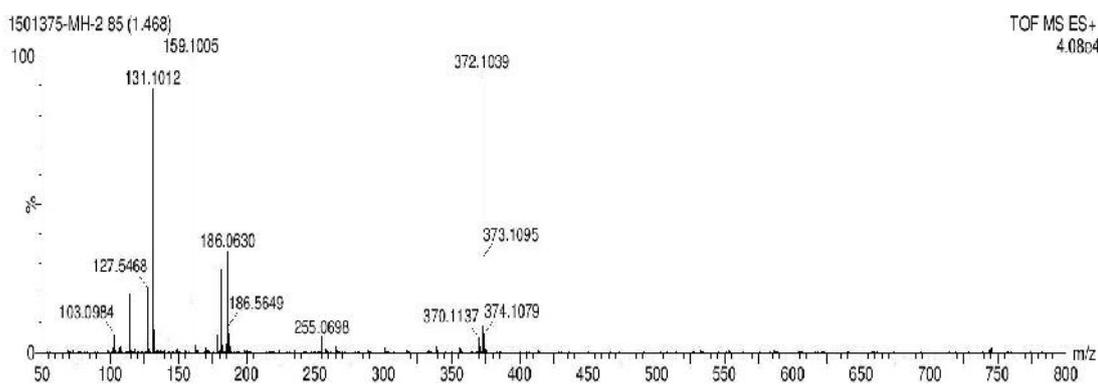


Fig. 3. LC-MS spectra of 1,2naphthoquinone with its molecular ion peak at 159 amu

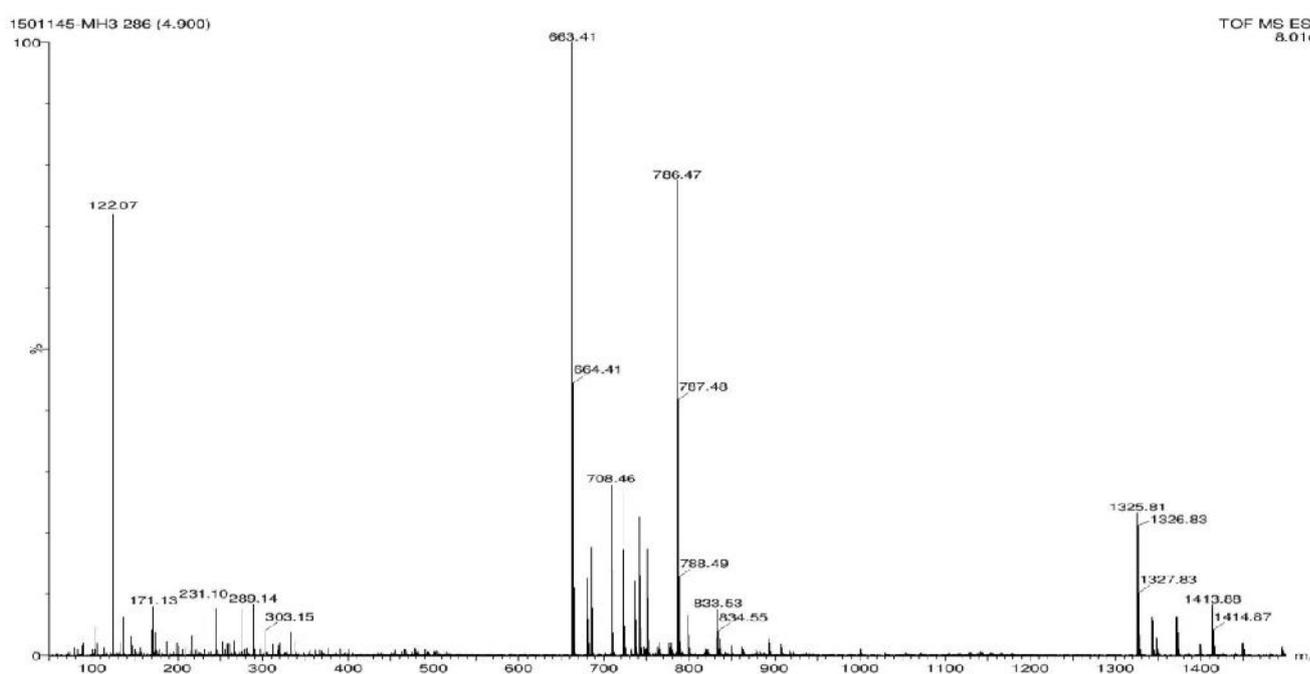


Fig. 4. LC-MS spectra of 4-methyl anisole molecular ion peak at 122 amu

NMR: (400 MHz  $CDCl_3$ )

1,2 naphthoquinone: 8.1(D, 1H), 7.2-7.6 (dd, 4H), 6.4-6.5(d,1H)

4-methyl anisole: 2.25(S, 3H), 3.7(S, 3H), 6.8-7.1(dd, 4H)

Also under the same experimental conditions an increase in  $[CAT]_0$  increased the value of  $k$  (Table 1). Plot of  $\log k$  Vs  $\log [CAT]$  were linear ( $R^2=0.991$ ) with a slope of 1.06 which indicated a first order dependence on  $[CAT]$  (Figure 7).

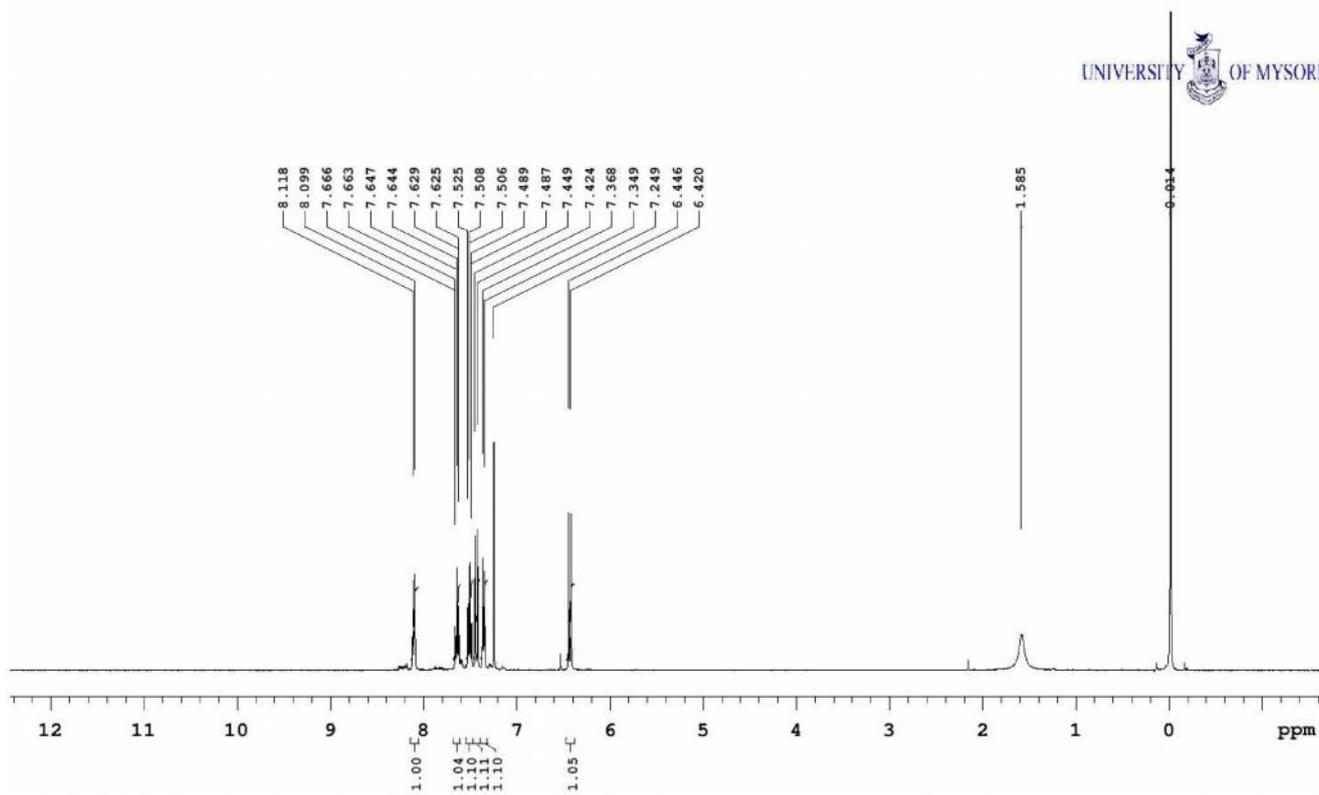


Fig. 5.  $H^1$ -NMR spectra of 1, 2 naphthoquinone

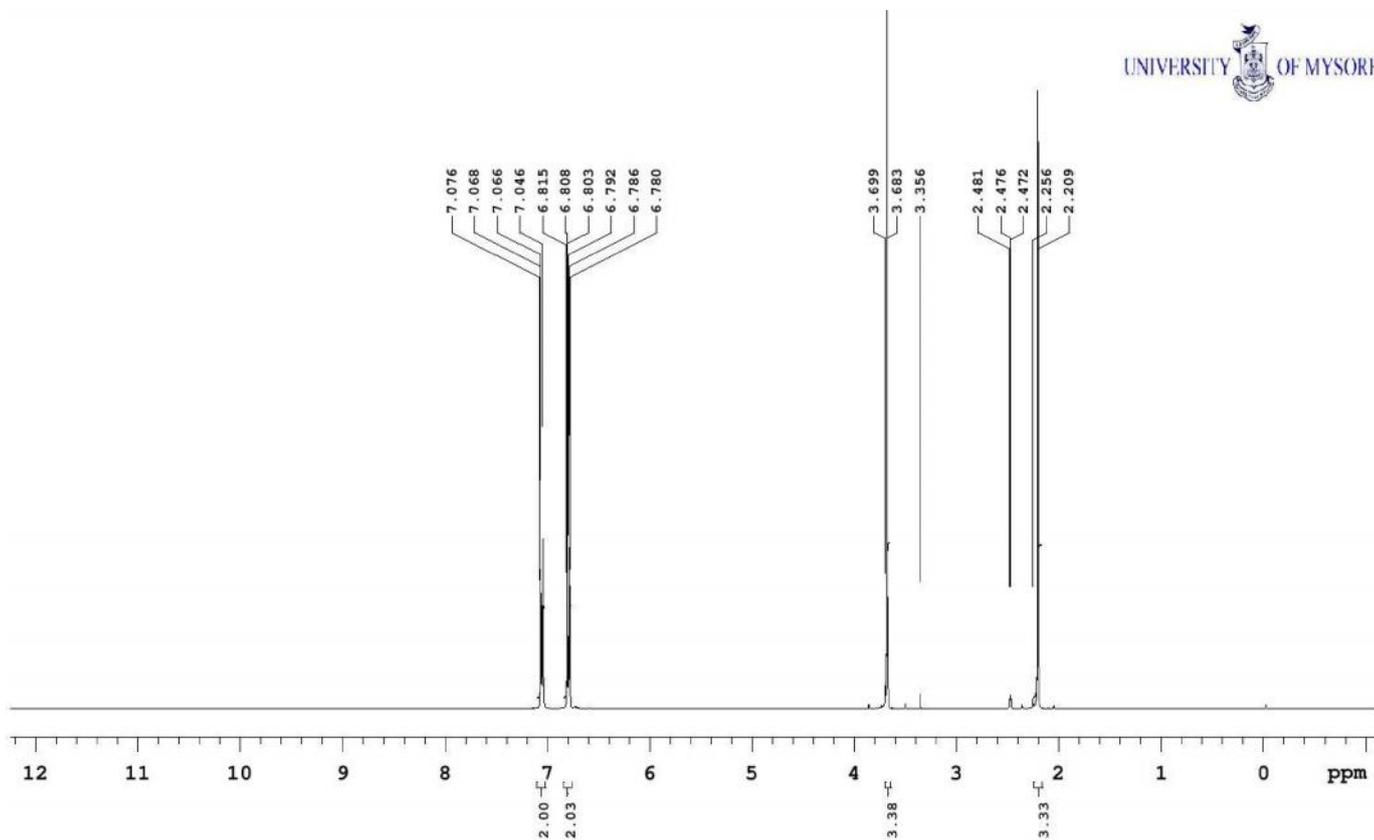


Fig. 6.  $H^1$ -NMR spectra of 4-methyl anisole

**Table 1. Effect of varying [AREd], [CAT], [HCl] on the reaction rate at 302k**

$10^5$ [AREd] (Mol dm <sup>-3</sup> )	$10^3$ [CAT] (Mol dm <sup>-3</sup> )	$10^3$ [HCl] (Mol dm <sup>-3</sup> )	$10^5 k$ (s <sup>-1</sup> )
2.0	2.0	4.0	18.79
3.0	2.0	4.0	18.08
4.0	2.0	4.0	17.79
5.0	2.0	4.0	16.87
6.0	2.0	4.0	15.89
4.0	0.4	4.0	3.50
4.0	0.8	4.0	6.18
4.0	1.2	4.0	9.51
4.0	1.6	4.0	14.69
4.0	2.0	4.0	17.79
4.0	2.4	4.0	22.49
4.0	2.0	3.0	19.31
4.0	2.0	4.0	17.79
4.0	2.0	5.0	16.35
4.0	2.0	6.0	15.99
4.0	2.0	7.0	15.03
4.0	2.0	8.0	14.58

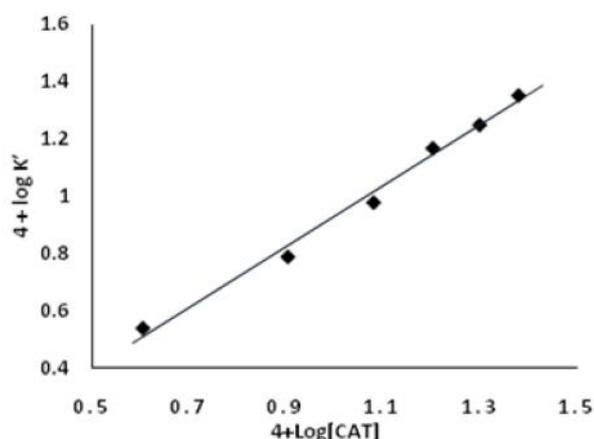


FIG. 7: Plot of log k' VS log [CAT]

**Effect of varying HCl concentration on the rate**

The effect of HCl on the rate of the reaction was studied by varying in the concentration range between  $3.0 \times 10^{-3}$ - $8.0 \times 10^{-3}$  mol dm<sup>-3</sup> (table 1). Plot of log k versus log [HCl] were linear ( $R^2=0.993$ ) with a slope of -0.30 which indicated an inverse fractional order dependence on [HCl] (Figure 8).

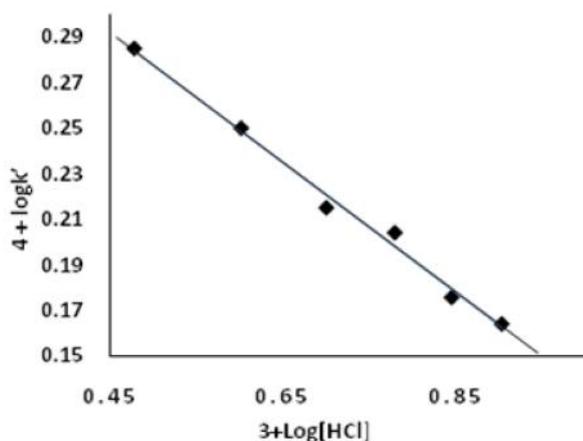


FIG. 8: Plot of log k' VS log [HCl]

**Effect of halide ions and ionic strength on the rate**

Addition of halide ions, Cl<sup>-</sup> and Br<sup>-</sup> ions in the form of their sodium salts ( $2.0 \times 10^{-3}$ - $10.0 \times 10^{-3}$  mol dm<sup>-3</sup>) had negligible effect on the reaction rate. This suggests that no interhalogen or free halogen is formed in the reaction sequence. Ionic strength ( $\mu$ ) of the medium was varied by varying the concentration of Sodium perchlorate (NaClO<sub>4</sub>) (0.1-0.4 mol dm<sup>-3</sup>). No significant effect was noticed. It indicates the involvement of non-ionic species in the rate determining step. Hence no attempt was made to keep ionic strength of the medium constant during kinetic runs.

**Effect of p-toluenesulphonamide and dielectric constant (D) on the rate**

Addition of the reaction product (PTS) retards the rate of the reaction (Table 2). Plot of log k Vs log [PTS] were linear ( $R^2=0.999$ ) with a slope of -0.576 which indicated an inverse fractional order dependence on [PTS] (Figure 9). The effect of solvent on the reaction kinetics has been discussed in detail in the well-known monographs of Moelwyn-Hughes (1961) Benson (1960) Frost and Pearson (1961) Laidler (1963) Amis (1966) and Entelis and Tiger (1976). The solvent composition was varied by adding methanol (0%-30%). The rate of the reaction decreased with the increase in the methanol content of the reaction medium (table 3) and plot of log k vs 1/D was linear (figure. 10  $R^2=0.9847$ ) with negative slope. Blank experiments with methanol indicated that the oxidation of methanol was negligible. The values of D for various MeOH-H<sub>2</sub>O mixtures reported in the literature (1932) were employed.

**Table 2. Effect of varying PTS on reaction rate with [AREd] =  $4.0 \times 10^{-5}$  mol dm<sup>-3</sup> [CAT] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> [HCl] =  $4.0 \times 10^{-3}$  mol dm<sup>-3</sup>**

$10^4$ [PTS] (mol dm <sup>-3</sup> )	$10^5 k$ (s <sup>-1</sup> )
0.5	15.13
1.0	10.39
1.5	8.04
2.0	6.82
2.5	6.05

**Table 3. Effect of varying Dielectric constant (D) of the medium on reaction rate with [AREd] =  $4.0 \times 10^{-5}$  mol dm<sup>-3</sup> [CAT] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> [HCl] =  $4.0 \times 10^{-3}$  mol dm<sup>-3</sup>**

MeOH(%V/V)	D	$10^5 k$ (s <sup>-1</sup> )	1/D	5 + log k
0	76.73	17.79	0.0130	1.25
10	72.37	14.31	0.0138	1.15
20	67.38	9.835	0.0148	0.99
30	62.71	5.583	0.0159	0.75

**Effect of temperature on the rate and calculation of activation parameters**

The reaction was studied at different temperatures in the range 302-318 K keeping other experimental conditions constant. Arrhenius plot of log k Vs 1/T were plotted (Figure 11) and with the help of the graph activation parameters were evaluated and average values for each parameter is reported along with errors (Table 4)

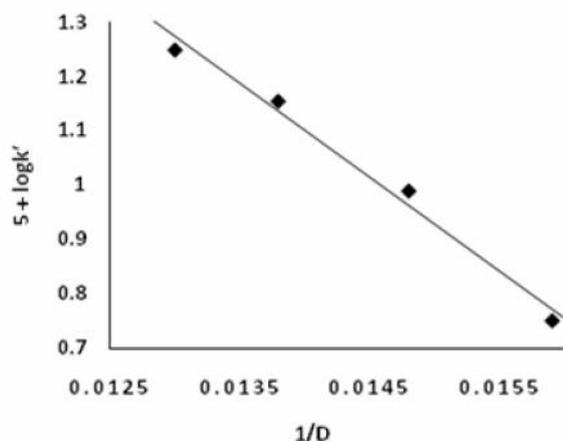


FIG. 10: Plot of log k' Vs 1/D

Table 4. Temperature dependence on reaction rate and values of composite activation parameters with  $[ARED] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[CAT] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[HCl] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$

Temperature (K)	$10^4 k \text{ (s}^{-1}\text{)}$	Activation parameters
302	1.78	$E_a \text{ (KJ mol}^{-1}\text{)} = 60.32$
306	2.59	$\Delta H^\ddagger \text{ (KJ mol}^{-1}\text{)} = 57.71 \pm (0.05)$
310	3.53	$\Delta G^\ddagger \text{ (KJ mol}^{-1}\text{)} = 97.06 \pm (0.8)$
314	4.70	$\Delta S^\ddagger \text{ (JK}^{-1}\text{mol}^{-1}\text{)} = -125.32 \pm (0.5)$
318	6.54	$\log A = 6.706 (\pm 0.01)$

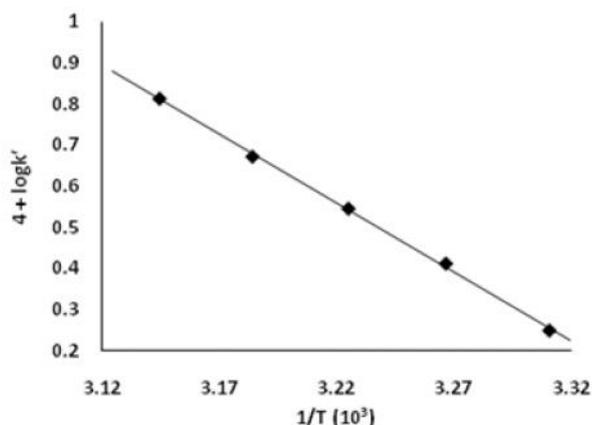


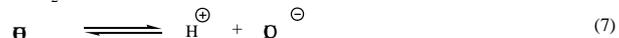
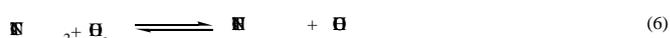
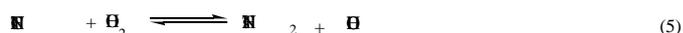
FIG. 11: Plot of log k' Vs 1/T

### Test for free radicals

Addition of reaction mixture to aqueous acrylamide monomer solutions did not initiate polymerization, indicating the absence of in situ formation of free radical species in the reaction sequence

## DISCUSSION

Chloramine-T behaves as a strong oxidizing species in aqueous solutions (Bishop and Jennings, 1958). Depending on the pH of the medium; CAT furnishes (Bishop and Jennings, 1958; Hardy and Johnston, 1972; Soper, 1924) following types of reactive species in solutions:

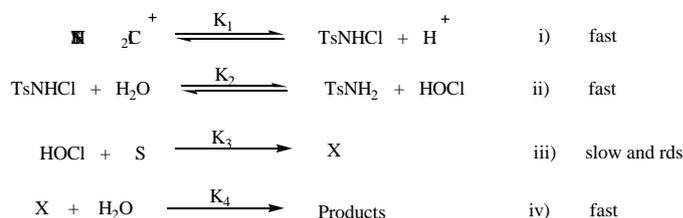


Therefore the possible oxidizing species in acidified CAT solutions are TsNHCl, TsNCl<sub>2</sub>, HOCl, and possibly H<sub>2</sub>O<sup>+</sup>Cl. Further, formation of species of the type TsNH<sub>2</sub>Cl<sup>+</sup> has been reported (Narayana and Rao, 1983; Subhashini *et al.*, 1985) with CAT and the protonation constant for the reaction,



Is found to be  $1.02 \times 10^2$  at 25<sup>o</sup>C

If TsNCl<sub>2</sub> were to be the reactive species, then the rate law predicts a second order dependence of rate on [CAT]<sub>o</sub>, which is contrary to the experimental observations. Since the rate of the reaction is retarded by the addition of TsNH<sub>2</sub>, HOCl is the most probable oxidizing reactive species for the oxidation of Allura red AC in the present system. From the above discussion and experimental facts, **scheme 1** is proposed to explain the reaction mechanism for the oxidation of Allura red AC by CAT in HCl medium



### Scheme 1: A general scheme for the oxidative decolorization of Allura red AC by CAT in HCl medium

In the first step there is a formation of an unprotonated CAT due to deprotonation of TsNH<sub>2</sub> Cl<sup>+</sup>. In the second step unprotonated CAT undergoes hydrolysis to give TsNH<sub>2</sub> and HOCl. Here HOCl is the most probable oxidizing species for the oxidation of Allura red AC. In the next step (rate determining step) the reactive species forms a complex (X) with Allura red AC (S) and finally the complex formed undergoes series of changes to give the oxidized products.

If [CAT]<sub>i</sub> is the total effective concentration of CAT, then

$$[\text{CAT}]_i = [\text{TsNH}_2\text{Cl}^+] + [\text{TsNHCl}] + [\text{HOCl}] \quad (10)$$

From step (i) of scheme 1,

$$K_1 = \frac{[\text{TsNHCl}][\text{H}^+]}{[\text{N}_2\text{C}^+]} \quad \text{or} \quad \text{N}_2\text{C}^+ = \frac{[\text{N}][\text{H}^+]}{K_1} \quad (11)$$

From step (ii) of scheme 1,

$$K_2 = \frac{[\text{HOCl}][\text{TsNH}_2]}{[\text{H}_2\text{D}]} \quad \text{or} \quad [\text{TsNHCl}] = \frac{[\text{HOCl}][\text{TsNH}_2]}{K_2[\text{H}_2\text{D}]} \quad (12)$$

By substituting for  $[\text{TsNHCl}]$  from equation (12) into equation (11) we get

$$[\text{H}_2\text{C}^+] = \frac{[\text{H}^+][\text{HOCl}][\text{TsNH}_2]}{K_1 K_2 [\text{H}_2\text{O}]} \quad (13)$$

By substituting for  $[\text{TsNH}_2\text{Cl}^+]$ ,  $[\text{TsNHCl}]$  and  $[\text{HOCl}]$  from equation (13) and (12) into equation (10) and solving for  $[\text{HOCl}]$ , we get

$$[\text{HOCl}] = \frac{k_1 k_2 [\text{CAT}][\text{H}_2\text{O}]}{[\text{H}^+][\text{TsNH}_2] + K_1[\text{TsNH}_2] + K_1 K_2 [\text{H}_2\text{O}]} \quad (14)$$

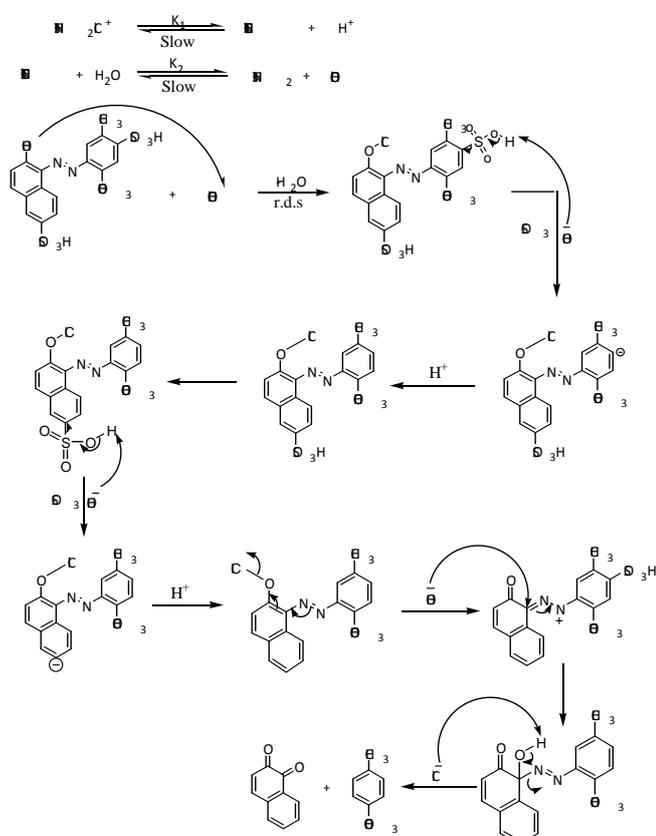
From slow step of Scheme 1,

$$\text{Rate} = k_3 [\text{HOCl}][\text{S}] \quad (15)$$

By substituting for  $[\text{HOCl}]$  from equation 14, the following rate law is obtained

$$\text{Rate} = \frac{k_1 k_2 k_3 [\text{CAT}][\text{S}][\text{H}_2\text{O}]}{[\text{H}^+][\text{TsNH}_2] + K_1[\text{TsNH}_2] + K_1 K_2 [\text{H}_2\text{O}]} \quad (16)$$

Rate law (16) satisfactorily fit well to the observed kinetic data wherein a first order dependence of rate on  $[\text{S}]$  and  $[\text{CAT}]$  and inverse fractional order on each  $[\text{TsNH}_2]$  and  $[\text{H}^+]$  on the rate of the reaction.



**Scheme 2. A detailed mechanism for the oxidative decolorization of Allura red AC by CAT in HCl medium**

## Conclusion

The kinetics of oxidative decolorisation of Allura red AC by CAT in HCl medium has been studied. In acid medium, the experimental rate law is found to be  $-d[\text{CAT}]/dt = K[\text{ARED}][\text{CAT}]^1[\text{H}^+]^{-2}[\text{PTS}]^{-2}$  where Y and Z are less than unity. The oxidation products were identified as 1, 2-naphthoquinone and 4-methyl anisole which are found to be toxic and allergic to human body. Thermodynamic parameters were calculated and suitable mechanism was proposed. HOCl is assumed to be the reactive species, which interacts with the food dye to give a complex which on further gets hydrolyzed to give the oxidized products. An appropriate rate law was derived which fits in to the proposed mechanism.

**Conflict of interest statement:** The authors declare that there are no conflicts of interest.

## Acknowledgements

One of the authors M.N.Kumarais grateful to the UGC F.No. 41-317/2012 (SR) Government of India, New Delhi, for financial support.

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