TRENDS IN SCIENCES 2022; 19(19): 6184 RESEARCH ARTICLE
https://doi.org/10.48048/tis.2022.6184

Chloramine-T Assisted Oxidative Decolourization of Tartrazine (Food Dye) in Acid Medium: Kinetic and Mechanistic Investigations

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Received: 1 July 2021, Revised: 17 September 2021, Accepted: 27 September 2021

Abstract

Tartrazine (TAZ) is a food color additive. It has been found to be contaminated with Benzidine or other carcinogens. It causes hypersensitivity reactions. The metabolites which are formed during digestion are responsible for the problems caused by these dyes. So, in the present work the kinetic and mechanistic aspects of oxidation of tartrazine have been studied with the help of mild oxidizing agent chloramine-T (CAT) in acid medium at 26 °C. The reaction exhibited 2nd-order dependence of rate with (CAT), inverse fractional order dependence of rate with (TAZ) and (H^+). 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 had no effect on the reaction rate. Addition of *p*-toluenesulphonamide (PTS), the reduction product retards the rate of reaction. Oxidation products were identified as 4-(5-Hydroxy-4-nitoso-pyrazol-1-yl)- benzenesulphonic acid and 4-amino-benzene sulphonic acid which are often allergic to human beings. These oxidation products were characterized by LC-MS. Activation parameters have been evaluated from Arrhenius-Eyring plots. The observed results have been explained by plausible mechanism and related rate law have been deduced.

Keywords: Tartrazine, Chloramine-T, Kinetics, Reaction mechanism, Oxidative decolorization

Introduction

Tartrazine also known as FD&C Yellow-5, is a synthetic lemon-yellow dye and it is used as a food colorant. It is not just in yellow food but it is also mixed with other colors to give various shades of green as well. Other than food, we find it in some drugs and vitamin supplements. In addition, it is used to color-soaps, cosmetics, moisturizers, shampoos and other hair care products. It is fed to chickens to make their egg yolks more yellow. The extensive use of tartrazine is mainly because of the fact that it is a cheap alternative to beta-carotene (100 % natural and beneficial to our health). Its chemical structure is similar to that of aspirin. So, people who are sensitive to aspirin are more likely to react to these dyes. People suffering from Asthma are also more likely to have a bad reaction to them. The molecules undergo oxidation to give simpler molecules which are not colored. Hence artificial food color elimination is a potentially valuable treatment. N-metallo-N-haloaryl sulphonamides generally known as N-haloamines contain halogen in the + 1 oxidation state and exhibit diverse behavior.

Chloramine-T (p-$CH_3C_6H_4SO_2NClNa.3H_2O$) is one the most important member of this class of compounds and behaves as oxidizing/analytical agent in both acidic and basic media [1-8]. It is commercially available, inexpensive, water tolerant, relatively nontoxic and easy to handle. Very limited information is available in the literature about the oxidative behavior of CAT towards food dyes. Very few literatures survey reveals on oxidation of amaranth by various oxidizing agents [9-11]. Recently, the kinetics and mechanistic investigation of oxidative decolourisation of Sunset Yellow by peroxydisulphate and CAT has been reported [12,13]. Even though the oxidation [14], degradation of tartrazine has been carried out by various methods [14-19] oxidation of tartrazine by CAT has not been reported. In view of the above, we systematically studied kinetics of oxidation of tartrazine by CAT in presence of different acids in order to understand the mechanistic aspects of these redox systems.

The main objective of this research was to elucidate the mechanism of oxidative decolorization of tartrazine and to obtain the rate law consistent with the experimental results.

Materials and methods

Materials

The oxidant (Chloramine-T hydrate 95 %), purchased from sigma Aldrich was recrystallized by the method applied by Morris *et al* [20] to get purified $NaC_7H_7SO_2NCl.3H_2O$. Further an aqueous solution of CAT was prepared, and was standardized iodometrically. tartrazine, also purchased from Aldrich was used as received without any further purification. Stock solutions of HCl, H_2SO_4, $HClO_4$, were prepared and their concentration were periodically determined. An aqueous solution of tartrazine, was freshly prepared whenever required. All other chemicals like PTS, NaCl, methanol used were of analytical grade and all solutions were prepared using triple distilled water.

Kinetic measurement

The kinetic measurements were made using UV-V is spectrophotometry at a constant temperature of 26 °C was maintained. All Kinetic runs were performed under pseudo 1st-order conditions i.e., an excess of CAT over TAZ is maintained in different acid medium. In certain cases, there is a possibility of degradation of Dye in the presence of sunlight. Hence the reactions were carried out in Pyrex boiling tubes **(**ground socket, with stopper) where the outer surface was coated black. Required amounts of TAZ, HCl and also water (to keep the total volume constant for all runs) were taken in 1 tube and the oxidant in the other. Both the tubes were thermostated at 26 °C for nearly 10 - 15 min in order to attain constant temperature. Later the reaction was initiated by the rapid addition of suitable amount of Oxidant in to the mixture containing TAZ. 3 mL of aliquot of the solution was pipetted into a cuvette and its absorbance was measured with the help of spectrophotometer. The absorbance was measured at λ_{max} = 427 nm (TAZ) for more than 2 half-lives (**Figure 1**). Plots of log (abs) Vs time was made to evaluate the pseudo 1st-order rate constants k′ (s^{-1}). **Figure 2** indicates the absorbance of decay of TAZ at different time intervals.

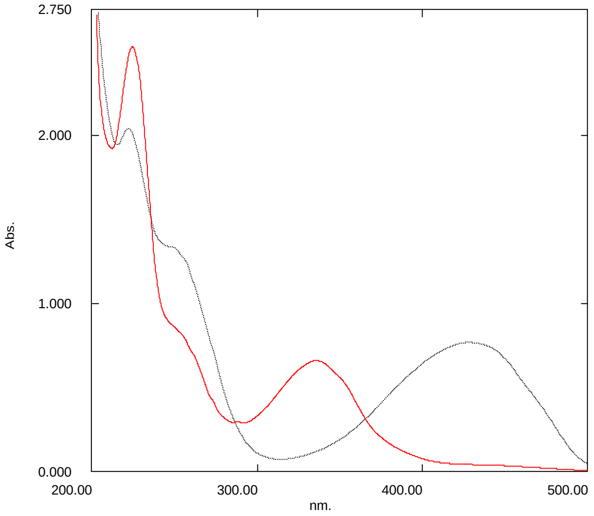


Figure 1 The disappearance of peak at 427 nm indicates the formation of products.

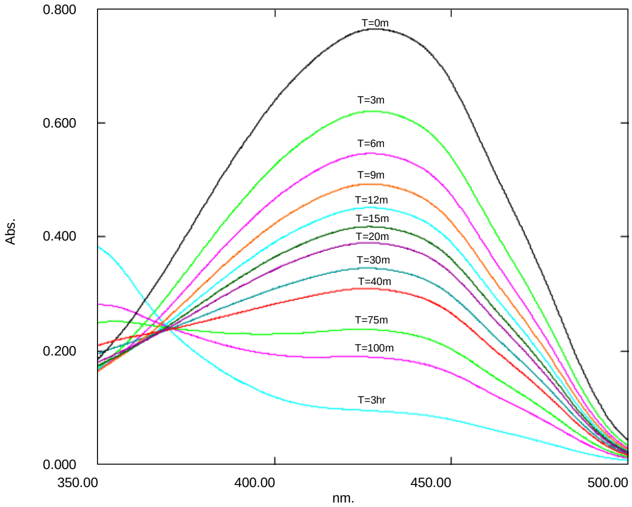


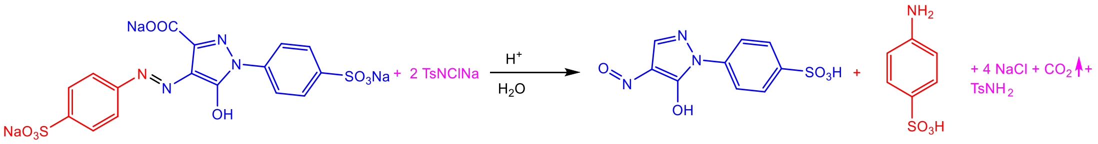
Figure 2 UV-Vis spectra of tartrazine at different time intervals.

Reaction stoichiometry

The reaction mixtures containing CAT and TAZ in 5×10^{-4} mol dm^{-3} HCl were allowed to react for 24 h at 26 °C. The unreacted oxidant in the reaction mixture was determined by iodometric titrations. The stoichiometry of the reaction was calculated with the help of the formula given below [21].

$E = (V_1 – V_2)$ Normality of $Na_2S_2O_3$ / 2 X Y

Where,
E = Number of moles of Chloramine-T required to oxidize 1 mol of the dye
V_1 = volume of $Na_2S_2O_3$ consumed for oxidant solution
V_2 = volume of $Na_2S_2O_3$ consumed after completion of reaction
X = volume of reaction mixture pipetted during titration
Y = molarity of the substrate
The analysis showed that 1 mole of tartrazine consumed 2 moles of CAT. The observed stoichiometry can be represented as below scheme (Scheme 1)



(1)

Scheme 1 Stoichiometry for the oxidation of tartrazine by CAT.

Characterization of products

The reaction mixture in stoichiometric proportion was allowed to react in the presence of acid for 24 h at 26 °C under stirred condition. Later the reaction products were neutralized with NaOH and extracted with ether. The organic products were identified by using TLC technique and separation was achieved using silica gel (60 - 100 mesh) column chromatography and using hexane/ethyl acetate (9:1) as mobile phase. The reaction products were identified as 4-(5-Hydroxy- 4-nitoso-pyrazol-1-yl)-benzenesulphonic acid and 4-amino benzene sulphonic acid. These products were separated by column chromatography and were confirmed by LC-MS. The mass spectrum showed a molecular ion peak at 269 [M^+] (**Figure 3**) and 170 [M^+] (**Figure 4**) clearly confirming 4-(5-Hydroxy-4-nitoso-pyrazol-1-yl)-benzenesulphonic acid and 4-amino-benzene sulphonic acid, respectively.

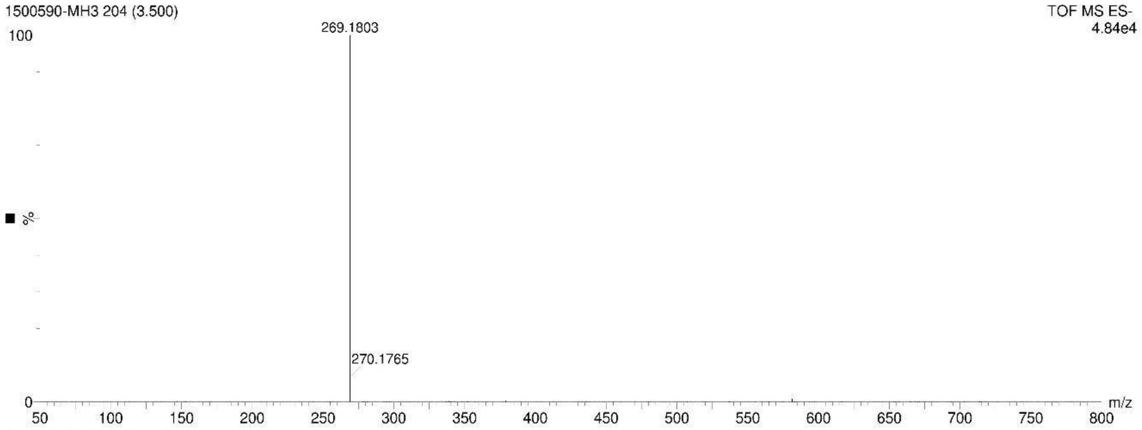


Figure 3 LC-MS of 4-(5-Hydroxy-4-nitoso-pyrazol-1-yl)-benzenesulphonic acid with its molecular ion peak at 269 amu in positive mode.

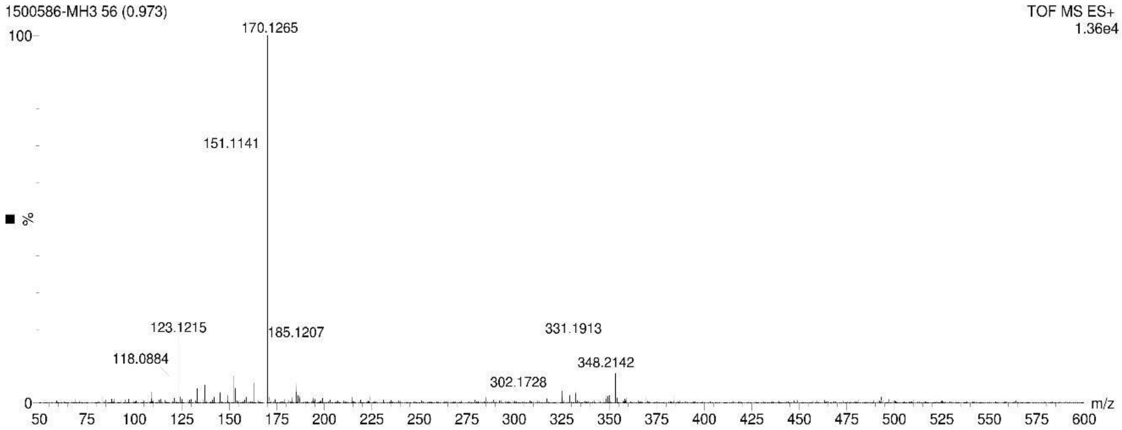


Figure 4 LC-MS of 4-amino benzene sulphonic acid with its molecular ion peak at 170 amu in positive mode.

Results and discussion

The detailed kinetic investigations were performed under pseudo 1st-order conditions of [CAT]>> [TAZ]. The kinetics of oxidation of TAZ with CAT has been investigated at several initial concentrations of the reactants in the presence of different acid medium at 26 °C.

Effect of reactant concentrations i.e. [TAZ], [CAT] AND [H$^+$] on the rate

With the oxidant in excess and keeping other parameters like [CAT]°, [H$^+$]° and temperature constant, plot of log (abs) Vs time were linear which indicates that the order of the reaction with respect to [TAZ] is one. The values of pseudo 1st-order rate constants (k′) were listed in **Tables 1 - 3**. Under the same experimental conditions, the values of k′ were calculated at different initial concentrations of CAT and it was observed that the value k′ increased with the increase in the initial concentration of CAT as shown in **Table 1**. Further, Plots of log k′ Vs log [CAT]° was found to be linear ($R^2 = 0.9975$) with a slope of 1.80, 1.87 and 1.82 in HCl, $HClO_4$ and H_2SO_4 respectively, showing a 2nd order dependence on [CAT] (**Figure 5**). The same procedure was followed at fixed [CAT]° and [TAZ]°, and by increasing the initial concentration of acid medium and it was observed that the rate of the reaction decreased with the increase in [H$^+$]° (**Table 2**). Plots of log k′ Vs log [H$^+$] were linear ($R^2 = 0.9949$) with slope of –0.70 in HCl, –0.82 in $HClO_4$ and –0.70 in H_2SO_4 (**Figure 6**), indicating inverse fractional-order dependence in all the 3 cases.

Table 1 Effect of [CAT] on rate of reaction in different acid medium at 26 °C with [HCl] = [$HClO_4$] = 1.0×10^{-3} M; [H_2SO_4] = 5×10^{-4} M; [TAZ] = 5×10^{-5} M.

10^4 [CAT] mol dm^{-3}	4+log [CAT]	HCl		$HClO_4$		H_2SO_4	
		10^4 k′ (s^{-1})	4+logk'	10^4 k′ (s^{-1})	4+logk'	10^4 k′ (s^{-1})	4+logk'
1.40	0.146	2.69	0.429	2.57	0.410	2.44	0.382
1.70	0.230	3.36	0.527	3.72	0.571	3.35	0.525
2.00	0.301	4.80	0.681	5.14	0.711	4.58	0.661
2.30	0.361	6.69	0.825	6.44	0.809	5.91	0.772
2.60	0.415	8.40	0.924	8.25	0.916	7.20	0.857
3.00	0.477	9.48	0.977	10.75	1.031	9.80	0.991

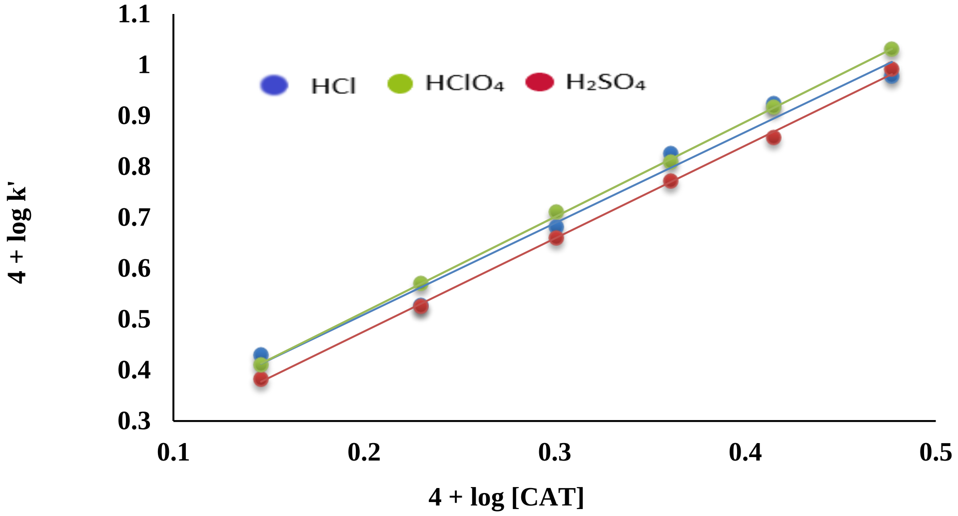


Figure 5 Plot of log k′ vs. log [CAT].

Table 2 Effect of [H$^+$] on rate of reaction in different acid medium at 26 °C with [CAT] = 2.0×10^{-4} M; [TAZ] = 5×10^{-5} M.

10^4 [H$^+$] mol dm^{-3}	5+log [H$^+$]	HCl		$HClO_4$		H_2SO_4	
		10^4 k′ (s^{-1})	4+log k'	10^4 k′ (s^{-1})	4+log k'	10^4 k′ (s^{-1})	4+log k'
0.50	0.146	8.57	0.933	9.60	0.982	4.58	0.661
0.75	0.230	6.17	0.790	7.00	0.845	3.56	0.551
1.00	0.301	4.80	0.681	5.14	0.711	2.88	0.459
1.50	0.361	3.63	0.560	3.91	0.592	-----	-----
2.00	0.415	2.95	0.470	3.09	0.450	-----	-----
2.50	0.477	2.39	0.378	2.67	0.426	-----	-----

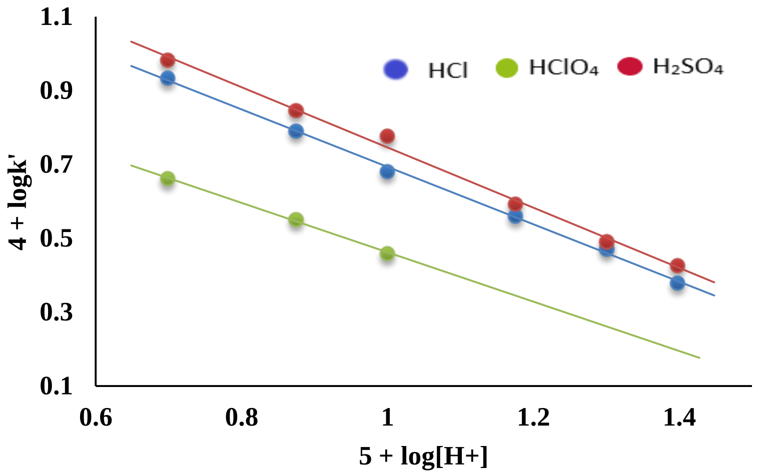


Figure 6 Plot of log k′ vs log [H$^+$].

Table 3 Effect of [TAZ] on the rate of reaction in different acid medium at 26 °C with [CAT] = 2.0×10^{-4} M; [HCl] = [HClO$_4$] = 1.0×10^{-3} M; [H$_2$SO$_4$] = 5×10^{-4} M.

10^5 [TAZ] moldm^{-3}	10^4 k′ (s^{-1})		
	HCl	HClO$_4$	H$_2$SO$_4$
4.0	4.90	5.22	4.43
4.5	4.83	5.17	4.51
5.0	4.80	5.14	4.58
6.0	4.78	5.13	4.50
7.0	4.71	5.01	4.44

Effect of varying [Cl$^-$], [NaClO$_4$] and [PTS] on the rate

The effect of halide ions and Ionic strength (I) of the medium was studied by the addition of sodium chloride (1.0 - 4.0×10^{-3} mol dm^{-3}) and sodium perchlorate (0.1 to 0.4 mol dm^{-3}), respectively. It was observed that rate of the reaction was not altered in both the cases. This indicated that no free chloride ion is formed in the reaction. 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, $\log k / k_o = 1.02\, Z_A Z_B (I)^{1/2}$ [22], a plot of log k versus $(I)^{1/2}$ will give a straight line of slope $1.02\, Z_AZ_B$ and intercept is log k_0. If one of the reactants is a neutral molecule, Z_AZ_B is 0 and the rate constant is expected to be independent of the ionic strength which holds good in the present case. Addition of reduction product (PTS) retards the rate of the reaction (**Table 4**). Plot of log k′ Vs log [PTS] were linear ($R^2 = 0.992$) with a slope of –0.45, –0.47 and –0.48 in HCl, HClO$_4$ and H$_2$SO$_4$, respectively. It shows an inverse fractional order dependence on [PTS] (**Figure 7**). It signifies the involvement of PTS in the step prior to the rate determining step in the proposed scheme.

Table 4 Effect of varying [PTS] on reaction rate with [TAZ] = 5.0×10^{-5} M; [CAT] = 2.0×10^{-4} M; [HCl] = [HClO$_4$] = 1.0×10^{-3} M; [H$_2$SO$_4$] = 5×10^{-4} M.

10^4 [PTS] mol dm^{-3}	5+log [PTS]	HCl		HClO$_4$		H$_2$SO$_4$	
		10^4 k′ (s^{-1})	4+logk'	10^4 k′ (s^{-1})	4+logk'	10^4 k′ (s^{-1})	4+logk'
1.00	1.000	3.99	0.601	4.22	0.625	4.10	0.612
1.50	1.176	3.22	0.508	3.40	0.531	3.39	0.530
2.00	1.301	2.89	0.461	3.00	0.477	2.95	0.469
2.50	1.398	2.62	0.418	2.67	0.426	2.63	0.420
3.00	1.477	2.43	0.386	2.52	0.401	2.43	0.389

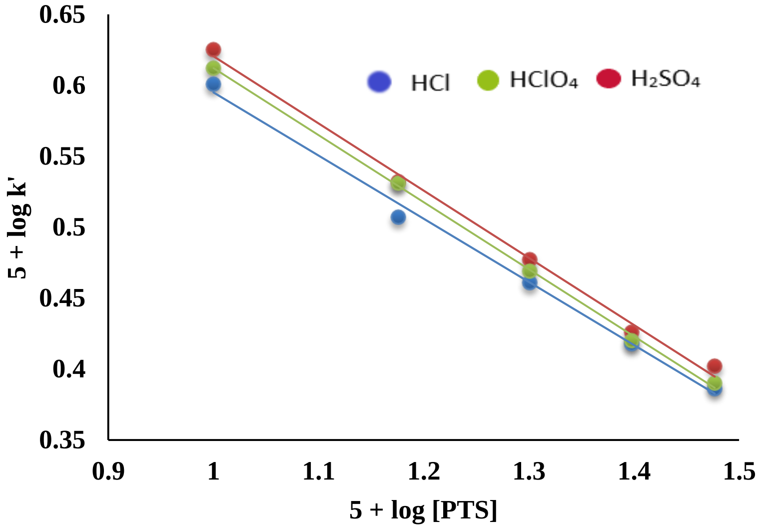


Figure 7 Plot of log k′ vs log [PTS].

Effect of solvent composition

The dielectric constant (D) of the reaction mixture was varied by changing the solvent composition with added methanol (0 - 30 % v/v). The permittivity of the reaction mixture was altered by the addition of methanol in varying proportions (v/v) and the values of dielectric constant of methanol water mixtures reported in the literature [23] were employed. The rate decreased with the increase in the methanol content (**Table 5**). The plots of log k′ Vs. 1/D gave a straight line (**Figure 8**) with negative slope (R^2 = 0.9822). The effect of solvent on the reaction kinetics has been discussed in detail in the various well-known monographs [23-27]. Variation of rate constant with dielectric constant can be explained with the help of the equation;

$\ln k = \ln k_o - (NZ_AZ_Be^2/ DRTr^\#)$ [28]

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 the limiting case of zero angle approach between 2 dipoles or an ion - dipole system [29] has shown that a plot of ln 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 2 dipoles-dipole, while a positive slope for a positive ion-dipole interaction. The former concept agrees with the present observations, i.e., a negative ion and a dipole interaction involved in the rate determining step.

Table 5 Effect of varying Dielectric constant (D) of the medium on reaction rate with [TAZ] = 5.0×10^{-5} M [CAT] = 2.0×10^{-4} M [HCl] = [$HClO_4$] = 1.0×10^{-3} M; [H_2SO_4] = 5×10^{-4} M.

% MeOH (v/v)	D	1/D	HCl		$HClO_4$		H_2SO_4	
			$10^4k'(s^{-1})$	4+logk'	$10^4k'(s^{-1})$	4+logk'	$10^4 k'(s^{-1})$	4+logk'
0	76.93	0.0130	4.80	0.681	5.14	0.711	4.58	0.661
10	72.37	0.0134	3.76	0.575	4.26	0.629	3.54	0.549
20	67.48	0.0148	2.15	0.332	2.64	0.421	2.02	0.305
30	62.71	0.0159	1.40	0.147	1.54	0.187	1.39	0.143

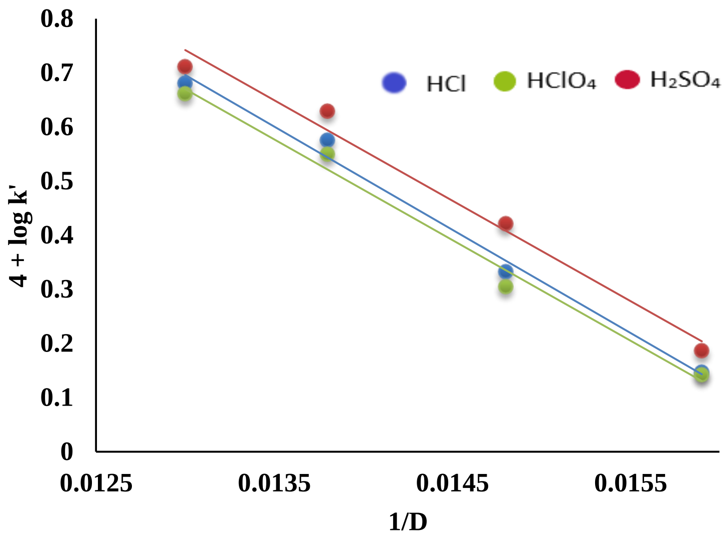


Figure 8 Plot of log k′ vs 1/D.

Effect of temperature

The reaction was studied at different temperatures (26 - 39 °C) and a plot of log k′ Vs 1/T (**Table 6**, **Figure 9**) known as Eyring plot allows the determination of activation parameters $\Delta S^{\#}$ and $\Delta H^{\#}$ from the temperature dependence of the rate constant; activation parameters for the reaction were computed (**Table 7**). $\Delta S^{\#}$ and $\Delta H^{\#}$ are the most important activation parameters and can be useful in understanding the events leading to the transition state. Low enthalpy of activation but a negative entropy of activation suggests an associative mechanism during the formation of the activated complex. The low enthalpy of activation is because of bonds do not need to be broken before the transition state, so it does not cost much to get there. However, a decrease in entropy means that energy must be partitioned into fewer states and hence it makes the reaction harder. The negative value of $\Delta S^{\#}$ also indicated that the transition state is highly solvated compared to the initial reactants.

Table 6 Temperature dependence on reaction rate and values of composite activation parameters for oxidation of tartrazine with [TAZ] = 5.0×10^{-5} M; [CAT] = 2.0×10^{-4} M; [HCl] = [$HClO_4$] =1.0×10^{-3} M; [H_2SO_4] = 5×10^{-4} M.

Temp. (K)	10^3(1/T) (K^{-1})	HCl		$HClO_4$		H_2SO_4	
		10^4 k′ (s^{-1})	4+logk'	10^4 k′ (s^{-1})	4+logk'	10^4 k′ (s^{-1})	4+logk'
299	3.344	4.80	0.681	5.14	0.711	4.58	0.661
303	3.300	6.20	0.792	6.27	0.797	6.19	0.792
307	3.257	8.74	0.941	8.96	0.952	9.29	0.968
311	3.215	10.77	1.032	10.91	1.038	10.86	1.036
315	3.174	13.99	1.146	14.61	1.165	14.32	1.156

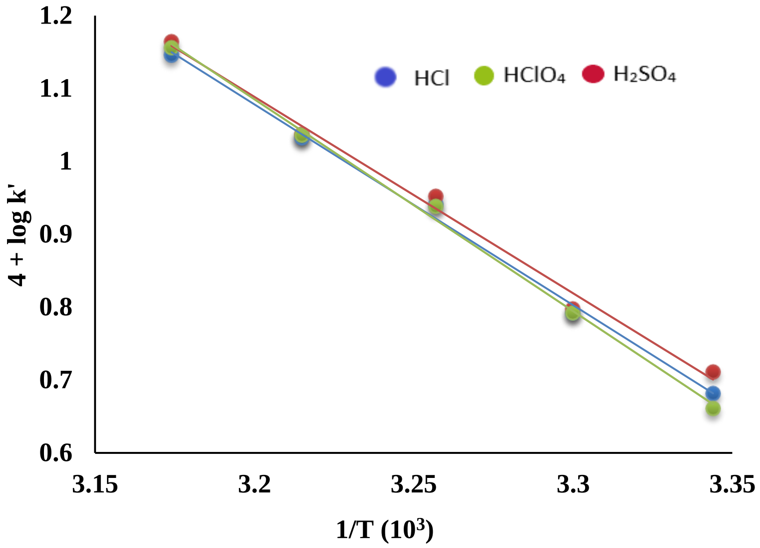


Figure 9 Plot of log k′ vs 1/T.

Table 7 Activation parameters for the oxidation of TAZ by CAT.

Medium	**Ea (kJ mol^{-1})**	**$\Delta H^{\neq}$ (kJ mol^{-1})**	**$\Delta G^{\neq}$ (kJ mol^{-1})**	**$\Delta S^{\neq}$ (JK^{-1} mol^{-1})**	**log A**
HCl	52.73	50.21 ± (0.05)	92.87 ± (0.06)	–140.79 ± (0.08)	5.88 ± (0.04)
$HClO_4$	51.62	49.09 ± (0.05)	92.86 ± (0.06)	–144.45 ± (0.10)	5.69 ± (0.05)
H_2SO_4	55.62	53.10 ± (0.04)	92.86 ± (0.08)	–131.23 ± (0.10)	6.38 ± (0.04)

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.

Discussions

Chloramine-T behaves as a strong electrolyte in aqueous solutions [30] and dissociates according to Eq. (2). The anion picks up a proton in acid solutions to give the free acid monochloramine-T [Eq. (3)]. Although the free acid has not been isolated there is experimental evidence for its formation in acid solutions. It undergoes disproportion giving rise to *p*-toluene sulphonamide and dichloramine-T [Eq. (4)]. Dichloramine-T and the free acid hydrolyse to give hypochlorous acid [Eqs. (5) and (6)]. Finally, HOCl ionizes according to Eq. (7). Depending on the pH of the medium; CAT furnishes [31,32] following types of reactive species in solutions:

$$\mathrm{TsNClNa} \rightleftharpoons \mathrm{TsNCl^{-}} + \mathrm{Na^{+}} \tag{2}$$

$$\mathrm{TsNCl^{-}} + \mathrm{H^{+}} \rightleftharpoons \mathrm{TsNHCl} \qquad \mathrm{Ka} = 2.82 * 10^{-5} \text{ at } 25^{0}\mathrm{C} \tag{3}$$

$$2\mathrm{TsNHCl} \rightleftharpoons \mathrm{TsNH_2} + \mathrm{TsNCl_2} \qquad K_d = 5.8 * 10^{-2} \text{ at } 25^{0}\mathrm{C} \tag{4}$$

$$\mathrm{TsNHCl} + \mathrm{H_2O} \rightleftharpoons \mathrm{TsNH_2} + \mathrm{HOCl} \qquad K_h = 8.0 * 10^{-7} \text{at } 25^{0}\mathrm{C} \tag{5}$$

$$\mathrm{TsNCl_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{TsNHCl} + \mathrm{HOCl} \tag{6}$$

$$\mathrm{HOCl} \rightleftharpoons \mathrm{H^{+}} + \mathrm{OCl^{-}} \tag{7}$$

$$\mathrm{HOCl} + \mathrm{H^{+}} \rightleftharpoons \mathrm{H_2OCl^{+}} \tag{8}$$

Therefore, the possible oxidizing species in acidified CAT solutions are TsNHCl, $TsNCl_2$, HOCl and possibly H_2OCl^+. Further, formation of species of the type $TsNH_2Cl^+$ has been reported [33] with CAT and the protonation constant for the reaction is found to be 1.02×10^2 at 25 °C.

$$\mathrm{TsNHCl} + \mathrm{H^{+}} \rightleftharpoons \mathrm{TsNH_2Cl^{+}} \tag{9}$$

If TsNHCl were to be the reactive species, then the rate law predicts a 1st order dependence of rate on $[CAT]_0$, which is contrary to the experimental observations. Also, if HOCl is the reactive species then the rate law would be a 1st order dependence on [CAT] and inverse fractional order on [PTS] once again which is contrary to the experimental observations. From the above observations we can clearly exclude TsNHCl and HOCl as active species. Since the rate of the reaction shows a 2nd order dependence of rate on $[CAT]_0$ and is retarded by the addition of $TsNH_2$, $TsNCl_2$ is the most probable oxidizing reactive species for the oxidation of tartrazine in the present system. Also, the reaction rate shows inverse fractional order on [H^+] and 1st order dependence on [TAZ]. From the above discussion and experimental facts, scheme 2 is proposed to explain the reaction mechanism for the oxidation of tartrazine by CAT in HCl medium.

$$\mathrm{TsNH_2Cl^{+}} \xrightleftharpoons{K_1} \mathrm{TsNHCl} + \mathrm{H^{+}} \qquad \text{i) fast}$$

$$2\mathrm{TsNHCl} \xrightleftharpoons{K_2} \mathrm{TsNH_2} + \mathrm{TsNCl_2} \qquad \text{ii) fast}$$

$$\mathrm{TsNCl_2} + \mathrm{S} \xrightarrow{k_3} \mathrm{X} \qquad \text{iii) slow and rate determining step}$$

$$\mathrm{X} + \mathrm{H_2O} \xrightarrow{k_4} \text{products} \qquad \text{iv) fast}$$

Scheme 2 A general reaction scheme for the oxidative decolorization of TAZ by CAT in acid medium.

In the 1st step $TsNH_2Cl^+$ undergoes deprotonation to give free acid of CAT. In the next step TsNHCl undergoes disproportion to form *p*-tolouenesulphonamide and dichloramine-T. The later species is found to be the probable active species for the oxidation of TAZ. In the 3rd step (rate determining step), $TsNCl_2$ interacts with the dye to give a complex, which further undergoes hydrolysis to give the oxidized products.

From the above-mentioned scheme 2, a suitable rate is deduced as follows.

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

$$[CAT]_t = [TsNH_2Cl^+] + [TsNHCl] + [TsNCl_2] \tag{10}$$

From step 1 and step 2 of scheme 2,

$$K_1 = \frac{[TsNHCl][\overset{+}{H}]}{[TsN\overset{+}{H}_2Cl]} \quad \text{or} \quad [TsN\overset{+}{H}_2Cl] = \frac{[TsNHCl][\overset{+}{H}]}{K_1} \tag{11}$$

$$K_2 = \frac{[TsNCl_2][TsNH_2]}{[TsNHCl]^2} \quad \text{or} \quad [TsNHCl] = \frac{[TsNCl_2]^{1/2}[TsNH_2]^{1/2}}{K_2^{1/2}} \tag{12}$$

By substituting for [TsNHCl] from Eq. (12) into Eq. (11), we get

$$[TsN\overset{+}{H}_2Cl] = \frac{[TsNH_2]^{1/2}\,[TsNCl_2]^{1/2}[\overset{+}{H}]}{K_1K_2^{1/2}} \tag{13}$$

Substituting for $[TsNH_2Cl^+]$ and [TsNHCl]] from Eqs. (13) and (12) into Eq. (10),

$$[CAT]_t = \frac{[TsNH_2]^{1/2}[TsNCl_2]^{1/2}[\overset{+}{H}]}{K_1K_2^{1/2}} + \frac{[TsNH_2]^{1/2}[TsNCl_2]^{1/2}}{K_2^{1/2}} + [TsNCl_2] \tag{14}$$

$$[CAT]_t = \frac{[TsNH_2]^{1/2}[TsNCl_2]^{1/2}[\overset{+}{H}] + K_1\,[TsNH_2]^{1/2}[TsNCl_2]^{1/2} + K_1K_2^{1/2}\,[TsNCl_2]}{K_1K_2^{1/2}} \tag{15}$$

Since the values of K_1, K_2 and $[TsNCl_2]$ are small, the 3rd term $K_1\,K_2\,[TsNCl_2]$ can be neglected.

Therefore Eq. (15) becomes,

$$[CAT]_t = \frac{[TsNH_2]^{1/2}[TsNCl_2]^{1/2}[\overset{+}{H}] + K_1\,[TsNH_2]^{1/2}[TsNCl_2]^{1/2}}{K_1K_2^{1/2}} \tag{16}$$

$$[CAT]_t = [TsNCl_2]^{1/2}\left\{\frac{[TsNH_2]^{1/2}[\overset{+}{H}] + K_1[TsNH_2]^{1/2}}{K_1K_2^{1/2}}\right\} \tag{17}$$

Rearranging Eq. (17) and squaring on both the sides,

$$[TsNCl_2] = \frac{K_1^2K_2[CAT]_t^2}{[TsNH_2][\overset{+}{H}]^2 + K_1^2[TsNH_2]} \tag{18}$$

Also from scheme 2,

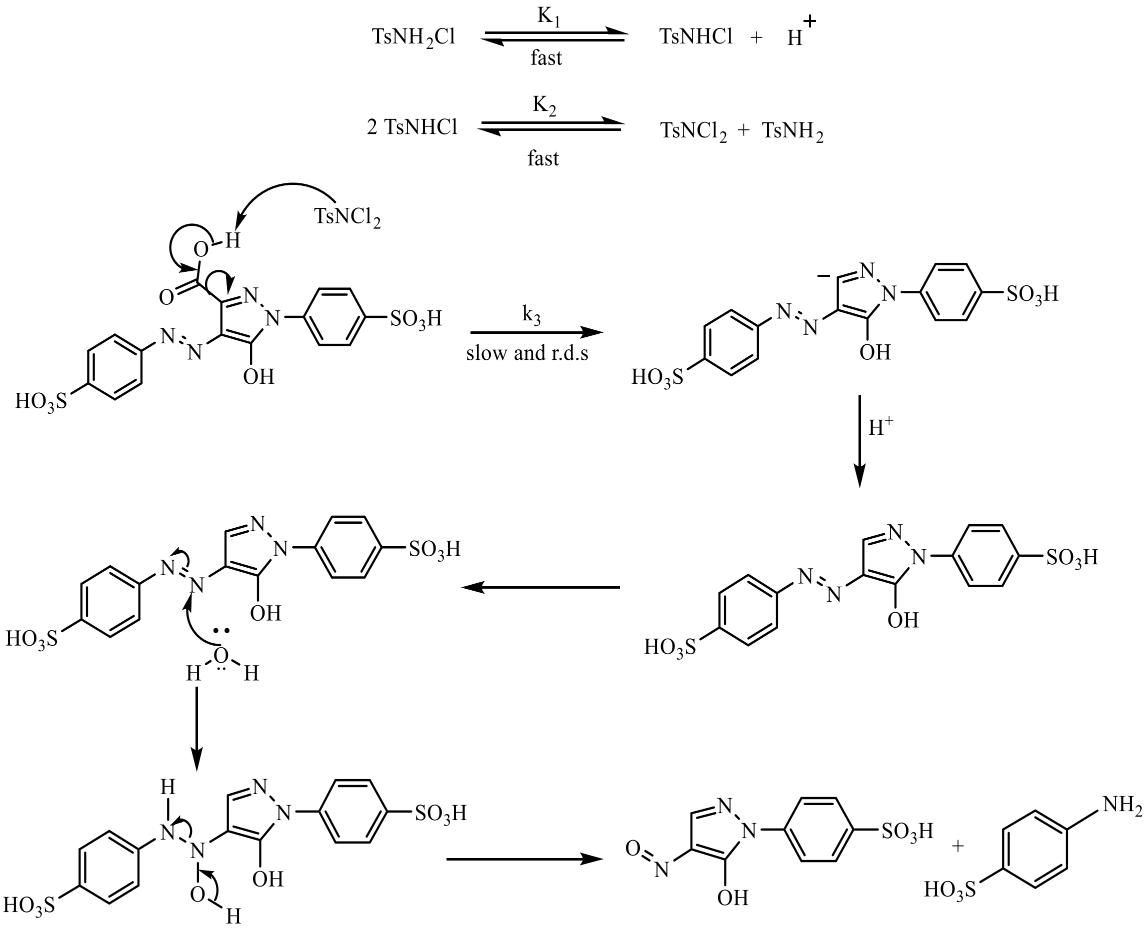
$$\text{rate} = k_3\,[TsNCl_2]\,[S] \tag{19}$$

By substituting for [$TsNCl_2$] from Eq. (18) into Eq. (19),

$$\text{Rate} = \frac{K_1^2 K_2 k_3\ [CAT]_t^2\ [S]}{[TsNH_2]\,[H]^2 + K_1^2\,[TsNH_2]} \tag{20}$$

The above rate law (Eq. (20)) is in good agreement with the experimental results i.e., 1st order for [S], 2nd order w.r.t [CAT] and inverse fractional order for [H^+] and [$TsNH_2$]. Detailed mechanism involving the electron transfer during the oxidation of TAZ by $TsNCl_2$ is shown in scheme 3.

According to Amis a plot of log k vs 1/D should give a straight line with a negative slope for dipole-dipole or negative ion-dipolar interaction and positive slope for positive ion-dipolar interaction. The former case which is observed in the present kinetics supports the negative ion - dipole interaction at the rate determining step. The ionic strength remains constant for dipole-dipole or ion dipole interaction and increases for ion-ion interaction. In the present studies the rateof the reaction remained constant with the increase in the ionic strength of the medium which clearly signifies the involvement of a neutral molecule in the rate determining step and finally theproposed mechanism is also supported by observed activation parameters for all the 3-acid media.



Scheme 3 A detailed mechanistic interpretation for the oxidative decolorization of TAZ by CAT in acid medium.

Conclusions

Tartrazine is an azo dye which is used in food and other consumable products. The dye gets oxidized into 4-(5-Hydroxy-4-nitoso-pyrazol-1-yl)-benzenesulphonic acid and 4-amino-benzene sulphonic acid. In the present work we have studied the kinetics of oxidation of tartrazine by using a mild oxidizing agent CAT in different acidic media. The reaction rate showed 1st order for [TAZ], 2nd order for [CAT] and inverse fractional order for $[H^+]$ and $[TsNH_2]$. Based on the experimental observation a plausible mechanism and appropriate rate law has been deduced.

Acknowledgements

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

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