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Kinetics and Mechanism of Oxidation of Alizarin Yellow R Dye by Chloramine-T in Hydrochloric Acid Medium. A Spectrophotmetric Study

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Abstract

Kinetics of oxidative decolorization of alizarin yellow R (AYR) by chloramine-T (CAT) in hydrochloric acid (HCl) medium at 304 K has been investigated spectrophotometrically at λ_{max}520 nm. The reaction showed first-order rate dependence on [CAT] and $[AYR]_o$ and fractional order dependence on [HCl]. Stoichiometry of the reaction was found to be 1:1 with respect to the substrate and oxidant respectively. The oxidation products were identified by spectral analysis. Variation of ionic strength had no effect on the rate. Addition of p-toluene sulphonamide (PTS) did not retard the rate of the reaction. Activation parameters have been computed. Probable mechanism and the relevant rate law have been deduced for the observed kinetic results.

Keywords: Alizarin Yellow R, CAT, Oxidation-kinetics, Acidic medium

Introduction

The ability of azo- dyes to produce brilliant shades as well as their low cost and simple synthetic processes are the main reasons for the huge production of these dyes all over the world.[1-4] The azo group is the chromophore of those dyes in which it is linked to benzene and naphthalene rings with lateral -SO_3H, COOH and -OH groups. the latter groups make them water soluble.[5,6] Alizarin yellow is a mordant dye and exists as a sodium salt. In its pure form, it is available in a brown crystalline solid. Alizarin yellow R is 2-hydroxy-4-((4-nitrophenyl))diazenyle) benzoic acid, its molecular mass is 287.21 g mol $^{-1}$ and its λ_{max} is 520 nm, The chemical structure of the azo-dye is givin in Fig.1:

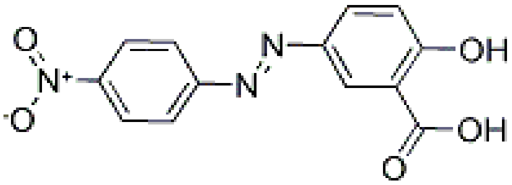

Fig.1: The chemical structure of AYR dye

The dye is soluble in water and suitable for dyeing different items like wool, nylon, leather, textiles and pharmaceuticals, along with its main use as a pH indicator.[7]

The alizarin yellow R (AYR) has been classified as a controlled product according to hazard criteria of the Controlled Products Regulations and the Material Safety Data Sheet (MSDS). It is found to be non-carcinogen material neither does not affect genetic and reproductive system.[8] The removal of Alizarin Yellow-R dye from the water using degradation technique has been carried out by several workers.[9-17] Chloramine-T CAT is a mild oxidant containing a strongly polarizable N- halogen bond where the halogen is in +1 oxidation state. CAT has been used as an oxidant in neutral, acidic and alkaline media.[18,19] It is also used as antiseptic and antipyretic drug.[20] An extensive literature survey revealed that there was no information about the oxidation of AYR by CAT.

Material and Methods

The stock solution of chloramine-T (SDF CHEM LIMITED) was prepared in double distilled water and

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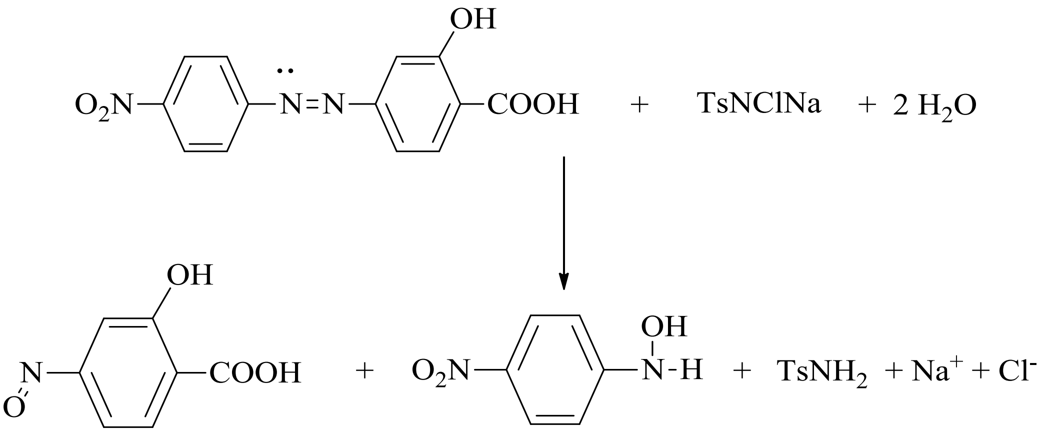
standardized iodometrically. Alizarin Yellow R (AZR) dye (LOBA CHEMIE) was used without further purification. Aqueous solutions of desired strengths were freshly prepared prior to use. Other reagents were of analytical grade.

Kinetic Measurement

The kinetic runs were performed under pseudo first-order conditions by ensuring an excess of CAT over Alizarin Yellow R (AZR) in hydrochloric acid (HCl) medium at 304 K using UV-Vis spectrophotometer (LM-1200) at λ_{max} 520 nm. A constant temperature was maintained with an accuracy of ± 0.1°C. Reactions were carried out in glass stoppered pyrex boiling tubes whose outer surface were coated black to eliminate any photochemical effects. The oxidant and requisite amounts of AYR, HCl solutions and water (to keep the total volume constant for all runs) were taken in separate tubes. The reactants were thermostated for nearly 30 minutes at 304 K. The reaction was initiated by the quick addition of a measured amount of oxidant to the stirred solution containing AYR. 4 mL aliquot of the reaction mixture solution was pipetted out into a cuvette and placed in the spectrophotometer for absorbance measurement.

Reaction Stoichiometry

Reaction mixtures with varying amounts of known excess of CAT over AYR in the presence of HCl solution (0.1 mol dm^{-3}) were equilibrated at 304 K for 24 h. The unreacted CAT was determined and the stoichiometry (number of moles of CAT consumed per mole of the AYR) was obtained. It was observed that one mole of AYR consumed one mole of CAT. The stoichiometry for the reaction is represented by in Eq.1.



(1)

Product Analysis

The reaction mixture under standard concentrations (concentration of CAT was kept in excess over that of AYR) was allowed to progress for 48 h at 304 K. The completion of the reaction was monitored by TLC and later the reaction products were neutralized by the addition of NaOH and were extracted with ethylacetate. The reaction products were characterized by LC-MS. The mass spectra showed a (M$^+$+1) ion peaks at 167 amu and 154 amu (Fig.2 and Fig.3) indicating the presence of 2-hydroxy-4-nitrosobenzoic acid and N-(4-nitrophenyl) hydroxyl amine respectively. The presence of PTS reduction products of CAT was also identified by paper chromatography using petroleum ether-$CHCl_3$-1-butonol (2:2:1 V/V) as the solvent system and iodine as spray agent. (R_f = 0.905) and also confirmed by LCMS spectrum (Fig.4) which shows a (M$^+$+1) ion peak at 172 amu.

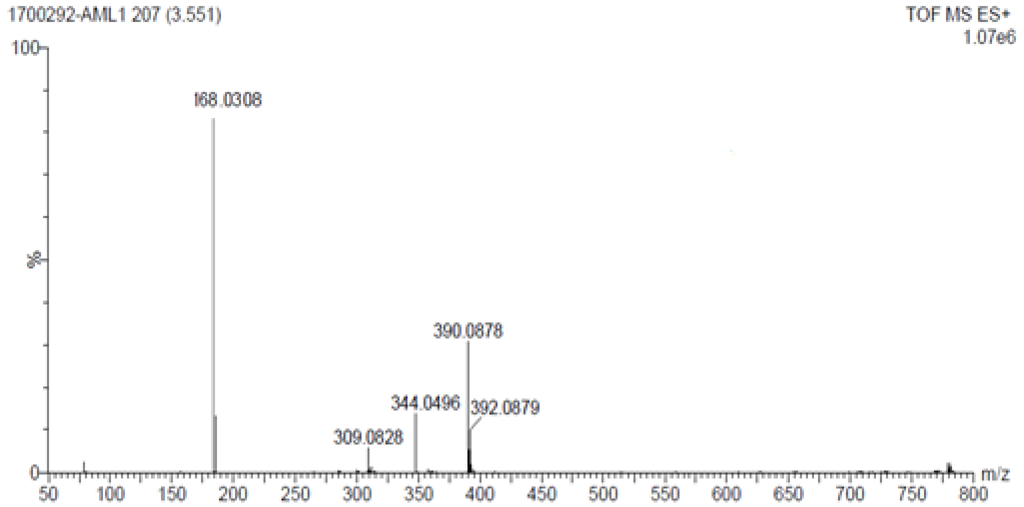


Fig. 2: The LC-Mass spectrum of 2-hydroxy-4-nitrosobenzoic acid with its M$^+$ ion peak at 168 amu

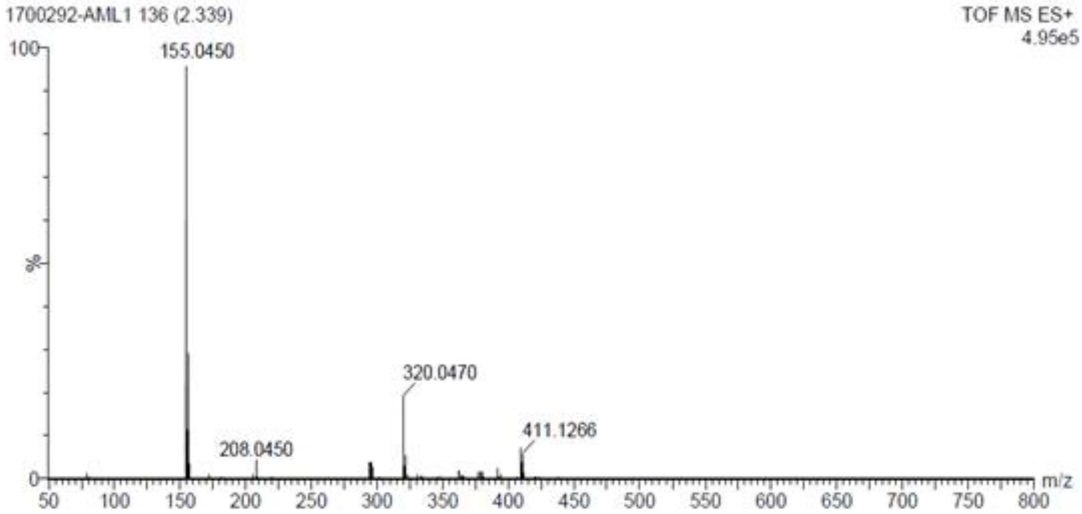


Fig.3: The LC-Mass spectrum of N-(4-nitrophenyl) hydroxyl amine with its M^{+1} ion peak at 155 amu

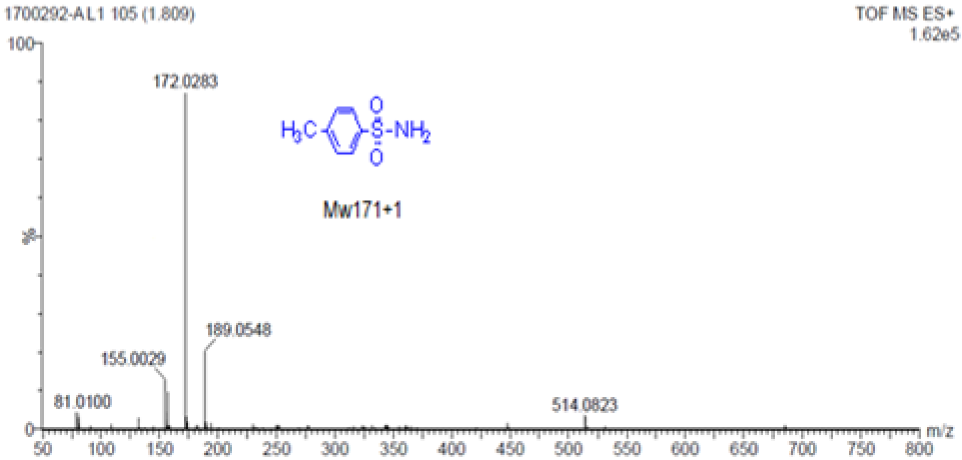


Fig.4: The LC-Mass spectrum of PTS with its M^{+1} ion peak at 172 amu

Results

Effect of reactant concentration on the rate of oxidation of AYR

At constant temperature, the standard run was carried out with concentration of CAT = 4×10^{-3}moldm^{-3} (in excess), AYR = 3×10^{-4} moldm^{-3} and HCl =3×10^{-3}moldm^{-3}. A plot of log (absorbance) versus time was linear indicating a first-order dependence of the reaction rate on [AYR]. The values (Table 1) of pseudo first-order rate constant ($k^{'}$) was unaltered with the variation in [AYR], confirming the first-order dependence of rate on [AYR]. Under the same experimental conditions, the rate of the reaction increased with the increase in the concentration of CAT (Table1). The plot of log $k^{'}$ versus log [CAT] was linear with slope of unity (Fig., R^2 = 0.992) confirming first order kinetics with respect to the oxidant

Effect of acid concentration on the rate of oxidation of AYR

The rate of the reaction increased with the increase in [HCl], the effect of [H^+] was studied by varying the acid concentration in the range 1.5×10^{-3}- 5×10^{-3} mol dm^{-3}. The plot of log $k^{'}$ vs log [H^+] was linear (Table 1, Fig 4, R_2=0.981) with a postive slope of 0.56 indicating a fractional-order dependence on the concentration of HCl.

Effect of ionic strength on the rate of oxidation of AYR

By keep all other experimental conditions constant, the ionic strength of the reaction system was varied by the addition of $NaClO_4$ in the range 0.1- 0.4 mol dm^{-3}. It was observed that the addition of $NaClO_4$ (Table 1) did not affect the rate of the reaction. Hence it was not necessary to keep the ionic strength constant for all the other kinetic runs.

Effect of halide ions on the rate of oxidation of AYR

The addition of Cl^- and Br^- in the form of NaCl and NaBr (1×10^{-2} to 8 $\times10^{-2}$ moldm^{-3}) had negligible (Table 1) effect on the rate. Hence, no free halogen or interhalogen is involved in the reaction system.

Effect of p-toluenesulphonamide (PTS) on the rate of oxidation of AYR

Addition of the reaction product (PTS) had no significant effect on the rate of the reaction (Table1), indicating that

[PTS] is not involved in the fast pre-equilibrium to the rate determining step.

Effect of Dielectric Constant (D) on the rate of Oxidation of AYR

The solvent composition was varied by adding methanol (0% - 30%). The rate of the reaction increased with the increase in the methanol content of the reaction medium and plot of log k' vs 1/D was linear (Table 2, Fig. 5. R^2= 0.980) with a postive slope. The values of D for various MeOH-H_2O mixtures reported in the literature**[21]** were employed for calculation.

Effect of solvent-isotope on the rate

As the rate of reaction depended on the $[H^+]$ ion, the solvent-isotope effect was studied in D_2O medium under standard conditions of [AYR] = 3×10^{-4}mol dm^{-3}, [CAT] = 4×10^{-3} $moldm^{-3}$ and [HCl] = 3×10^{-3}mol dm^{-3}. The rate constant values were $3.45\times10^{-4}s^{-1}$ in H_2O medium and $9.19\times10^{-4}s^{-1}$ in D_2O medium. Therefore, the solvent isotope effect, k_{H2O} / k_{D2O}, was found to be 0.37. That the value being lower than 1 is due to the greater acidity of D_3O^+ compared to H_3O^+.

Effect of temperature on the rate and calculation of activation parameters

The reaction was studied ad different temperatures in the range 296-312 K keeping other experimental conditions constant. Arrhenius plot of log k' vs 1/T was plotted (Table 4, Fig. 6, R^2 = 0.990) and with the help of the graph activation parameters were evaluated. The average values for each parameter is tabled in (Table 3). Addition of reaction mixture to aqueous acrylamide monomer solutions did not initiate polymerization of the latter, indicating the absence of in-situ formation of free radical species in the reaction sequence.

Discussion

Chloramine-T exists as a strong oxidizing species in aqueous solutions.[22] Depending on the pH of the medium, CAT releases[22-25] the following types of reactive species in solutions:

$$\mathrm{TsNClNa} \rightleftharpoons \mathrm{Ts\overset{-}{N}Cl} + \mathrm{Na^+} \qquad (2)$$

$$\mathrm{Ts\overset{-}{N}Cl} + \mathrm{H^+} \rightleftharpoons \mathrm{TsNHCl} \qquad (3)$$

$$2\,\mathrm{TsNHCl} \rightleftharpoons \mathrm{TsNH_2} + \mathrm{TsNCl_2} \qquad (4)$$

$$\mathrm{TsNHCl} + \mathrm{H_2O} \rightleftharpoons \mathrm{TsNH_2} + \mathrm{HOCl} \qquad (5)$$

$$\mathrm{TsNCl_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{TsNHCl} + \mathrm{HOCl} \qquad (6)$$

$$\mathrm{HOCl} \rightleftharpoons \mathrm{H^+} + \mathrm{\overset{-}{O}Cl} \qquad (7)$$

$$\mathrm{HOCl} + \mathrm{H^+} \rightleftharpoons \mathrm{H_2\overset{+}{O}Cl} \qquad (8)$$

Therefore, the possible oxidizing species in acidified CAT solutions are TsNHCl, $TsNCl_2$, HOCl, and possibly H_2O^+Cl. Further, formation of species of the type $TsNH_2Cl^+$ has been reported[26,27] with CAT and the protonation constant for the reaction,

$$\mathrm{TsNHCl} + \mathrm{H^+} \rightleftharpoons \mathrm{Ts\overset{+}{N}H_2Cl} \qquad (9)$$

is found to be 1.02×10^2 at 25^0C

If $TsNCl_2$ were to be the reactive species, the rate law would predict a second order dependence of rate on $[CAT]_o$, which is contrary to the experimental observations. Since the rate of the reaction is not retarded by the addition of $TsNH_2$, HOCl can be rejected as oxidizing species, Therefore, based on the kinetic results $TsNH_2Cl^+$ is taken as the oxidizing reactive species for the oxidation of Alizarin yellow R in the present system. Scheme.1 is proposed to explain the mechanism of oxidation of AY R by CAT in HCl medium.

$$\mathrm{TsNHCl + H^+ \underset{fast}{\overset{k_1}{\rightleftharpoons}} Ts\overset{+}{N}H_2Cl} \qquad \text{(i)}$$

$$\mathrm{TsNH_2Cl + S \underset{slow}{\overset{k_2}{\rightleftharpoons}} X} \qquad \text{(ii) r.d.s}$$

$$\mathrm{X + H_2O \longrightarrow products} \qquad \text{(iii)}$$

Scheme.1

$TsNH_2Cl^+$ is formed from the protonation reaction of TsNHCl (step ii) which reacts with AYR to give complex (X). the complex (X) undergoes hydrolysis to give final products.

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

$[CAT] = [TsNHCl] + [TsN^+H_2Cl]$ (10)

From step (i)

$$[\mathrm{TsNHCl}] = \frac{[\mathrm{Ts\overset{+}{N}H_2Cl}]}{K_1\,[H^+]} \qquad (11)$$

By substituting for [TsNHCl] from Eq.11 into Eq.10

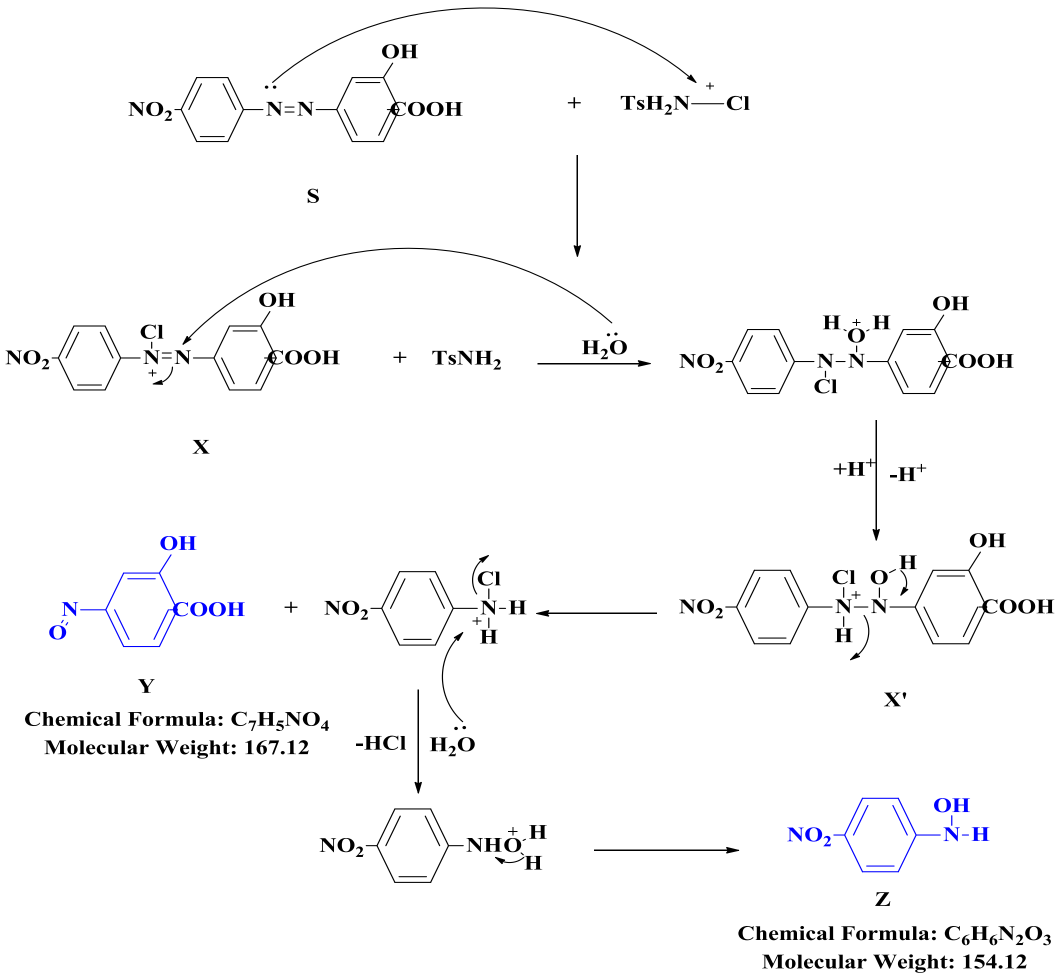
$$[\mathrm{Ts\overset{+}{N}H_2Cl}] = \frac{K_1\,[CAT]_t\,[H^+]}{1+[H]K_1} \qquad (12)$$

From r.d.s step (ii), $\mathrm{Rate} = k_2\,[\mathrm{Ts\overset{+}{N}H_2Cl}][S]$ (13)

By substituting for $[TsNH_2Cl]$ from Eq.12 into Eq.13 we got

$$\mathrm{Rate} = \frac{k_2\,K_1\,[CAT]_t\,[H^+]\,[S]}{1+[H^+]K_1} \qquad (14)$$

Rate law (14) satisfactorily explains the observed kinetic data, wherein a first-order dependence of rate on [S] and [CAT] and fractional-order on $[H^+]$ is indicated. As the reaction is H^+ catalyzed in the present study. Solvent-isotope effect was studied the nature of bond-breaking in rds showed that the rate of the reaction is higher in D_2O medium. For a reaction involving a fast equilibrium H^+ (or OH^- ion) transfer, the rate increases in D_2O medium since D_3O^+ (or OD^-) is a stronger acid or (a stronger base than H_3O^+ or OH^-) ions.[28] The observed solvent isotope effect of $k_{H2O} / k_{D2O} < 1$ is due to the greater acidity of D_3O^+ compared to H_3O^+. The observed mechanism is also supported by the solvent methanol effects on the rate of the reaction. According to Amis,[29] 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 positive dielectric effect observed in the present study, supports the positive ion-dipole interaction at 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. The ionic strength remains constant for dipole-dipole or ion dipole interaction and increases for ion-ion interaction.[30] In the present study, the rate constant remained unchanged with the increase in the ionic strength of the medium which indicated that AYR dye reacts as neutral molecule in the rate determining step. The proposed mechanism is also supported by observed activation parameters. The activation parameters like energy of activation and other thermodynamic parameters are moderate. The energy of activation value suggests that the reaction is enthalpy controlled. The negative value 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. A detailed reaction mechanism is represented in Scheme 2.



Y Chemical Formula: $C_7H_5NO_4$
Molecular Weight: 167.12

Z Chemical Formula: $C_6H_6N_2O_3$
Molecular Weight: 154.12

Scheme .2: A detailed reaction scheme of the oxidation of AYR by CAT in HCl medium

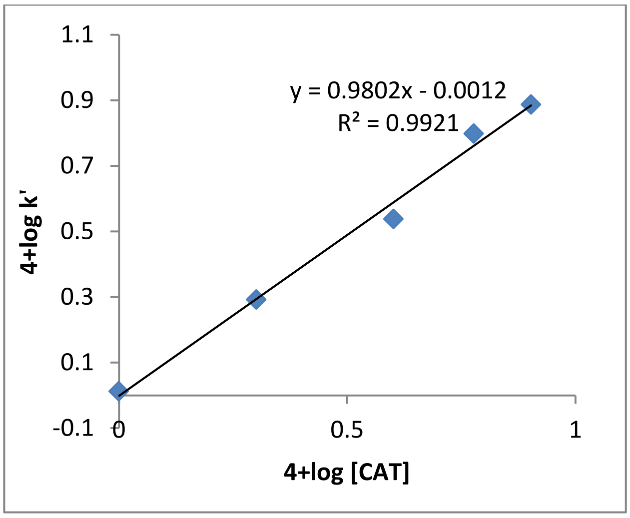
Tables and Plots:

Table 1: Effect of variation of reactants on the oxidation reaction rate

$[AYR] = 3.0 \times 10^{-4}$ moldm^{-3}, $[CAT]_o = 4.0 \times 10^{-3}$ mol dm^{-3},
$[HCl] = 3.0\times 10^{-34}$ moldm^{-3}, T=304 K

[AYR] ×10^{4} moldm^{-3}	[CAT]×10^{3} moldm^{-3}	[HCl]×10^{3} moldm^{-3}	k×10^{4} s^{-1}
1.0	4.0	3.0	3.38
2.0	4.0	3.0	3.41
3.0	4.0	3.0	3.45
4.0	4.0	3.0	3.29
5.0	4.0	3.0	3.39
3.0	1.0	3.0	1.028
3.0	2..0	3.0	1.958
3.0	4.0	3.0	3.454
3.0	6.0	3.0	6.281
3.0	8.0	3.0	7.709
3.0	4.0	1.5	2.167
3.0	4.0	2.0	2.851
3.0	4.0	3.0	3.454
3.0	4.0	4.0	3.872
3.0	4.0	5.0	4.841
(a) 0.1	(a) 0.2	(a) 0.3	3.45
(b) 1.0	(b)2.0	(b) 4.0	3.45
(c) 1.0	(c) 2.0	(c) 6.0	3.45
(d) 1.0	(d) 1.5	(d) 2.0	3.45

a = [$NaClO_4$], b = [NaCl], c = [NaBr] and d = [PTS]



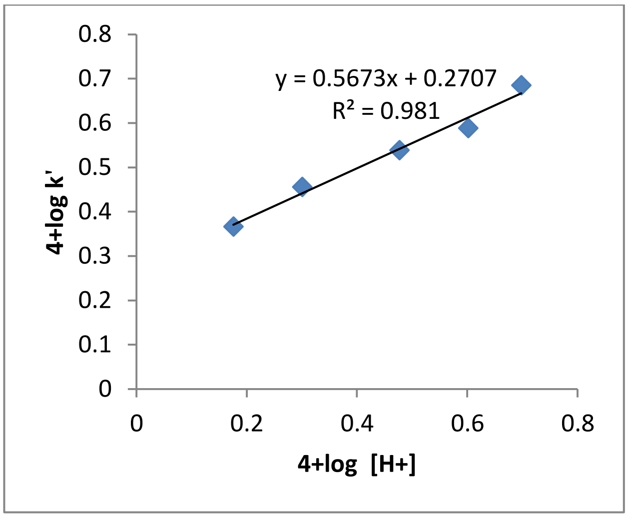


Fig.5: Plot of log k vs log [CAT] **Fig .6:** Plot of log k vs log [H$^+$]

Table 3: Effect of dielectric constant on the rate of oxidation

$[AYR]_o$ = 3.0 X 10^{-4} mol dm^{-3}, $[HCl]_o$ = 3.0 X 10^{-3} mol dm^{-3}, $[CAT]_o$ = 4.0 X 10^{-3} mol dm^{-3}, T= 304 K

% MeOH (v/v)	D	1/D	10^4 k$'$ (s^{-1}) 4+logk'	
0	76.73	0.0130	3.454	0.538
10	72.37	0.0138	4.092	0.612
20	67.48	0.0148	4.875	0.688
30	62.71	0.0159	6.486	0.812

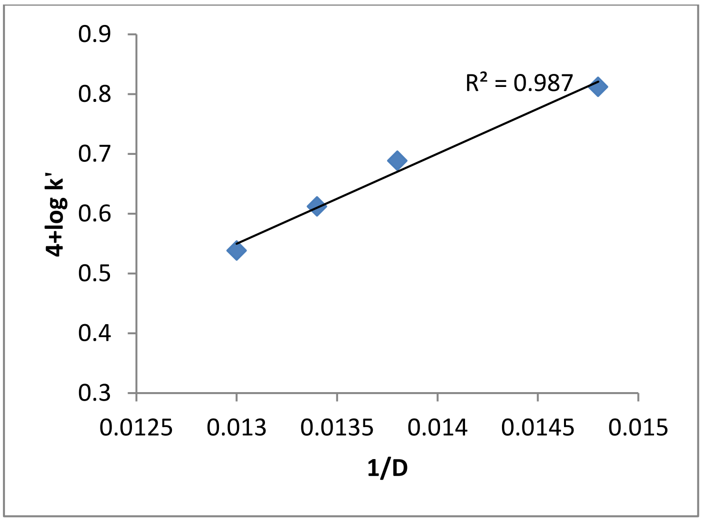


Fig .7: Plot of log k vs 1/D

Table 4: Effect of temperature on the rate of oxidation

$[AYR]_o$ = 3.0 X 10^{-4} mol dm^{-3}, $[HCl]_o$ = 3.0 X 10^{-3} mol dm^{-3}, $[CAT]_o$ = 3.0 X 10^{-3} mol dm^{-3}, T= 304 K

Temperature (K)	10^3(1/T) (K^{-1})	10^4 k$'$ (s^{-1}) 4+logk'	
296	3.37	2.04	0.311
300	3.33	2.61	0.415
304	3.28	3.45	0.538
308	3.24	5.09	0.707
312	3.20	6.13	0.788

R2 = 0.990

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
49.32	47.71	95.06	-173.32	8.71

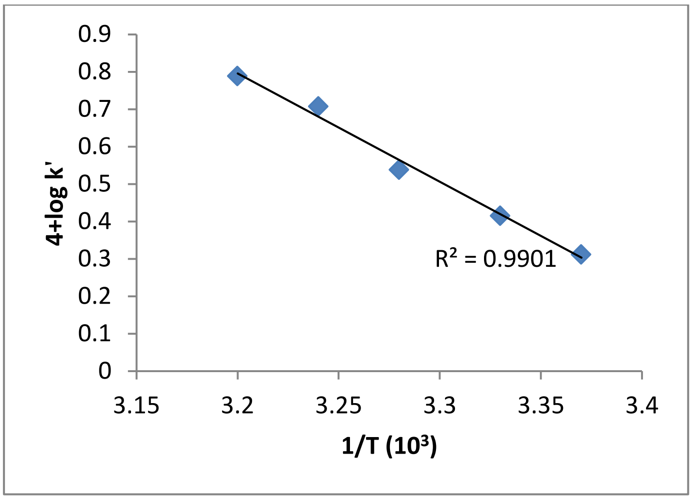


Fig .8: Arrhenius plot of log k vs 1/T

Conclusion

The kinetics of oxidative decolorisation of Alizarin yellow R (AYR) by CAT in HCl medium has been studied. The experimental rate law was found to be - d[CAT] /dt= $k[AYR]^1 [CAT]^1[H^+]^{0.56}$, The oxidation products were identified to be 2-hydroxy-4-nitrosobenzoic acid and N-(4-nitrophenyl) hydroxyl amine. Thermodynamic parameters were calculated and suitable mechanism was proposed. TsNHCl is assumed to be the reactive species, which interacts with the azo dye to give a complex which on further gets hydrolyzed to give the oxidized products. An appropriate rate law was derived which fits into the proposed mechanism.

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