Oxidative Decolorization of Azo Dye Acid Orange 7 With Acidified Chloramine-T: Kinetic And Mechanistic Approach

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***Abstract:-*. The kinetics of oxidative decolorization of Acid orange 7 (AO7) by chloramine-T(CAT) in $HClO_4$ medium has been investigated spectrophotometrically (λ_{max} = 482 nm) at 298 K. Kinetic runs were performed under pseudo first-order conditions of $[CAT]_o >> [AO7]_o$. The reactions show first-order dependence on $[CAT]_o$ and [AO7] and a fractional-order dependence on $[HClO_4]$. Stoichiometry of the reaction was found to be 1:1 and the oxidation products were identified. The reaction was studied at different temperatures and various activation parameters have been computed. Effects of p-toluenesulfonamide, halide ions, ionic strength and dielectric constant of the medium have been investigated. Reaction mixture fails to induce polymerization of acrylonitrile. Plausible mechanism and related rate law have been deliberated for the observed kinetics.**

Key Words: Decolorization, Acid orange 7, oxidation-kinetics, chloramine-T, acid medium

I. INTRODUCTION

Color is the main petition of any textile. No issue how tremendous its constitution, if unsuitably colored it is bound to be a malfunction as a commercial fabric. Fabrication and utilize of imitation dyes for structure dyeing has therefore become huge production today. Simulation dyes have provided prevalent evolution of colorfast and shades. However their venomous life has become a core of unsympathetic disquiet to environmentalists. Use of replicated dyes has an objectionable result on all forms of life. Existence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals and certain supplementary chemicals all cooperatively make the textile runoff exceptionally noxious.

Seepage containing azo dyes discharged by dye, textile and food processing industries origin key environmental harms and reduction of toxicity caused by these dyes is a chief concern in waste water handling. Acid orange 7 is one of the harmful dye effluents from textile industries and removal of this dye by simple, cost effective method is most required for healthy public. Azo dyes contain one or more azo groups (-N=N-) as the primary chromophore form a largest class of synthetic dyes and some monoazo dyes are widely used as colorants in common foods and drugs [1]. The discharge of highly colored synthetic dye effluents is damaging the receiving water bodies, since these dyes in water strongly absorb sunlight, which decreases the intensity of light absorbed by water plants and phytoplankton, reducing photosynthesis and the oxygenation of water reservoirs [2, 3]. In addition, dyes used in the textile industry may be toxic to aquatic organisms and can be resistant to natural biological degradation [2,4,5]. Effluents containing azo dyes are commonly treated using physico-chemical methods such as adsorption, photodegradation and coagulation. All these processes are expensive and complicated. Therefore, there is a need for inexpensive and simple methods to abolish harmful dyes in effluents.

The oxidation of azo dyes has attracted much attention in recent years [6-11]. The literature review shows that there is no information on the oxidative decolorization of AO7 from kinetic and mechanistic view point. Consequently, this research program is designed through oxidative decolorization kinetic studies to determine the mechanism of this reaction.

The effectiveness of the proposed process was evaluated by its ability to decrease in color and total organic carbon content. The high efficiency observed with the dye model showed that this economic, easily operated and maintained treatment process can also be employed in the remediation of effluents.

The diverse nature of the chemistry of N-haloamines is a result of their ability to act as sources of halonium cations, hypohalites and N-anions which act both as electrophiles and nucleophiles [10-14]. They behave as mild oxidants and are suitable for the limited oxidation of several functional groups. Consequently, these reagents react with a wide variety of functional groups affecting an array of molecular transformations. Generally, these haloamines undergo two-electron change while dihaloamines are four-electron oxidants [10]. The reduction products are the respective sulfonamide and NaCl or HCl. The prominent member of this class of compounds is sodium N-chloro-4-methylbenzenesulfonamide, commonly known as CAT ($p-CH_3C_6H_4SO_2NClNa.3H_2O$) is a by-product in the manufacture of saccharin. The redox potential of CAT/p-toluenesulfonamide is pH dependent [11] and decreases with increase in pH of the medium (1.139 V at pH 0.65, 1.778 V at pH 7.0 and 0.614 V at pH 9.7). The nature of active oxidizing species of CAT depends on the pH of the medium and the reaction condition. CAT is a source of positive halogen and has been exploited as oxidant for a variety of substrates in both acidic and alkaline media [10, 11, 14-20]. Although a large number of various substrates have been oxidized by CAT, very few oxidation kinetic investigations of dyes with CAT are carried out. Preliminary experimental results revealed that the oxidation of AO7 by CAT in alkaline medium is too slow to be measured but the reaction is facile in the presence of an acid. Hence, the present kinetic investigations have been carried out in acid medium.

In the light of available information in this communication we report on the detailed kinetics of AO7 oxidation by CAT in $HClO_4$ medium at 298 K in order to (i) elucidate a plausible mechanism, (ii) design appropriate kinetic model, (iii) ascertain the reactive species, (iv) characterize the oxidation products and (v) develop an optimum condition for the facile oxidation of the substrate.

II. EXPERIMENTAL

Materials

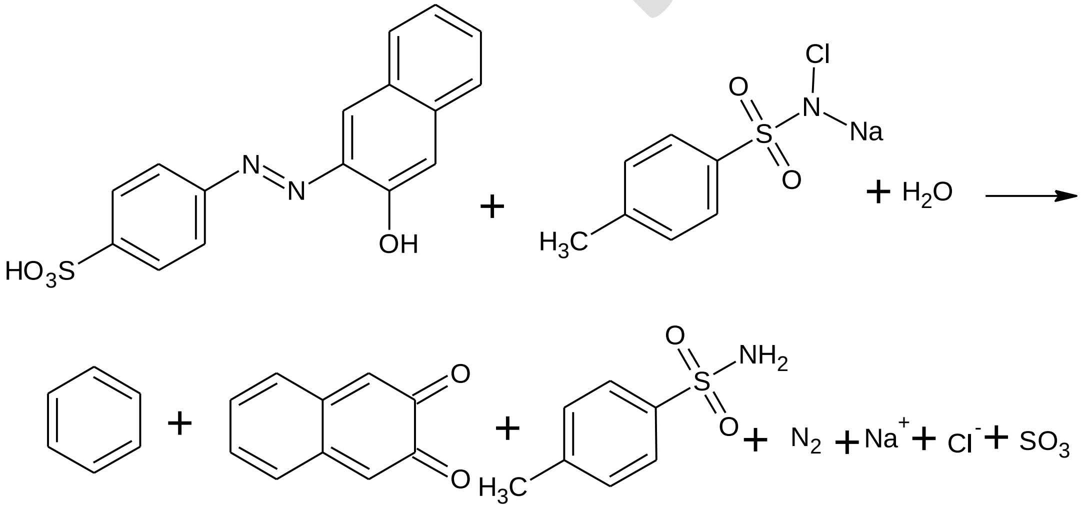
CAT (Merck) and AO7 (S.d. fine-chem Ltd.) were used as received. The concentrations of stock solutions were periodically determined. An aqueous solution of dye was freshly prepared whenever required. Solvent isotope studies were made in D_2O (99.24% purity) medium supplied by Bhabha Atomic Research Centre, Mumbai, India. Reagent grade chemicals and double distilled water were used throughout.

Kinetic measurement

The kinetic runs were performed under pseudo first-order conditions with a known excess of $[\mathrm{CAT}]_o$ over $[\mathrm{AO7}]_o$ at 298 K using a Digital Spectrophotometer (166, Systronics, India). In the present study, the kinetic experiments were carried out between 288 and 313 K. For this purpose, a Raaga Ultra Cold Chamber with digital temperature control (India) was used. A constant temperature was maintained with an accuracy of ± 0.1 ◦C. Reactions were carried out in glass stoppered Pyrex boiling tubes whose outer surfaces were coated black to eliminate any photochemical effects. The oxidant as well as requisite amounts of dye and $HClO_4$ solutions and water (to keep the total volume constant for all runs) taken in separate tubes were thermostatted for 30 min at 298 K. The reaction was initiated by the rapid addition of a measured amount of oxidant to the stirred reaction mixture. Immediately, the solution was pipetted into a cuvette placed in the spectrophotometer. Absorbance measurements were made at 482 nm (λ_{max} of AO7) for nearly three half lives. The absorbance readings at $t = 0$ and $t = t$ are D_0 and D_t. Plots of log D_0/D_t versus time were made to evaluate the pseudo-first-order rate constants ($k^{\prime}$) which were found to be reproducible within ± 4-5%. Regression analysis of the experimental data was carried out by using *fx* −100W scientific calculator.

Reaction stoichiometry

Reaction mixtures containing different ratios of CAT to AO7 were equilibrated at 298 K in 1.00×10^{-4} mol dm^{-3} $HClO_4$ for 48 h. Iodometric titrations of unreacted CAT showed that one mole of AO7 consumed one mole of CAT confirming the following stoichiometry:



Product Analysis

The reaction mixture in 1:1 ratio under stirred condition was allowed to progress for 48 h at 298 K. After the reaction, solution was neutralized with NaOH and the products were extracted with ether. The organic products were subjected to spot tests and chromatographic analysis (TLC technique), which revealed the formation of oxidation products, namely benzene and 1,2-naphthoquinone. These oxidation products were separated by column chromatography and identified melting point of 1,2-naphthoquinone is 125 ^{o}C (lit. m.p.124-126 ^{o}C) ,boiling point of benzene is 80 ^{0}C (lit. b.p.80.1 ^{o}C). These two products were further confirmed by GC-MS data obtained on a 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer. The mass spectrum was obtained using the electron impact ionization technique. The mass spectra showed parent molecular ion peaks at 77 and 158 amu, confirming benzene and 1,2-naphthaquinone, respectively (Figs. 1 and 2). Further, it was noticed that there was no further reaction between benzene and 1,2-naphthoquinone with CAT under the present set of experimental conditions.

p-Toluenesulfonamide was extracted with ethyl acetate and detected by paper chromatography [18]. Benzyl alcohol saturated with water was used as the solvent with 0.5 % vanillin in 1% HCl solution in ethanol as spray reagent (R_f = 0.905). Further the parent molecular ion peak of 171 amu (Fig. 3) confirms *p*-toluenesulfonamide. All other peaks observed in GC-Mass spectrum can be interpreted in accordance with the observed structure.

III. RESULTS AND DISCUSSION

Effect of reactant concentration on the rate

The oxidation of AO7 by CAT was kinetically investigated at different initial concentrations of the reactants in $HClO_4$ medium at 297 K. Under pseudo first-order conditions of $[AO7]_o$ << $[CAT]_o$ at constant $[AO7]_o$, $[HClO_4]$ and temperature, plots of log (absorbance) versus time were linear (r > 0.9901), indicating a first-order dependence of rate on $[AO7]_o$. The pseudo first-order rate constants ($k^{/}$) are listed in Table 1. Further, the values of $k^{/}$ remain unaltered with variation in $[AO7]_o$, confirming the first-order dependence of the rate on $[AO7]_o$.

Under the same experimental conditions, an increase in $[CAT]_o$ increased the rate (Table 1). A plot of log $k^{/}$ versus log $[CAT]_o$ was linear (r = 0.9976) having a slope equal to unity, indicating a first-order dependence of the reaction rate on $[CAT]_o$. Further, a plot of $k^{/}$ versus $[CAT]_o$ was linear (r = 0.9983) passing through the origin, confirming the first-order dependence on $[CAT]_o$. At constant $[CAT]_o$, $[AO7]_o$, and temperature, the rate of the reaction increased with increase in $[HClO_4]$ (Table 1). A plot of log $k^{/}$ versus log $[HClO_4]$ was linear with a slope of 0.60, indicating a fractional-order dependence on $[HClO_4]$.

Effects of halide and p-toluene sulfanamide concentration on the rate

Addition of *p*-toluenesulfonamide (PTS or $TsNH_2$), reduction product of CAT (1.0 x 10^{-3} - 8.0 x 10^{-3} mol dm^{-3}), to the reaction mixture did not affect the rate significantly. It indicates that PTS is not involved in any step prior to the rate-determining step (rds) in the scheme proposed.

Effect of ionic strength of the medium on the rate

Addition of halide ions, Cl^- or Br^-, in the form of their sodium salts (1.0 x 10^{-3} - 8.0 x 10^{-3} mol dm^{-3}) showed no pronounced effect on the rate. This indicates that the halide ions play no role in the reaction. The ionic strength of the reaction medium was varied from 0.1 to 0.3 mol dm^{-3} with $NaClO_4$ solution keeping other experimental conditions constant. It was found that addition of $NaClO_4$ showed negligible effect on the reaction rate, indicating the involvement of nonionic species in the rate-determining step. Hence no attempts were made to keep the ionic strength of the medium constant for kinetic runs.

Effect of dielectric constant of the medium on the rate

The dielectric constant (D) of the medium was varied by adding MeOH (0-30 % v/v) to the reaction mixture with all other experimental conditions being held constant. The rate decreased with increase in MeOH content (Table 2, Fig. 4). A plot of log $k^{/}$ versus 1/D was linear (r = 0.9978) with a negative slope. It was further noticed that no reaction of the dielectric with the oxidant under the experimental conditions employed. The values of the dielectric constant of CH_3OH - H_2O mixtures reported in the literature [22] were employed.

Effect of solvent isotope on the rate

As the oxidation of AO7 by CAT was accelerated by $[H^+]$, the solvent isotope effect was studied in D_2O as the solvent medium, with AO7 as a probe. Values of $k^{/}$ (H_2O) and $k^{/}$ (D_2O) were 4.81 x 10^{-4} s^{-1} and 4.96 x 10^{-4} s^{-1}, giving a solvent isotope effect $k^{/}$ (H_2O) / $k^{/}$ (D_2O) = 0.96.

Effect of temperature on the rate

The effect of temperature on the reaction rate was studied by performing the kinetic runs in the range of 288-313 K, keeping other experimental conditions constant. From the linear Arrhenius plot of log $k^{/}$ versus 1/T (r = 0.9930, Fig. 5), values of activation parameters (E_a, $\Delta H^{\neq}$, $\Delta G^{\neq}$, $\Delta S^{\neq}$ and log A) for the overall reaction were evaluated. These data are presented in Table 3.

Test for free radicals

Addition of the reaction mixture to the acrylamide monomer did not initiate polymerization, indicating the absence of free radicals in the reaction mixture. Control experiments performed with solutions containing all the components of the reaction mixture except the oxidant and with the individual oxidant solutions were found to be negative.

Reactive species of CAT

Chloramine-T (TsNClNa) behaves as a strong electrolyte [21] in aqueous solutions, and depending upon the pH of the medium, it furnishes the following types of reactive species in solutions (Eqns 2-8).

$$\mathrm{TsNClNa} \rightleftharpoons \mathrm{TsNCl}^- + \mathrm{Na}^+ \qquad (2)$$

$$\mathrm{TsNCl}^- + \mathrm{H}^+ \rightleftharpoons \mathrm{TsNHCl} \qquad (3)$$

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

$$\mathrm{TsNCl_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{TsNHCl} + \mathrm{HOCl} \qquad (5)$$

$$\mathrm{TsNHCl} + \mathrm{H_2O} \rightleftharpoons \mathrm{TsNH_2} + \mathrm{HOCl} \qquad (6)$$

$$\mathrm{HOCl} \rightleftharpoons \mathrm{H}^+ + \mathrm{OCl}^- \qquad (7)$$

$$\mathrm{HOCl} + \mathrm{H}^+ \rightleftharpoons \mathrm{H_2OCl}^+ \qquad (8)$$

CAT dissociates according to equilibrium (2) and the anion picks up a proton from acid (Eq. 3) to give free acid TsNHCl whcih undergoes disproportionation [23-25] via reaction (4) giving rise to dichloramine-T and the parent amide. The free acid and dichloramine-T undergo hydrolysis (Eqns. (5) and (6)). Finally the hypohalous acid undergoes ionization according to reaction 7. Possibly the hypohalous acid with a proton gives H_2OCl^+ species (Eqs. 7 and 8). Consequently, the possible oxidizing species in acidified CAT solutions are TsNHCl, $TsNCl_2$, HOCl and possibly H_2OCl^+.

Absence of a retardation effect by the p-toluene sulfonamide rules out the involvement of HOCl in the reaction sequence. Bishop and Jennings [23] have shown in aqueous solutions of CAT, at pH > 3, the concentration of anion $TsNCl^-$ is greater than that of the free acid. Hence the protonation equilibrium (3) involving the anion can be assumed in aqueous acidic solution.

Reaction scheme

Since reaction rate shows fractional-order dependence on the concentration of acid, based on the kinetic data and above discussion, the conjugate free acid TsNHCl is assumed to be most active oxidizing species in the present investigations and Scheme 1 is proposed to explain the reaction mechanism for the oxidation of AO7 by CAT in $HClO_4$ medium.

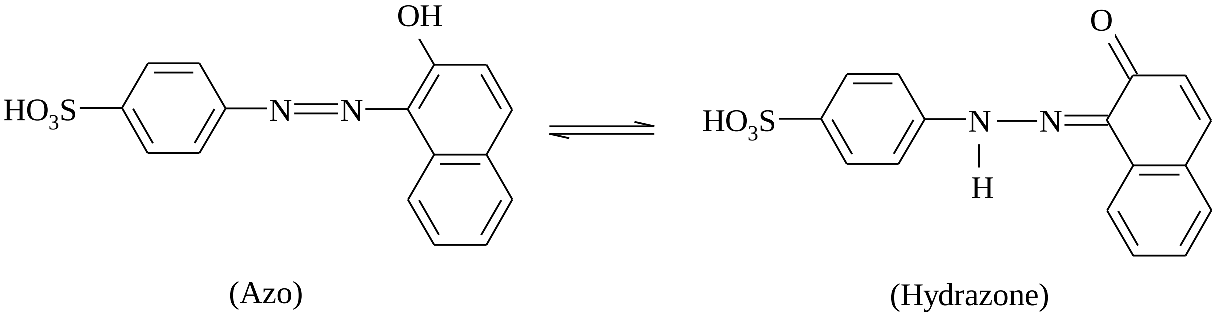
$$\mathrm{TsNCl}^- + \mathrm{H}^+ \overset{K_1}{\rightleftharpoons} \mathrm{TsNHCl} \qquad \text{(i) fast}$$

$$\mathrm{TsNHCl} + \mathrm{AO7} \xrightarrow{k_2} \underset{\text{(Complex)}}{\mathrm{X}} \qquad \text{(ii) slow \& rate determining}$$

$$\mathrm{X} \xrightarrow{k_3} \text{Products} \qquad \text{(iii) fast}$$

Scheme 1**.** Reaction Scheme for the oxidation of AO7 by CAT in acid medium.

Dyes such as AO7 containing hydroxyl groups conjugated to azo group exhibit azo-hydrazone tautomerism as shown below.



In the present case, the azo form of the dye reacts with the conjugate acid of the oxidant to form AO7-CAT complex (X) with the elimination of $TsNH_2$. The complex in acid medium undergoes protodesulfonation followed by hydrolysis and cleavage of azo bond to yield the ultimate products benzene and 1,2-naphthaquinone as shown in scheme 2.

Kinetic rate law

A detailed mode of oxidation of AO7 by CAT in acid medium is depicted in Scheme 2, where the structure of the intermediate complex X is shown. In a fast initial equilibrium (step (i) of Scheme 1), the anion $TsNCl^-$, in acid accelerating step generates the active oxidizing species TsNHCl. In a slow / rate determining step (step (ii)), the lone pair of electrons on oxygen of AO7 attacks the positive chlorine of TsNHCl forming an intermediate species X. This intermediate complex X (step (iii)) undergoes hydrolysis followed by several fast steps leading to the formation of naphthaquinone and benzene as end products.

If $[CAT]_t$ represents the total concentration of the oxidant, then from steps (i) and (ii) of Scheme 1

,

$$[CAT]_t = [TsN^-Cl] + [TsNHCl] \qquad (9)$$

From step (i)

$$K_1 = \frac{[TsNHCl]}{[TsNCl^-]\,[H^+]}$$

Or

$$[TsNCl^-] = \frac{[TsNHCl]}{K_1\,[H^+]} \qquad (10)$$

By substituting $[TsN^-Cl]$ from equation (10) into equation (9), we get

$$[\mathrm{CAT}]_t = \frac{[\mathrm{TsNHCl}]}{1 + K_1\,[\mathrm{H}^+]} + [\mathrm{TsNHCl}] \qquad (11)$$

From equation (11), [TsNHCl] is given as

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

Rate of the reaction is given by slow/rate determining step, then

$$\mathrm{Rate} = k_2\,[\mathrm{TsNHCl}]\,[\mathrm{AO7}] \qquad (13)$$

By substituting for [TsNHCl] from Eqn 12 into Eqn 13, the following rate law is obtained:

$$\mathrm{Rate} = \frac{K_1 k_2\,[\mathrm{CAT}]_t\,[\mathrm{AO7}]\,[\mathrm{H}^+]}{1 + K_1\,[\mathrm{H}^+]} \qquad (14)$$

The above rate law (14) is in good agreement with the experimental results, wherein a first order dependence of rate on each $[\mathrm{CAT}]_o$ and $[\mathrm{AO7}]_o$ and a fractional order dependence on $[\mathrm{H}^+]$.

Since rate = $[\mathrm{CAT}]_t$, Eqn 14 can be transformed into Eqn 15:

$$\frac{1}{k^{/}} = \frac{1}{K_1 k_2\,[\mathrm{AO7}]\,[\mathrm{H}^+]} + \frac{1}{k_2\,[\mathrm{AO7}]} \qquad (15)$$

A plot of $1/k^{/}$ versus 1/[AO7] passes through the origin confirming observed kinetics. Further from the slope and intercept of the linear plot of $1/k^{/}$ versus $1/[\mathrm{H}^+]$, values of protonation constant (K_1) and dissociation constant (k_2) were found to be 0.05735 $\mathrm{dm}^3\,\mathrm{mol}^{-1}$ and 0.055 $\mathrm{dm}^3\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$, respectively.

Effect of dielectric constant

Several approaches have been put forward to explain quantitatively the effect of dielectric constant of the medium on the rates of reactions in solutions. For the limiting case of zero angle of approach between two dipoles or an ion-dipole system, Amis [26] has shown that a plot of log $k^{/}$ against 1/D gives a straight line with a negative slope (Figure 4; r > 0.9943) for the reaction between a negative ion and a dipole or between two dipoles, while a positive slope indicates a reaction between a positive ion and a dipole. The negative dielectric effect in the present studies is in agreement with dipole-dipole nature of the rate determining step in the proposed scheme and the reaction pathways suggested explaining the kinetic results.

Solvent isotope studies

Reactions in aqueous medium that are susceptible to acid-base catalysis have been studied in heavy water (D_2O) after equilibrium. Since most oxidation reactions of organic compounds involve the cleavage of C-H bond, deuterium isotope effect on such reactions gives information regarding the nature of the rate determining step. In the present investigations, solvent isotope studies have shown that the rate of reaction is higher in D_2O medium. For a reaction involving a fast equilibrium with H^+ or OH^- ion transfer, the rate increases in D_2O medium since D_3O^+ and OD^- are a stronger acid and a stronger base respectively, than H_3O^+ and OH^- ions [27-28]. The observed solvent isotope effect of $k^{/}(H_2O) / k^{/}(D_2O) < 1$ is due to the greater acidity of D_3O^+ compared to H_3O^+. However, the magnitude of increase in rate in D_2O is small as compared to the expected value which is 2-3 times greater. This may be due to the fractional-order dependence of the rate on $[H^+]$. Hence, this observation supports the proposed mechanism.

The negligible influence of variation of ionic strength and addition of p-toluenesulfonamide and halide ions are in agreement with the proposed mechanism. The proposed mechanism is also supported by the moderate value of energy of activation and other thermodynamic parameters (Table 3). The fairly high positive values of $\Delta G^{\neq}$ and $\Delta H^{\neq}$ indicate that the transition state is solvated while the negative entropy of activation reflects the formation of a compact and ordered transition state. Further, the experimental observation shows that there is no effect of p-toluenesulfonamide, halide ions and ionic strength on the reaction rate which also substantiates the proposed mechanism.

CONCLUSION

The kinetics of oxidation of AO7 by chloramine-T in acid medium obeys the rate law $-d[CAT] / dt = k\,[CAT]_o\,[AO7]_o\,[acid]^{0.60}$. Oxidation products were identified by GC-MS analysis. The present method developed for the oxidative decolorization of AO7 with CAT offers several advantages including cost effective and relatively non-toxic reagents, which make the reaction process simple, smooth and environmentally benign. Furthermore, the simple and elegant method developed in the present research can be adopted for treating the AO7 dye present in industrial effluents to minimize the toxicity caused by this dye.

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10^3 [CAT]$_o$ (mol dm^{-3})	10^4 [AO7]$_o$ (mol dm^{-3})	10^3 [HClO$_4$] (mol dm^{-3})	10^4 $k^{/}$ (s^{-1})
0.40	0.80	0.40	1.74
0.80	0.80	0.40	4.81
1.60	0.80	0.40	9.30
2.00	0.80	0.40	11.5
3.20	0.80	0.40	18.6
0.80	0.40	0.40	4.78
0.80	0.80	0.40	4.85
0.80	1.60	0.40	4.89
0.80	2.00	0.40	4.73
0.80	3.20	0.40	4.88
0.80	0.80	0.20	2.88
0.80	0.80	0.40	4.81
0.80	0.80	0.80	7.17
0.80	0.80	1.60	10.2
0.80	0.80	3.20	18.3

Table 1. Effect of variation of CAT, AO7 and HClO$_4$ concentrations on the reaction rate at 297 K.

% MeOH (v/v)	D	$10^4 k^{/}$ (s^{-1})
0	76.7	4.81
5	74.5	2.15
10	72.3	1.04
15	69.7	0.36
20	67.5	0.13

$[CAT]_o = 8.00 \times 10^{-4}$ mol dm^{-3}, $[AO7]_o = 8.00 \times 10^{-5}$ mol dm^{-3}, $[HClO_4] = 4.00 \times 10^{-4}$ mol dm^{-3}.

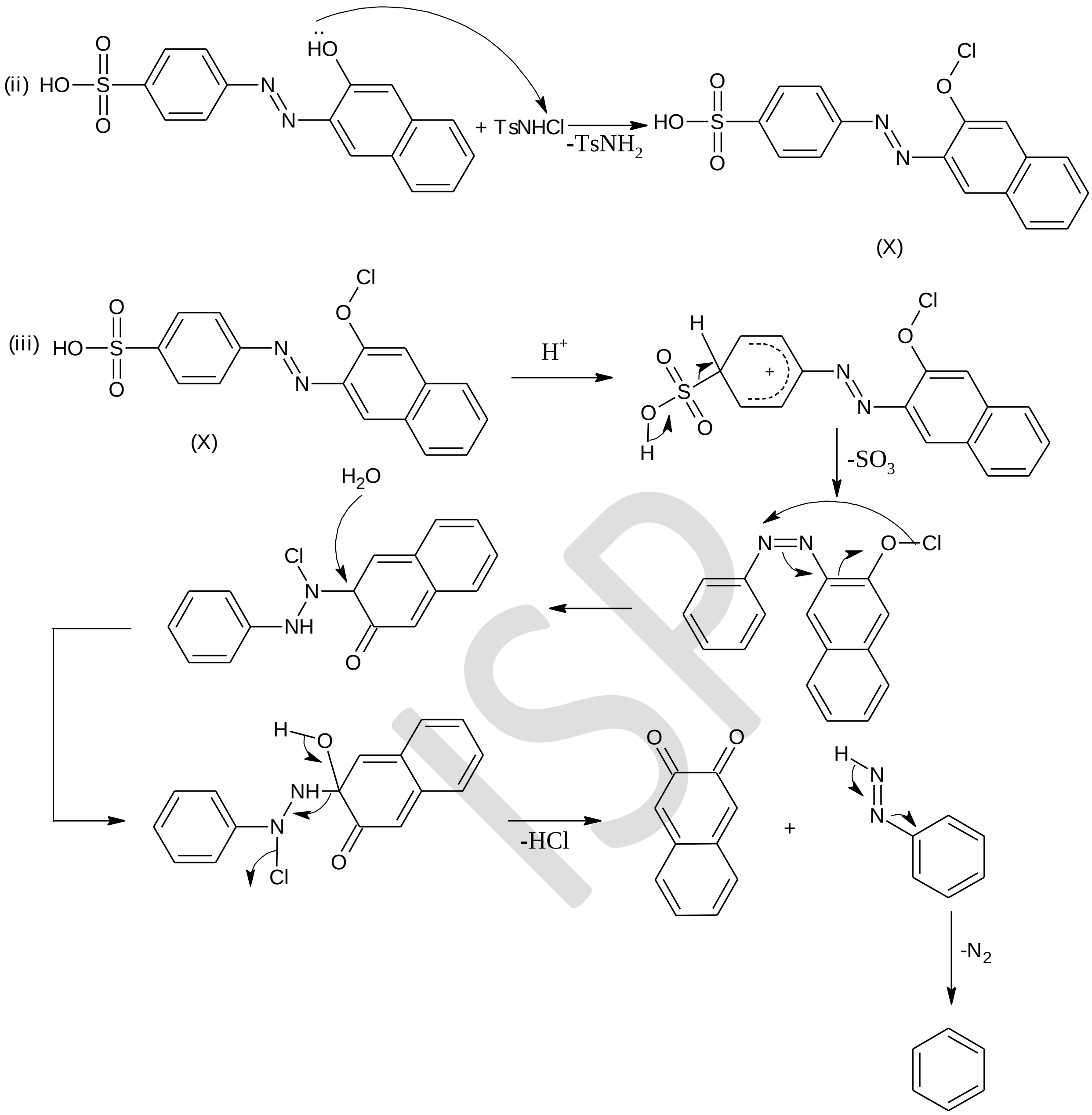
Table 2. Effect of varying dielectric constant (D) of medium on the rate of reaction at 297 K

Temperature (K)	$10^4 k^{/}$ (s^{-1})
288	1.84
293	3.16
298	4.81
308	12.6
313	23.4
E_a (kJ mol^{-1})	71.7
$\Delta H^{\neq}$ (kJ mol^{-1})	69.2
$\Delta G^{\neq}$ (kJ mol^{-1})	91.8
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	-75.4

$[CAT]_o = 8.00 \times 10^{-4}$ mol dm^{-3}; $[AO7]_o = 8.00 \times 10^{-5}$ mol dm^{-3}; $[HClO_4] = 4.00 \times 10^{-4}$ mol dm^{-3}.

Table 3. Temperature dependence on the reaction rate and activation parameters for the oxidation of AO7 by CAT acid medium

(i) $TsNCl^- + H^+ \longrightarrow TsNHCl$



Scheme 2. A detailed mechanistic interpretation for the oxidation of acid orange 7 by CAT in acid medium.

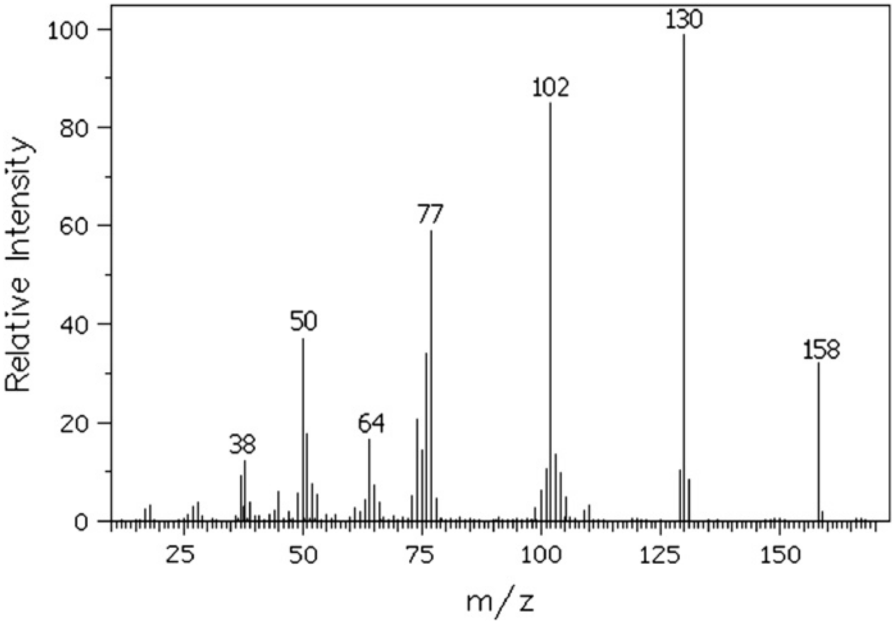


Figure 1. GC-Mass spectrum of naphthaquinone with its molecular ion peak at158 amu.

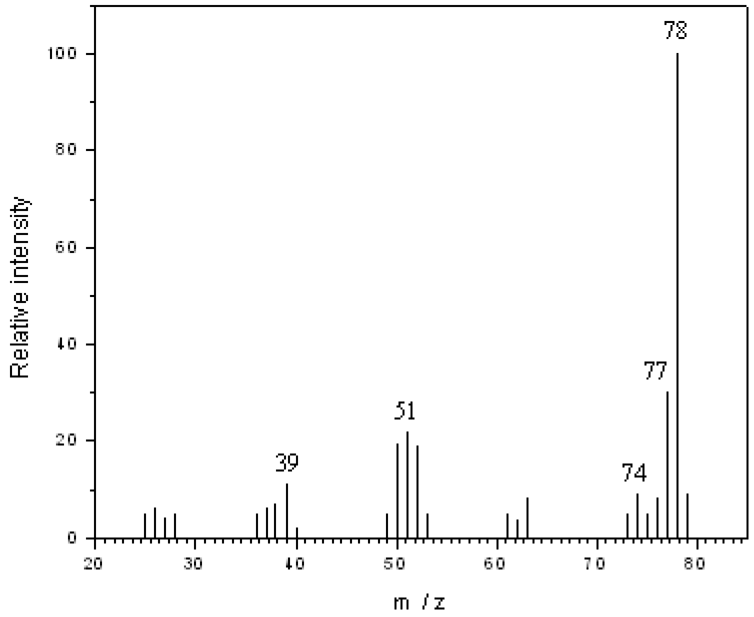


Figure 2. GC-Mass spectrum of benzene with its molecular ion peak at 78 amu.

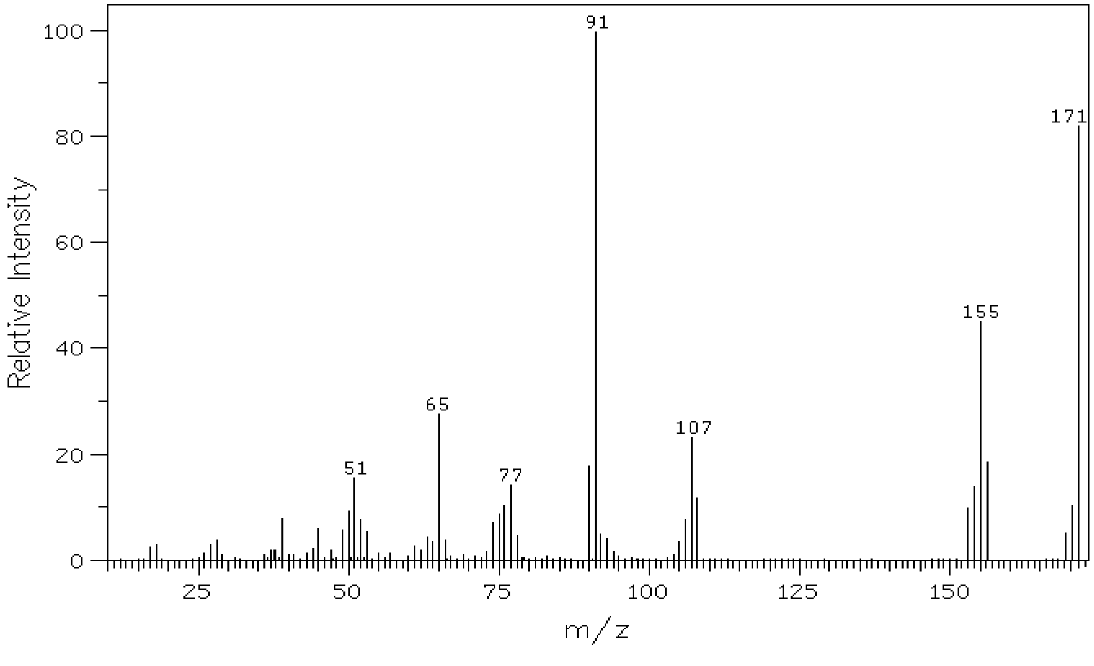


Figure 3. GC-Mass spectrum of p-toluenesulfonamide with its parent molecular ion peak at 171 amu

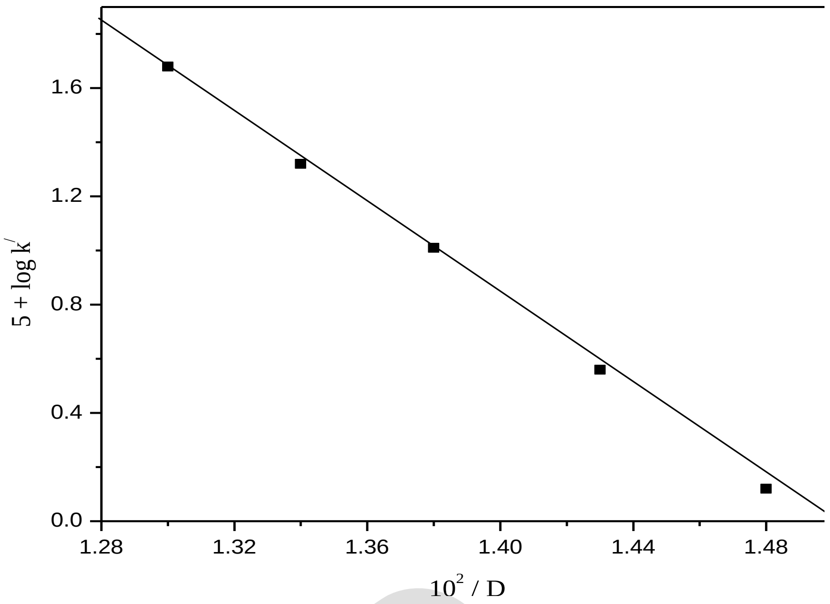


Figure 4. Arrhenius plot of log $k^{/}$ versus 1/D.

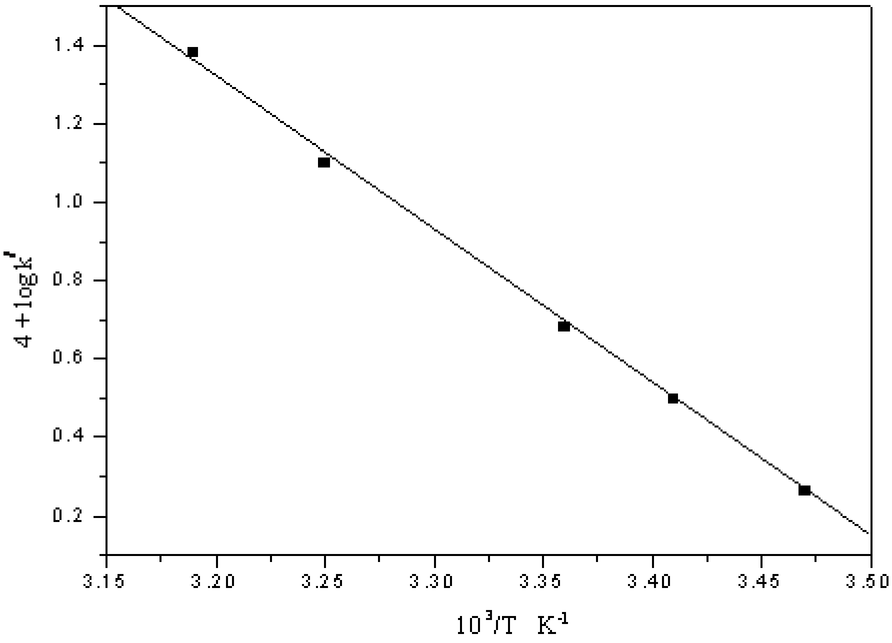


Figure 5. A plot of log $k^{/}$ versus 1/T