Spectrophotometric Kinetics and Mechanistic Chemistry of Oxidative Decolorization of Disperse Orange 13 by Sodium N-halo-p-toluenesulfonamides in Acid Medium

J.P. Shubha[a*], Y. Madhusudhan, R. Raveesha[b] and Puttaswamy[c]

[a]*Department of Chemistry, Don Bosco Institute of Technology, Kumbalagodu, Bangalore, India*

[b] *Q C Department, Apotex pharmachem Ind. Pvt. Ltd., Bommasandra Industrial area, Jigani Link Road, Bangalore, India*

[b]*Department of Chemistry, Central College Campus, Bangalore University, Bangalore, India*

Abstract: **The kinetics of oxidative decolorization of disperse orange 13 (DO13) by chloramine-T (CAT) and bromamine-T (BAT) in acid medium has been investigated spectrophotometrically (λ_{max} = 427 nm) at 298 K. UV-visible spectrophotometry was used as a basic analytical approach in the present kinetic study. Kinetic runs were performed under pseudo first-order conditions of $[oxidant]_o \gg [DO13]_o$. Under identical experimental conditions, reactions with both the oxidants follow identical kinetics with a first-order dependence on each $[oxidant]_o$ and $[DO13]$ and a fractional-order dependence on $[HClO_4]$. Stoichiometry of the reaction was found to be 1:4 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. The rate of oxidation of DO13 is about 2 times faster with BAT as compared to CAT. This may be attributed to the difference in electrophilicities of Cl^+ and Br^+ ions and also the van der Waal's radii of chlorine and bromine. Plausible mechanism and related rate law have been deliberated for the observed kinetics.**

Key words: Azo dyes, Disperse orange 13, Chloramine-T, Bromamine-T, Oxidation-Kinetics, Decolorization, Acid Medium.

I. INTRODUCTION

Variety of dyes used in textile industry usually have a synthetic origin and multifaceted aromatic molecular structures which make them more stable and more complicated to be biodegraded [1-3]. Colored industrial effluent is the most apparent indicator of water pollution and the discharge of highly colored synthetic dye effluents is aesthetically displeasing and cause considerable damage to the aquatic life. The effluents are strongly colored which not only created environmental and aesthetic problems, but also posed a great potential toxic threat to ecological human health as most of these dyes are toxic and carcinogenic. Predominantly azo dyes which contain one or more nitrogen to nitrogen double bonds (-N=N-) constitutes a significant portion that are widely used in industries today. The strong electron-withdrawing character of the azo group stabilizes these aromatic pollutants against conversions by oxygenases. Therefore, azo dyes are not readily degraded under aerobic conditions. Hence, removal of azo dye effluents generated by food and dye industries is a main issue in waste water treatment. These effluents are commonly treated using physico-chemical methods such as adsorption, photo degradation and coagulation. All of these processes are expensive and complicated. Therefore, there is a need for economical and simple methods to abolish harmful dyes in effluents [1-9].

Disperse orange 13 is a synthetic di-azo dye used in textiles and other dyeing processes [1]. An extensive literature survey reveals that there are no reports on the oxidation of DO13 by any oxidants from the standpoint of the kinetic and mechanistic approach. Hence, it was felt advisable to investigate the oxidative decolorization of DO13 with N-haloamines to explore the kinetic and mechanistic aspects of its redox chemistry.

The most important aim of this work was to promote the decolorization of DO13 by relatively non toxic N-haloamine, has a low energy cost and is economical. The effectiveness of the proposed process was evaluated by its capability to promote decreases 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 could also be employed in the remediation of effluents.

The sodium salts of arylhalosulfonamides usually recognized as organic haloamines have engrossed the concentration of chemists, as adaptable redox titrants [10]. The miscellaneous chemical behaviour of organic haloamines is credited in common to their capability to act as halonium cations, hypohalites, N-anions which act both as bases and nucleophiles, and nitrenoids in restrictive cases [11]. As a result, these compounds react with an ample range of functional groups and influence a variety of molecular changes. Organic haloamines are gentle oxidants

containing a strongly polarized N-linked halogen which is in +1 state. The area under discussion has been broadly reviewed and well deliberated [10-14]. The vital chlorine compound of this set is sodium N-chloro-p-toluenesulfonamide or chloramine-T (CAT), is a byproduct in the manufacture of saccharin. This reagent has been subjugated as an oxidant for a diversity of substrates in both acidic and alkaline media [10-20]. The bromine analogue of CAT, bromamine-T (BAT) is gaining significance as a mild oxidant and is found to be a enhanced oxidizing agent than the chloro derivative [12-14,21-23]. This reagent can be easily prepared by the bromination of CAT. Although BAT is an improved oxidant compare to CAT, an extensive literature analysis reveals that only intermittent references are accessible about the oxidative behavior of BAT from the kinetic and mechanistic points of vision. This aroused our attention to carry out the detailed kinetic study on the oxidation of DO13 by the closely associated reagents CAT and BAT in acid medium to discover the mechanistic aspects of these oxidations and also to assess their relative rates. The studies extended to the pertinent kinetic features of CAT and BAT and to identify the reactive oxidizing species of these oxidants in aqueous acid medium.

In the beam of accessible information and in extension of our research curiosity on the kinetic and mechanistic investigations of oxidation of various substrates in general and dyes in particular by CAT and BAT, the title reaction was undertaken. Accordingly, in this communication we report on the comprehensive kinetics of DO13 oxidation by CAT and BAT in $HClO_4$ medium at 298 K.

II. EXPERIMENTAL

2.1 Materials

Chloramine-T (E. Merck) and Disperse orange 13 (Sigma) were used as received. Bromamine-T was obtained [24] by the partial debromination of dibromamine-T (DBT) by 4 mol dm^{-3} NaOH. The purity of these reagents was checked iodometrically to determine the active halogen content. Aqueous solution of these oxidants was standardized by the iodometric method and stored in brown bottles to prevent any of its photochemical corrosion. Solvent isotope studies were made with D_2O (99.4 %) supplied by BARC, Mumbai, India. Analytical grade chemicals and double distilled water was used throughout.

2.2 Kinetic measurements

Kinetic measurements were carried out using a UV–Visible spectrophotometer (Digital Spectrophotometer 166, Systronics, India). In the present study, the kinetic experiments were carried out between 288 and 308 K. For this purpose, a Raagaa Ultra Cold Chamber with digital temperature control (Chennai, India) was used. The temperature was maintained constant with an accuracy of ± 0.1 ^{0}C. Detailed kinetic runs were performed under pseudo first-order conditions of $[oxidant]_0 >> [DO13]_0$ at 298 K. Reactions were conceded in glass stoppard pyrex boiling tubes whose outer surfaces were coated black to prevent photochemical effects. The oxidant as well as the requisite amounts of DO13, $HClO_4$ 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. Instantaneously, 4 cm^3 of the solution was pipetted into a cuvette placed in the UV-Vis spectrophotometer and absorbance measurements were made at 427 nm (λ_{max} for DO13) for more than two 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 ($k^/$) which were found reproducible within ±4–5%.

2.3 Reaction stoichiometry

Reaction mixtures containing different ratios of oxidant to DO13 in presence of 1.2 x 10^{-3} mol dm^{-3} $HClO_4$ were equilibrated at 293 K for 24 h. The unreacted oxidant in the reaction mixture was determined by iodometric titration. This analysis showed that in both the cases one mole of DO13 consumed four mole of oxidant and the observed reaction stoichiometry is represented as:

$$(1)$$
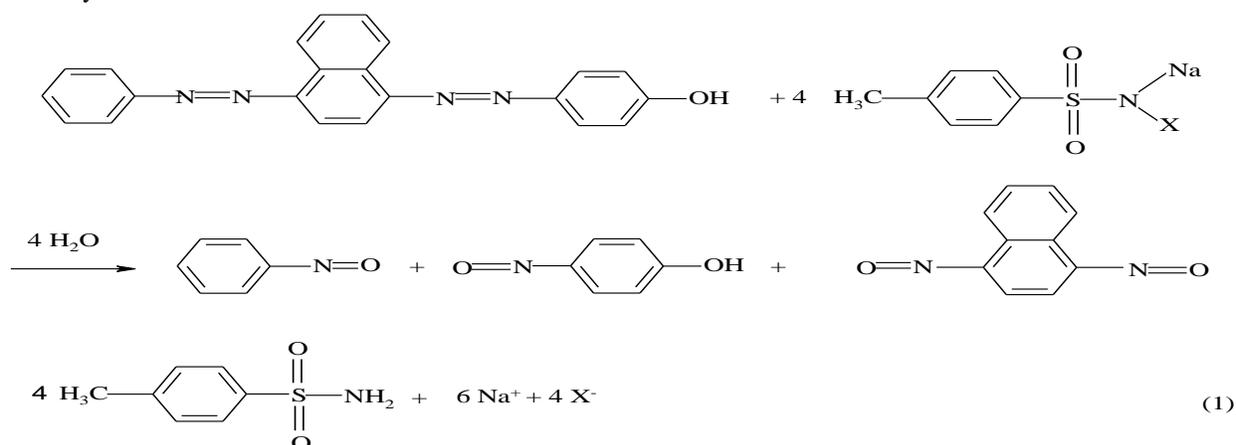
Where X= Cl or Br.

2.4 Product analysis

In the stoichiometric proportion, the reaction mixtures containing different concentrations of oxidant and substrate in 1.2 x 10^{-3} mol dm^{-3} $HClO_4$ under stirred condition was allowed to react for 24 h at 298 K. After completion of the reaction (monitored by thin layer chromatography), the reaction products were neutralized with alkali and extracted with ether. The organic products were subjected to spot tests [25] and chromatographic analysis, which revealed the formation of nitrosobenzene, nitrosophenol and dinitrosonaphthalene as the oxidation products of DO13 and p-toluenesulfonamide as the reduction product of the oxidant. These compounds were confirmed by mass spectral analysis. It was noticed that there was no reaction between the products and oxidant under the current set of experimental conditions.

p-toluenesulfonamide was extracted with ethyl acetate and detected by paper chromatography [26]. Benzyl alcohol saturated with water was used as the solvent system with 0.5 % vanillin in 1 % HCl solution in ethanol as spray reagent (R_f = 0.905) and it was further confirmed by mass spectral investigation.

III.   RESULTS AND DISCUSSION

3.1. Effect of reactant concentration on the rate

The kinetics of oxidation of DO13 by CAT and BAT (hereafter edited as oxidant) have been investigated at several initial concentrations of the reactants, under pseudo first-order conditions of [oxidant]$_o$ >> [substrate]$_o$, in presence of $HClO_4$ at 298 K in both cases. The kinetic and mechanistic features for the oxidation of DO13 with the closely related compounds CAT and BAT in $HClO_4$ medium are same under identical experimental conditions but the comparative rates of oxidation of DO13 by BAT are about three-fold faster than CAT.

Under the conditions [oxidant]$_0$ >> [DO13]$_0$ at constant [oxidant]$_0$, [$HClO_4$], temperature, plots of log (absorbance) versus time were linear (r>0.9876) indicating a first-order dependence of rate on [DO13]$_0$ in both the cases. The linearity of these plots in both cases, together with the constancy of the slopes obtained at different [DO13]$_0$, substantiates the first-order dependence of rate on [DO13]$_0$. The pseudo first-order rate constants (k$^/$) obtained are recorded in Table 1. Under the same experimental conditions the rate of reaction increased in [oxidant]$_0$ (Table 1) and plots of log k$^/$ versus log [oxidant] were linear (r>0.9895) with unit slopes in both the cases. This establishes that the order of the reaction is first-order with respect to [oxidant]$_0$. Further, plots of k$^/$ versus [oxidant]$_0$ were linear (r>0.9990) passing through the origin corroborate the first-order dependence on [oxidant]$_0$.

The rate of reaction augmented with increase in [$HClO_4$] (Table 1) and plots of log k$^/$ versus log [$HClO_4$] were linear (r > 0.9799) with slopes of 0.65 and 0.52 for CAT and BAT, showing a fractional-order dependence on [$HClO_4$].

3.2. Effects of halide ions and p-toluenesulfonamide concentration 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, representing the participation of nonionic species in the rate-determining step. Hence no attempts were made to maintain the ionic strength of the medium stable for kinetic runs. Addition of p-toluenesulfonamide (TsNH$_2$) to the reaction mixture (5.0 x 10^{-3} mol dm^{-3}) did not influence the rate significantly indicates that TsNH$_2$ is not involved in any step prior to the rate determining step of the proposed scheme.

3.3. Effect of dielectric constant of the medium on the rate

The dielectric constant (D) of the medium was mottled by adding MeOH (0-30 % v/v) to the reaction mixture with all other experimental conditions being held constant but the rates were not considerably altered with both the oxidants.

3.4. Effect of solvent isotope on the rate

Since the oxidation of DO13 by CAT and BAT was increased with H^+ ions, the solvent isotope effect was studied in D_2O as the solvent medium for both the oxidants. The rate constants for CAT and BAT revealed that k$^/$ (H_2O) was equal to 4.66 x 10^{-4} s^{-1} and 8.80 x 10^{-4} s^{-1}, and k$^/$ (D_2O) was 5.25 x 10^{-4} s^{-1} and 10.65 x 10^{-4} s^{-1}, respectively. Thus, the solvent isotope effect, k$^/$ (H_2O) / k$^/$ (D_2O) were found to be 0.88 and 0.82 for CAT and BAT.

3.5. Effect of temperature on the rate

The reaction was studied at different temperatures (288-313 K), keeping other experimental conditions constant. From Arrhenius plots of log k$^/$ vs. 1/T (r > 0.9934), composite activation parameters (E_a, $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$ and log A) were computed for the oxidation of DO13 by CAT and BAT. These data are summarized in Table 2.

3.6. Test for free radicals

Alkene monomers such as acrylonitrile and freshly prepared 10% acrylamide solution were added to the reaction mixture to instigate polymerization by free radicals

formed *in situ*. The lack of polymerization indicated the absence of free radicals in the reaction mixture. This clearly ruled out the possibility of free radical mechanism. The controlled experiments were also performed under similar reaction conditions without oxidant.

3.7. Reactive species of sodium n-halo-p-toluenesulfonamides

Organic N-haloamines are sources of positive halogens and these reagents have been exploited as oxidant for a variety of substrates in both acidic and alkaline media [11-13]. Since organic N-haloamines have analogous chemical properties, it is predicted that identical equilibria exist in aqueous acidic and basic solutions of these compounds [27,28]. Chloramine-T and bromamine-T act as oxidizing agents in acidic and alkaline media[2] with a two electron change per mole giving p-toluenesulfonamide (PTS) and NaCl or NaBr. The redox potential of CAT-PTS couple is pH dependent [22] and decreases with increase in pH of the medium (E_{redox} 1.138 V, 1.778 V, 0.614 V and 0.5 V at pH 0.65, 7.0, 9.7 and 12, respectively). In view of the homogeneity in properties of CAT and BAT, similar redox potential behaviour can be expected for BAT also. The nature of the active oxidizing species and mechanism depends on the nature of halogen atom, the groups attached to the nitrogen and the reaction condition. The species accountable for such oxidizing character may be different depending on the pH of the medium.
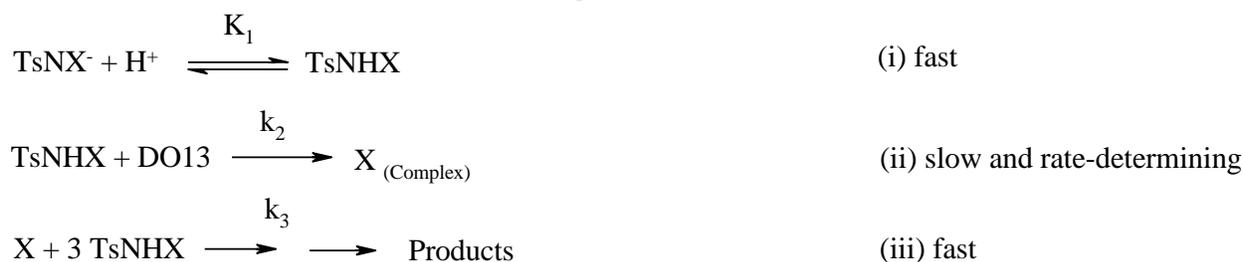
Chloramine-T and bromamine-T (TsNXNa) are moderately strong electrolytes [28] in aqueous solutions (TsNXNa $\rightleftharpoons$ TsN$^-$X + Na$^+$), and depending on the pH of the medium, these reagents furnish different types of reactive species in solutions [24, 27-31]. The possible oxidizing species present in acid medium are TsNHX, TsNX$_2$, HOX and also perhaps H$_2$OX$^+$.

3.8. Reaction scheme

In the present studies, the first-order dependence of rate on [oxidant]$_o$ and no effect of rate on [TsNH$_2$] clearly ruled out the opportunity of both TsNX$_2$ and HOX as reactive species. The probability of the dichloro compound as the reactive species is ruled out, since clear first-order plots are obtained for the desertion of the [substrate]. Added p-toluenesulfonamide does not hinder the reaction indicating that HOX is not primarily involved in the rate determining step. Further, Bishop and Jennings [28] have shown in their studies on aqueous solutions of CAT, that pH~ 3-4, the concentration of anion TsN$^-$Cl is greater than that of the free acid.

$$TsNCl^- + H^+ \rightleftharpoons TsNHCl \qquad (1)$$

Hence a protonation equilibrium (2) suggesting the anion can be assumed as the reactive oxidizing species. Since organic haloamines have similar chemical properties, the same equilibria can be expected for BAT also.

$$TsNX^- + H^+ \xrightleftharpoons{K_1} TsNHX \qquad \text{(i) fast}$$

$$TsNHX + DO13 \xrightarrow{k_2} X_{(Complex)} \qquad \text{(ii) slow and rate-determining}$$

$$X + 3\ TsNHX \xrightarrow{k_3} \longrightarrow Products \qquad \text{(iii) fast}$$

Scheme 2. A general reaction scheme for the oxidation of DO13 by CAT and BAT in acid medium.

3.9. Kinetic rate law

A detailed mode of oxidation of DO13 by CAT and BAT in acid medium is depicted in Scheme 3, where the structure of the intermediate complex x is shown.
Assuming a total efficient concentration of oxidant

$$[oxidant]_t = [TsN^-X] + [TsNHX] \qquad (2)$$

By substituting for [TsN⁻X] from equilibrium (i) of Scheme 1 in Eq. (3) and solving for [TsNHX], we get

$$[TsNHX] = \frac{K_1 \, [oxidant]_t + [H^+]}{1 + K_1 \, [H^+]} \qquad (3)$$

From slow and rate-determining step of Scheme 1

$$\text{Rate} = -d[oxidant]_t / dt = k_2[oxidant] \, [TsNHX] \qquad (4)$$

By substituting for [TsNHX] from Eq. (3) into Eq. (4), the following rate law is obtained:

$$\text{Rate} = \frac{K_1 \, K_2 \, [oxidant] \, [DO13] \, [H^+]}{1 + K_1 \, [H^+]} \qquad (5)$$

Rate law (5) is in good conformity with the experimental information.

　　　In the present investigations, disparity of dielectric constant of the medium does not have an effect on the rate appreciably. The effect of varying solvent composition and dielectric constant on the rate of reaction has been described in several studies [32-36]. For limiting case of zero angle of approach between two dipoles or an ion-dipole system, Amis [35] has shown that a plot of log $k^/$ versus $1/D$, gives a straight line with a negative slope for a reaction between a negative ion and a dipole or between two dipoles, where a positive slope results for a positive ion-dipole interaction. The total absence of the effect of varying dielectric constant on the rate cannot be explained by the Amis theory [35]. Applying the Born equation, Laidler [36] has anticipated the following equation for a dipole-dipole interaction:

$$\ln k^/ = \ln k_o + 3 / 8kT \, (2/D - 1) \, [\mu^2_A / r^3_A + \mu^2_B / r^3_B - \mu^2_{\neq} / r^3_{\neq}] \qquad (6)$$

where k_o is the rate constant in a medium of infinite dielectric constant, μ represents the dipole moment and r refers to the radii of the reactants and activated complex. It can be seen from Eq. (15) that the rates should be greater in a medium of lower dielectric constant when $r^3_{\neq} = r^3_A + r^3_B$ representing that the extent of charge scattering in the transition state is different. On the other hand, $r^3_{\neq} \approx r^3_A + r^3_B$ implies the absence of a dielectric effect of the solvent on the rate, as was observed in the present investigations, signifying that the transition state is not very much different from the reactants with respect to the size and charge of the transition state and the reactants.

　　　Reactions in aqueous medium that are vulnerable to acid-base catalysis have been studied in heavy water (D_2O) after equilibrium. Since the majority oxidation reactions of organic compounds involve the cleavage of C-H bond, deuterium isotope effect on such reaction gives information regarding the nature of the rate limiting 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 H^+ or OH^- ion transfer, the rate increases in D_2O medium since D_3O^+ or OD^- are a stronger acid and a stronger base respectively, than H_3O^+ and OH^- ions [37-39]. The observed solvent isotope effect of $k^/$ (H_2O) and $k^/$ (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 (expected value is 2-3 times greater). This may be due to the fractional order dependence of rate on [H^+]. Hence, this observation supports the planned mechanism.

3.10. Relative reactivity of CAT and BAT

　　　Association of the rates of reaction of CAT and BAT shows that the oxidation of AB is about two fold faster in BAT compared to CAT, under identical set of experimental circumstances. This is approved by the relative magnitudes of activation energies (Table 2). This tendency may be accredited to the disparity in elctrophilicities of the halocations, Cl^+ and Br^+ ions, involved in the oxidation processes and, is also related to the ease with which these species are generated in reactions. In these oxidation reactions, the electronegativity values of Br^+ and Cl^+ play a vital role. Bromine has the elctronegativity of 2.7, while chlorine has a higher value of 2.8. As the elcetronegativity increases the electropositive nature decreases. Since the halo cations are the reactive species in these oxidation reactions, the electropositive nature is in the order: Br > Cl. Therefore the reactivity of BAT is more compared to CAT. This trend may also be due to the moderate difference in the van der Waals's radii of bromine and chlorine. A similar behaviour has been in the oxidation of several other substrates using CAT and BAT. The facts furnished in the present research and the literature reports [13,14, 21,23, 40-42] led to conclude that BAT is a stronger oxidant compared to CAT.

The negligible influence of difference of ionic strength and addition of p-toluenesulfonamide and halide ions are in conformity with the proposed mechanism. The proposed mechanism is also supported by the sensible value of energy of activation and other thermodynamic parameters (Table 2). The moderately high positive values of $\Delta G^{\neq}$ and $\Delta H^{\neq}$ designate the transition state is solvated while the negative entropy of activation replicates the formation of a dense and planned transition state. Further, the experimental observation demonstrates that there is no effect of p-toluenesulfonamide, halide ions and ionic strength on the reaction rate which also substantiates the predictable mechanism.

In the present redox system the optimum conditions for the controlled oxidation of DO13 by CAT and BAT to corresponding nitroso compounds were established in acid medium. Accordingly, this redox system can be scaled up to industrial process. Furthermore, DO13 is one of the chief components in the effluents of various industries and is environmentally unsafe and also carcinogenic compound. Hence, the present simple method developed can be adopted for treating the DO13 dye present in industrial effluents to reduce toxicity caused by this dye. Also, this method offers several advantages including short reaction time, cost helpful and reasonably non-toxic reagents which make the reaction process trouble-free, neat and environmentally kind.

IV. CONCLUSIONS

The kinetics of oxidation of DO13 by CAT and BAT in acid medium obeys the rate law $-d[\text{oxidant}] / dt = k\ [\text{oxidant}]_o [\text{DO13}]_o\ [H^+]^x$, where x= 0.53 and 0.65 for CAT and BAT respectively. Oxidation products were identified by GC-MS analysis. The present method developed for the oxidative decolorization of DO13 with CAT and BAT offers several advantages including cost efficient and fairly non-toxic reagents, which make the reaction course simple, smooth and environmentally compassionate. Furthermore, the simple and well-designed method developed in the present research can be implemented for treating DO13 present in industrial effluents to diminish the toxicity caused by this dye.

ACKNOWLEDGEMENTS

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Table 1. Effect of Variation of oxidant, DO13 and $HClO_4$ concentrations on the reaction rate at 298 K.

10^3 [oxidant]$_o$ (mol dm^{-3})	10^4 [DO13]$_o$ (mol dm^{-3})	10^3 [HClO$_4$] (mol dm^{-3})	$10^4 k'$ (s^{-1}) CAT	$10^4 k'$ (s^{-1}) BAT
0.6	2.0	2.0	1.08	4.65
1.5	2.0	2.0	2.52	6.67
2.5	2.0	2.0	4.66	8.80
4.0	2.0	2.0	6.92	12.6
5.0	2.0	2.0	8.75	17.4
2.5	0.5	2.0	4.25	8.20
2.5	1.0	2.0	4.92	7.98
2.5	2.0	2.0	4.66	8.17
2.5	3.0	2.0	4.75	8.26
2.5	5.0	2.0	4.15	8.08
2.5	2.0	0.5	1.98	5.26
2.5	2.0	1.0	3.14	6.65
2.5	2.0	2.0	4.66	8.80
2.5	2.0	4.0	6.32	10.8
2.5	2.0	5.0	8.23	13.7

[oxidant]$_o$ = 2.5 x 10^{-3} mol dm^{-3}; [DO13]$_o$ = 2.0 x 10^{-4} mol dm^{-3}; [HClO$_4$] = 2.0 x 10^{-3} mol dm^{-3}.

Table 2. Temperature dependence on the reaction rate and activation parameters for the oxidation of DO13 by CAT and BAT in acid medium.

Temperature (K)	$10^4 k'$ (s^{-1}) CAT	$10^4 k'$ (s^{-1}) BAT
283	3.46	4.65
288	4.15	4.86
298	4.66	8.17
303	5.18	12.8
313	6.35	24.8
E_a (kJ mol^{-1})	20.1	17. 0
$\Delta H^{\neq}$ (kJ mol^{-1})	17.6	14.6
$\Delta G^{\neq}$ (kJ mol^{-1})	92.3	91.0
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	-249	-255
Log A	5.30	4.38

[oxidant]$_o$ = 2.5 x 10^{-4} mol dm^{-3}; [DO13]$_o$ = 2.0 x 10^{-3} mol dm^{-3}; [HClO$_4$] = 2.0 x 10^{-3} mol dm^{-3}.

(i) $TsNX^- + H^+ \rightleftharpoons^{K_1} TsNHX$

(ii)

(iii)

Where R is C_6H_5- and R^1 is C_6H_5OH -

Scheme 3. Detailed mechanistic interpretation for the oxidation of DO13 by CAT and BAT in acid medium.