Oxidative Decolorization Kinetics of Xylidine Ponceau by Bromamine-B in Acid Medium: Spectrophotmetric and Mechanistic Chemistry

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Abstract: - **Easy oxidative decolorization system has been urbanized for the removal of xylidine ponceau (XP) dye present in dissipate water. The kinetic and mechanistic features of the present redox design have also been examined. Kinetics and oxidative decolorization of XP with bromamine-B in $HClO_4$ medium at 298 K has been investigated spectrophotometrically at λ_{max} 388 nm. The reaction show first-order dependence each on $[BAB]_o$ and $[XP]_o$. Reaction proceeds with fractional-order dependence with respect to $[HClO_4]$. Activation parameters have been evaluated. The oxidation products were identified. The present kinetic data have been explained by suitable mechanism and related rate law is deduced.**

Key words: Azo dyes, xylidine ponceau, bromamine-B, oxidation-kinetics, decolorization, waste water treatment, acid medium.

I. INTRODUCTION

Multiplicity of dyes used in stuff engineering customarily have a reproduction source and resourceful aromatic molecular structures which make them more constant and more complex to be biodegraded [1-3]. Decorated industrial dirt is the most evident pointer of water contamination and the emancipation of extremely dyed synthetic color effluents is visually distressing and origin substantial injury to the water life. The effluents are muscularly colored which not only created environmental and aesthetic problems, but also pretense a great potential toxic risk to natural human health as most of these dyes are noxious and carcinogenic. Primarily azo dyes which contain one or more nitrogen to nitrogen double bonds (-N=N-) constitute a chief segment that are largely used in industries currently. The strong electron-withdrawing eminence of the azo group stabilizes these aromatic contaminants next to conversions by oxygenases. Therefore, azo dyes are not readily mottled under aerobic conditions. Hence, removal of azo dye effluents generated by food, textile and dye industries is a main concern in waste water management. These effluents are generally treated using physico-chemical methods such as adsorption, photo degradation and coagulation. All of these processes are classy and difficult.

Therefore, there is a need for realistic and easy methods to eradicate destructive dyes in effluents [1-10].

Xylidine ponceau (XP) is a mono azo dye used in textiles and other dyeing processes [1]. Comprehensive literature review reveals that there is no information on the oxidation of XP by any oxidants from the perspective of the kinetic and mechanistic approach. Hence, it was felt advantageous to scrutinize the oxidative decolorization of XP with bromamamine-B to determine the kinetic and mechanistic aspects of its redox chemistry.

The most significant intend of this work was to support the decolorization of XP by reasonably non toxic N-haloamine is economical. The competence of the projected method was evaluated by its latent to endorse decreases in color and total organic carbon substance. The efficiency observed with the dye replica showed that this financially viable, easily operated and preserved dealing could also be occupied in the remediation of effluents.

The chemistry of a class of N-metallo-N-haloarylsulfonamides, known as N-haloamines, attracted the attention of many investigators due to their diverse behaviour. Their versatile nature is attributed to their ability to act both as bases and nucleophiles [11]. As a result of this, these compounds cooperate with a wide range of functional groups in aqueous, moderately aqueous and non-aqueous media in presence of acids or alkalis, bringing about collection of molecular renovation. Monohaloamines in common undergo two electron changes while dihaloamines act as four electron oxidants. The reduction products obtained are the respective sulfonamide and sodium chloride [12]. The dominant members of this class of chlorocompounds are chloramine-T (CAT) and chloramine-B (CAB). A review of literature reveals that although the reaction of aromatic sulfonyl chloramines have been known and extensively investigated, [11, 13-17] there is not much of information [18-21] available on the reaction of corresponding bromamines, bromamine-T and bromamine-B. Sodium N-bromobenzenesulfonamide or bromamine-B (BAB; $C_6H_5SO_2NBrNa$ 1.5 H_2O BAB) has

gained importance as a mild oxidant and it can be readily prepared by brominating CAB. Bromamine-B is found to be a most potential oxidant among these N-haloamines. There are but a very few reports [22-25] on the kinetics of oxidation of organic substrates by BAB as compared to the studies with other haloamines as oxidants from mechanistic vision. For these grounds, it was felt motivating to explore the mechanism of oxidation of XP with this reagent. Accordingly, in this communication we report on the comprehensive kinetics of XP oxidation by BAB in $HClO_4$ medium at 298 K.

II. EXPERIMENTAL

2.1 Materials

Bromamine-B was prepared [26] by the partial debromination of dibromamine-B (DBB) as follows. Pure chlorine was bubbled through an aqueous solution of chloramine-B (30 g in 560 mL water) and liquid bromine (6 mL) was added drop wise with invariable stirring. A yellow precipitate of DBB formed was washed well with H_2O, filtered under suction, and dried in a vacuum desiccator. Dibromamine-B (31.5 g) was digested in batches with constant stirring in 50 mL of 4 mol dm^{-3} NaOH. The resulting mass was cooled in ice, filtered under suction, and the product (BAB) was dried over anhydrous calcium chloride. The purity of BAB was tested iodometrically through its active bromine content and its FT-IR spectrum. Aqueous solutions of BAB were prepared, standardized whenever required by the iodometric method and preserved in brown bottles to prevent its photochemical corrosion.28 Xylidine ponceau (Sigma Aldrich, gift sample) was used as received and aqueous solution of the dye was prepared fresh just before use. 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. The regression coefficient (r) was calculated using f_x – 350TL scientific calculator.

2.2 Kinetic measurements

Kinetic measurements were carried out using a 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 $[BAB]_0 >> [XP]_0$ at 298 K. Reactions were conceded in glass stoppard pyrex boiling tubes whose outer surfaces were coated black to avoid photochemical effects. The oxidant as well as the requisite amounts of XP, $HClO_4$ 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 measured amount of oxidant to the stirred reaction mixture. Immediately, 4 cm^3 of the solution was pipetted into a cuvette positioned in the UV-Vis spectrophotometer and absorbance dimensions were made at 388 nm (λ_{max} for XP) 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 BAB to XP in presence of 1.2 x 10^{-3} mol dm^{-3} $HClO_4$ were equilibrated at 293 K for 24 h. The unreacted BAB in the reaction mixture was determined by iodometric titration. This analysis showed that in both the cases one mole of XP consumed four mole of BAB and the observed reaction stoichiometry is represented as:
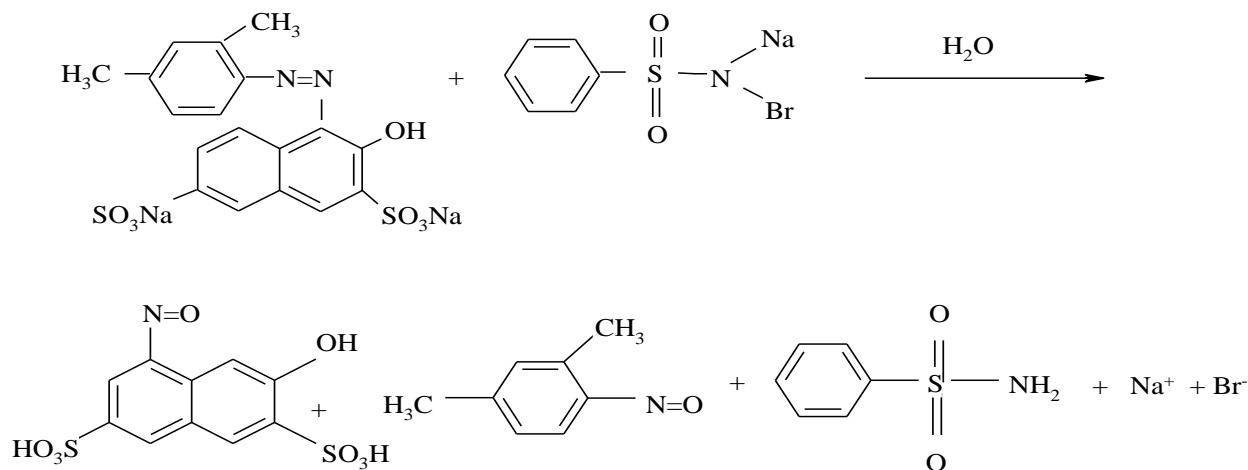
2.4 Product analysis

In the stoichiometric proportion, the reaction mixtures containing different concentrations of oxidant and substrate in 1.2×10^{-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 [27] and chromatographic analysis, which revealed the formation of nitroso compounds as the oxidation products of XP and benzene sulfonamide 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. Benzenesulfonamide, a reduction product of BAB, was also extracted with ethyl acetate and identified [24, 25] by TLC using pet. ether-CHCl$_3$-1-butanol (2:2:1, v/v) as a solvent system and iodine as a spray reagent (Rf = 0.88). It was further confirmed by GC-MS which showed a molecular ion peak of 157 amu (Figure 1).

III. RESULTS AND DISCUSSION

3.1. Effect of reactant concentration on the rate

The kinetics of oxidation of XP by BAB has 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. Under this conditions at constant [oxidant]$_0$, [HClO$_4$], temperature, plots of log (absorbance) versus time were linear (r>0.9952) indicating a first-order dependence of rate on [XP]$_0$. The linearity of the plot with the constancy of the slope obtained at different [XP]$_0$, substantiates the first-order dependence of rate on [XP]$_0$. The pseudo first-order rate constants (k$'$) obtained are recorded in Table 1. Under the same experimental conditions the rate of reaction increased in [BAB]$_0$ (Table 1) and plot of log k$'$ versus log [BAB] was linear (r>0.9955) with unit slope. This establishes that the order of the reaction is first-order with respect to [BAB]$_0$. Further, plot of k$'$ versus [BAB]$_0$ were linear (r>0.9980) passing through the origin corroborate the first-order dependence on [BAB]$_0$.

The rate of reaction augmented with increase in [HClO$_4$] (Table 1) and plots of log k$'$ versus log [HClO$_4$] was linear (*r* > 0.982) with slope of 0.69, 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 (1.0×10^{-3} - 8.0×10^{-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 assorted from 0.1 to 0.4 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 benzenesulfonamide (PhSO$_2$NH$_2$) to the reaction mixture (5.0×10^{-3} mol dm^{-3}) did not influence the rate significantly indicates that PhSO$_2$NH$_2$ 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. Values of dielectric constnt of MeOH-H$_2$O mixture reported in the literature [24] were used.

3.4. Effect of solvent isotope on the rate

Since the oxidation of XP by BAB was increased with H$^+$ ions, the solvent isotope effect was studied in D$_2$O as the solvent medium for both the oxidants. The rate constant revealed that k$'$ (H$_2$O) was equal to 3.85×10^{-4} s^{-1} and k$'$ (D$_2$O) was 4.22×10^{-4} s^{-1}. Thus, the solvent isotope effect, k$'$ (H$_2$O) / k$'$ (D$_2$O) was found to be 0.91.

3.5. Effect of temperature on the rate

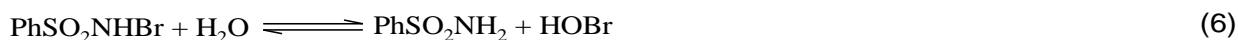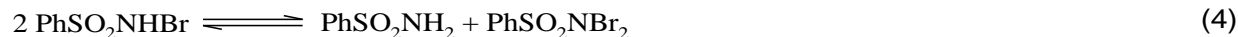The reaction was studied at different temperatures (288-313 K), keeping other experimental conditions constant. From Arrhenius plot of log k$'$ vs. 1/T (*r* > 0.9934), composite activation parameters (E$_a$, $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$ and log A) were computed for the oxidation of XP by BAB. 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 initiate 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 BAB

Organic haloamines have homogeneous chemical properties and hence it is expected that similar equilibria exist in solutions of these compounds.[28-31] Bromamine-B, which is analogous to chloramine-T and chloramine-B, behaves like a strong electrolyte both in acidic and alkaline media [28]. The oxidation potential of BAB/ PhSO$_2$NH$_2$ is pH dependent [11] and decreases with increase in the pH of the medium (1.4 V at pH 0.65 and 0.50 V at pH 12.0). In acid solutions, BAB exists in the following equilibria:
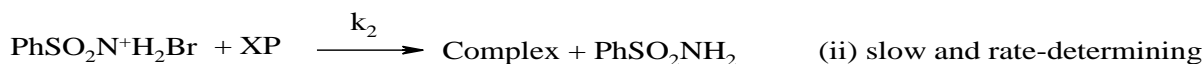
$$\text{PhSO}_2\text{NBrNa} \rightleftharpoons \text{PhSO}_2\text{NBr}^- + \text{Na}^+ \tag{2}$$

$$\text{PhSO}_2\text{NBr}^- + \text{H}^+ \rightleftharpoons \text{PhSO}_2\text{NHBr} \tag{3}$$

$$2\,\text{PhSO}_2\text{NHBr} \rightleftharpoons \text{PhSO}_2\text{NH}_2 + \text{PhSO}_2\text{NBr}_2 \tag{4}$$

$$\text{PhSO}_2\text{NBr}_2 + \text{H}_2\text{O} \rightleftharpoons \text{PhSO}_2\text{NHBr} + \text{HOBr} \tag{5}$$

$$\text{PhSO}_2\text{NHBr} + \text{H}_2\text{O} \rightleftharpoons \text{PhSO}_2\text{NH}_2 + \text{HOBr} \tag{6}$$

$$\text{HOBr} \rightleftharpoons \text{H}^+ + \text{OBr}^- \tag{7}$$

$$\text{HOBr} + \text{H}^+ \rightleftharpoons \text{H}_2\text{OBr}^+ \tag{8}$$

The possible oxidizing species in acidified BAB solutions are therefore the free acid (PhSO$_2$NHBr), dibromamine-B (PhSO$_2$NBr$_2$), hypobromous acid (HOBr) and possibly H$_2$O$^+$Br. The involvement of PhSO$_2$NBr$_2$ in the mechanism should correspond to a second-order rate law, which is contrary to the experimental observations. If HOBr were the primary oxidizing species, a first-order retardation of the rate by the added benzenesulfonamide would be expected, which is conflicting the investigations. Since pKa of

PhSO$_2$NHBr is 4.95 at 298 K, it is likely that under the present acidic conditions BAB may exist32 primarily as PhSO$_2$NHBr and any dependence of rate on [H$^+$] could be attributed to the addition of a second proton to PhSO$_2$NHBr. Furthermore, Narayanan and Rao [32] and Subhashini et al [33] have reported that monochloramines can be further protonated at pH 2 as shown in eq. (9) and eq. (10) for chloramine-T and chloramine-B, respectively

$$\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCl} + \text{H}^+ \rightleftharpoons (\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2\text{Cl})^+ \tag{9}$$

$$\text{PhSO}_2\text{NHCl} + \text{H}^+ \rightleftharpoons (\text{PhSO}_2\text{NH}_2\text{Cl})^+ \tag{10}$$

The second protonation constants for CAT and CAB are 102 M^{-1} and 61 ± 5 M^{-1} respectively at 298 K. Because organic haloamines have similar chemical properties, it is reasonable to expect the formation of an identical species of the type PhSO$_2$NH$_2$Br$^+$ for BAB also. In the present investigations, the acceleration of rate by H$^+$ ion indicates that PhSO$_2$NH$_2$Br$^+$ is the active oxidizing species. Further, variations of ionic strength of the medium or addition of the reaction product, benzenesulfonamide have virtually no effect on the rate. Based on the preceding discussion and experimental facts, Scheme 1 is proposed to explain the reaction mechanism for the oxidation of XP by BAB in HClO$_4$ medium.

A detailed mode of oxidation of XP by BAB in acid medium and the structure of intermediate are depicted in Scheme 2. In Scheme 2, an initial equilibrium involves protonation of PhSO$_2$NHBr forming the active oxidizing species of BAB, PhSO$_2$NH$_2$Br$^+$ (step (i)). In the next slow/rate determining step (step (ii)), nucleophilic attack on the positive bromine of PhSO$_2$NH$_2$Br$^+$ by a lone pair of electrons on nitrogen atom of XP, results in the formation of a complex cation X with the elimination of PhSO$_2$NH$_2$. In the next step (step (iii)), followed by several fast steps, the complex cation X undergoes hydrolysis leading to the formation of N-oxide with the elimination of HBr.

$$\text{PhSO}_2\text{NHBr} + \text{H}^+ \xrightleftharpoons{K_1} \text{PhSO}_2\text{N}^+\text{H}_2\text{Br} \qquad \text{(i) fast}$$

$$\text{PhSO}_2\text{N}^+\text{H}_2\text{Br} + \text{XP} \xrightarrow{k_2} \text{Complex} + \text{PhSO}_2\text{NH}_2 \qquad \text{(ii) slow and rate-determining}$$

$$\text{Complex} + \text{H}_2\text{O} \xrightarrow{k_3} \longrightarrow \longrightarrow \text{Products} \qquad \text{(iii) fast}$$

Scheme 1. General reaction scheme for the oxidation of XP by BAB in $HClO_4$ medium.

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

$$[BAB]_t = [PhSO_2NHBr] + [PhSO_2NH_2Br^+] \quad (11)$$

From step (i) of Scheme 1

$$[PhSO_2NHBr] = \frac{[PhSO_2N^+H_2Br]}{K_1 [H^+]} \quad (12)$$

$$[PhSO_2N^+H_2Br] = \frac{K_1 [BAB]_t [H^+]}{1 + K_1 [H^+]} \quad (13)$$

By substituting for $[PhSO_2NHBr]$ from equation (12) into equation (13) and solving for $[PhSO_2N^+H_2Br]$, we get

$$[PhSO_2N^+H_2Br] = \frac{K_1 [BAB]_t [H^+]}{1 + K_1 [H^+]} \quad (14)$$

From slow/rate-determining (step (ii)) of Scheme 1,

$$\text{rate} = k_2 [PhSO_2N^+H_2Br] [XP] \quad (15)$$

By substituting for $[PhSO_2N^+H_2Br]$ from equation (14) into equation (15), the following rate law (16) is obtained,

$$\text{rate} = \frac{K_1 k_2 [BAB]_t [XP] [H^+]}{1 + K_1 [H^+]} \quad (16)$$

Rate law (16) is in good agreement with the experimental results, wherein a first-order dependence each on $[BAB]_o$ and $[XP]_o$, and fractional-order on $[H^+]$ was observed.

3.8 Solvent Isotope Effect

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 [34-36]. 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:

$$\ln k' = \ln k_o + 3 / 8kT \, (2/D - 1) \, [\mu^2_A / r^3_A + \mu^2_B / r^3_B - \mu^2_{\neq} / r^3_{\neq}] \quad (17)$$

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. (17) 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.

3.9 Dielectric constant effect

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, 38]. 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.

The negligible influence of difference of ionic strength and addition of benzenesulfonamide 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 benzenesulfonamide, 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 XP by BAB were established

in acid medium. Accordingly, this redox system can be scaled up to industrial process. Furthermore, XP 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 XP 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 XP by BAB in acid medium obeys the rate law $-d[oxidant] / dt = k \ [BAB]_o \ [XP]_o \ [H^+]^{0.61}$. Oxidation products were identified by spot test spectral analysis. The present method developed for the oxidative decolorization of XP with BAB 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 XP present in industrial effluents to diminish the toxicity caused by this dye.

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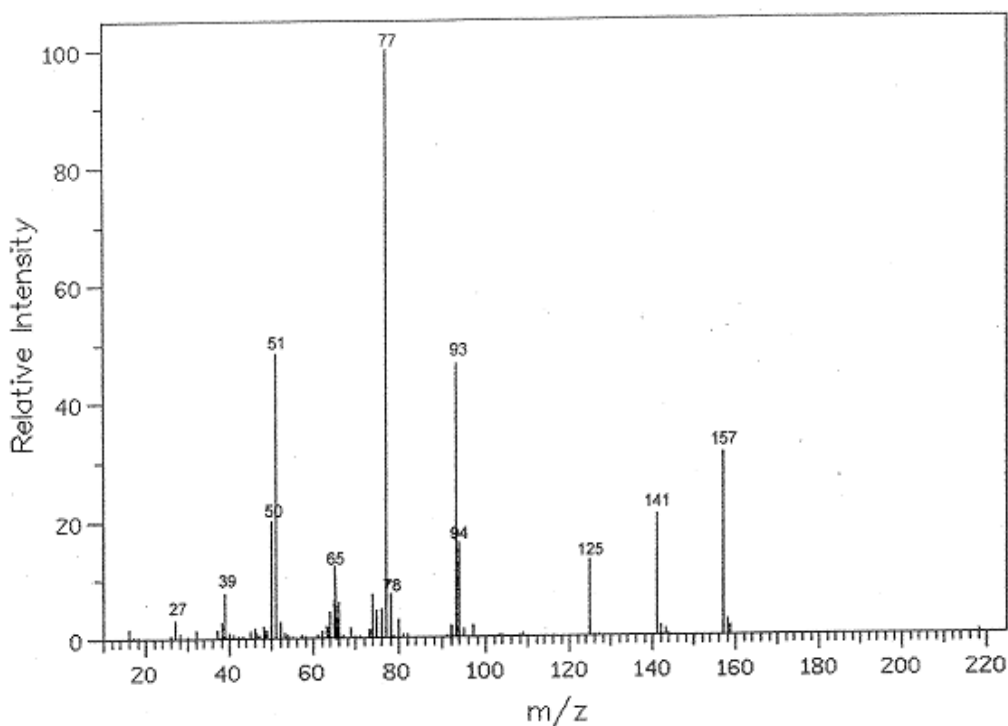
Fig. 1 Mass spectrum of benzenesulfonamide with its molecular ion peak at 157 amu.

(i) $PhSO_2NHBr + H^+ \rightleftharpoons PhSO_2N^+H_2Br$ (over arrow: K_1)
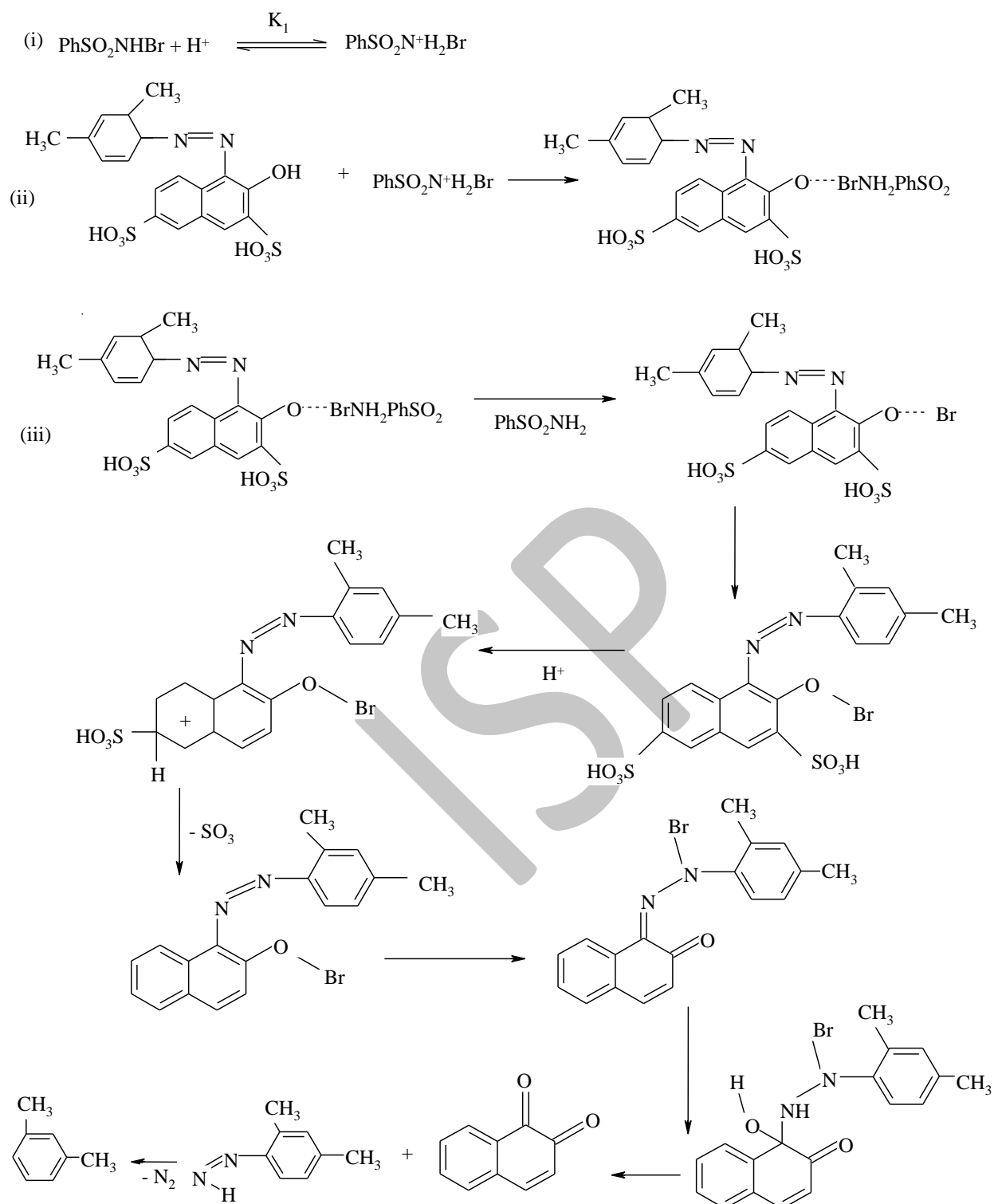
Scheme 3. Detailed mechanistic interpretation for the oxidation of XP by BAB in acid medium.

Table 1. Effect of variation of BAB, XP and $HClO_4$ concentrations on the reaction rate at 298 K.

10^3 [BAB]$_o$ (mol dm^{-3})	10^4 [XP]$_o$ (mol dm^{-3})	10^3 [HClO$_4$] (mol dm^{-3})	$10^4 k'$ (s^{-1})
0.5	2.0	4.0	1.32
1.0	2.0	4.0	2.59
1.5	2.0	4.0	3.85
3.0	2.0	4.0	7.26
5.0	2.0	4.0	12.4
1.5	0.5	2.0	3.25
1.5	1.0	2.0	3.92
1.5	2.0	4.0	3.85
1.5	3.0	2.0	3.75
1.5	5.0	2.0	3.54
1.5	2.0	1.5	1.62
1.5	2.0	2.0	2.57
1.5	2.0	4.0	3.85
1.5	2.0	6.0	4.76
1.5	2.0	8.0	5.92

Table 2. Temperature dependence on the reaction rate and activation parameters for the oxidation of XP by BAB in acid medium.

Temperature (K)	$10^4 k'$ (s^{-1})
283	1.52
288	2.18
298	3.85
303	4.83
313	7.74
E_a (kJ mol^{-1})	39.1
$\Delta H^{\neq}$ (kJ mol^{-1})	36.7
$\Delta G^{\neq}$ (kJ mol^{-1})	92.4
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	-187
Log A	8.57

[BAB]$_o$ = 1.5 x 10^{-4} mol dm^{-3}; [XP]$_o$ = 2.0 x 10^{-3} mol dm^{-3}; [HClO$_4$] = 4.0 x 10^{-3} mol dm^{-3}.

REFERENCES

[1] H. Zollinger, Colour chemistry: Synthesis, properties and applications of organic   dyes and pigments, New York, VCH, 1981.

[2] J. Perkowski, S. Ledakowicz. *Fibres Text East Eur.* **2002,** *10*, 68-72.

[3] B.D.Waters, Colour in Dyehouse Effluent, Cooper, P. Ed. Society of Dyers and Colourists, Bradford, **1995**.

[4] C.I. Pearce, J.R. Lloyd; Guthrie, J.T. *Dyes Pigments* **2003**, *58*, 179-196.

[5] G.D.A.Umbuzeiro, H.S.Freeman, S.H.Warren, D.P.De Oliveira, Y.Terao, T. Watanabe, L.D. Claxton *Chemosphere* **2005**, *60,* 55-64.

[6] J.Oakes, P. Gratton, *J. Chem. Soc. Perkin Trans 2* **1998**, 2201-2206 and references therein.

[7] E.N. Abrahat; Dyes and their intermediates, London, UK Edward AQrnolds Ltd. 1977.

[8] O. Ligrini, E. Oliveros, A. Braun, *Chem Rev* **1993**, *93,* 671-698.

[9] J.J.Roxon, A.J. Ryan, S.E.Wright, *Food Cosmet Toxicol* **1967,** *5*, 367-369.

[10] V.J. Jennings, *Critical Rev Anal-Chem* **1947,** 407-419.

[11] Campbell, M. M.; Johnson, G. *Chem. Rev*. **1978**, *78*, 65.

[12] Murthy, A. R. V.; Rao, B. S. *Proc Indian Acad. Sci.* **1952**, *35*, 69.

[13] Banerji, K. K.; Jayaram, B.; Mahadevappa, D. S. *J. Sci. Ind. Res.* **1987**, *46*, 65.

[14] Brenner, D. H. *In. Synth. Reagents* **1985**, *6*, 9.

[15] Gowda, B. T.; Mahadevappa, D. S. *J. Chem. Soc. Perkin Trans.II* **1983**, 323.

[16] Geethanjali, A. *Synlett.* **2005**, *18*, 2857.

[17] Kolvari, E.; Ghorbani-Choghamarani, A.; Salehi, P.; Shirini, F.; Zolfigol, M. A. *J. Iran.Chem. Soc.* **2007**, *4*, 126.

[18] Puttaswamy.; Mahadevappa, D. S.; Rangappa, K. S. *Bull. Chem. Soc. Japan* **1989**, *62*,3343.

[19] Ananda, S.; Jagadeesha, M. B.; Puttaswamy.; Venkatesha, B. M.; Vinod, T. K.; Gowda, N. M. M. *Int. J. Chem. Kinet.* **2000**, *32*, 776.

[20] Shashikala, V.; Rangappa, K. S. *J. Carbohyd. Chem.* **2002**, *21*, 219.

[21] Puttaswamy.; Jagadeesh, R. V. *Appl. Catal. A: Gen.* **2005**, *292*, 259.

[22] Meenakshisundaram, SP.; Markkandan, R. *Indian J. Chem.* **2005**, *44A*, 71.

[23] Usha, K. M.; Gowda, B. T. *J. Che. Sci.* **2006**, *118*, 351.

[24] Shubha J P, Puttaswamy, Bull. Korean, Chem. Soc., 2009, 30(9), 1939.

[25] Shubha J.P., Y. Madhusudhan, Puttaswamy, Int. J. Inno. Res. Sci., 2015, 4(3), 817-828.

[26] Ahmed, M. S.; Mahadevappa, D. S. *Talanta* **1980**, *27*, 669.

[27] Feigl F, Spot tests in Organic Analysis, 7th Edn., pp. 479-481. Elsevier, Amsterdam.

[28] Morris, J. C.; Salazar, J. A.; Wineman, M. A. *J. Am. Chem. Soc.***1948**, *70*, 2036.

[29] Bishop, E.; Jennings, V. J. *Talanta* **1959**, *1*, 197.

[30] Hardy, F. F.; Johnston, J. P. *J. Chem. Soc. Perkin Trans II* **1973**, 742.

[31] Pryde, B. G.; Soper, F. G. *J. Chem. Soc.* **1962**, 1582.

[32] Narayanan, S. S.; Rao, V. R. S. *Radio Chim. Acta* **1983**, *32*, 211.

[33] Subhashini, M.; Subramanian, M.; Rao, V. R. S. *Talanta* **1985**, *32*, 1082.

[34] Moelwyn-Hughes, E.A. The kinetics of reaction in solutions, Oxford, Clarender Press, 374-381, 1947.

[35] Amis, E.S. Rates *Anal Chem* **1955,** *27,* 1672-1679.

[36] Laidler, K.J. Chemical kinetics New Delhi, Tata Mc Graw-Hill, 211-228,1955.

[37] Collins CJ, Bowman NS Isotope Effects in Chemical Reactions New York, Van- Nostrand, 267, 1970.

[38] Kohen, A, Limbach, H.H. Isotope Effects in Chemistry and Biology. Florida, CRC Press, 827-844, 2006.