

Kinetics and Mechanistic Chemistry of Sodium N-Halobenzenesulfonamides Oxidative Decolorization of Azo Dye Acid Orange 10 in Acid Medium: Spectrophotometric Approach

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ABSTRACT: The kinetics of oxidative decolorization of acid orange 10 (AO10) by chloramine-B and bromamine-B in HClO₄ medium has been investigated spectrophotometrically ($\lambda_{\max} = 475$ nm) at 298 K. Kinetic runs were performed under pseudo first-order conditions of $[\text{oxidant}]_0 \gg [\text{AO10}]_0$. Under identical experimental conditions, reactions with both the oxidants follow identical kinetics with a first-order dependence on each $[\text{oxidant}]_0$ and $[\text{AO10}]_0$ and a fractional-order dependence on $[\text{HClO}_4]$. 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. The rate of oxidation of AO10 is about two-fold faster with BAB as compared to CAB. 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 dye, acid orange 10, Chloramine-B, Bromamine-B, Oxidation-Kinetics, 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].

Acid orange 10 (AO10, orange G) is used in textile fabrics. [1]. Extensive literature survey reveals that there are no reports on the oxidation of AO10 by any oxidants from the standpoint of the kinetic and mechanistic approach. Hence,

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it was felt advisable to investigate the oxidative decolorization of AO10 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 AO10 by 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 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 [10]. As a result of this, these compounds interact with a wide range of functional groups in aqueous, partially aqueous and non-aqueous media in presence of acids or alkalis, bringing about an array of molecular transformations. In general monohaloamines undergo two electron change while dihaloamines act as four electron oxidants. The reduction products obtained are the respective sulfonamide and sodium chloride [11]. 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 [10, 12-16] there is not much of information [17-20] available on the reaction of corresponding bromamines, bromamine-T and bromamine-B. Sodium N-bromobenzenesulfonamide or bromamine-B (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 few reports [21-22] on the kinetics of oxidation of organic substrates by BAB as compared to the studies with other haloamines as oxidants from mechanistic view point. For these reasons, it was felt interesting to investigate the mechanism of oxidation of AO10 with this reagent.

In the light of existing information and in continuation of our research interest on the kinetic and mechanistic investigations of oxidation of various substrates in general and dyes in particular by CAB and BAB, the title reaction was undertaken. Accordingly, in this communication we report on the comprehensive kinetics of AO10 oxidation by CAB and BAB in HClO₄ medium at 298 K.

II. EXPERIMENTAL

Chloramine-B (E. Merck) and acid orange 10 (Sigma Aldrich) were used as received. Bromamine-B was prepared [23] 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 dropwise with constant stirring. A yellow precipitate of DBB formed was washed well with H₂O, 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 deterioration [24]

Solvent isotope studies were made with D₂O (99.4 %) supplied by BARC, Mumbai, India. Analytical grade chemicals and double distilled water was used throughout.

Kinetic measurements

Kinetic measurements were carried out using a UV-Visible spectrophotometer (Elico SL159). 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 °C. Detailed kinetic runs were performed under pseudo first-order conditions of $[\text{oxidant}]_0 \gg [\text{AO10}]_0$ 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 AO10, HClO₄ 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 cm³ of the solution was pipetted into a cuvette placed in the UV-Vis spectrophotometer and absorbance measurements were

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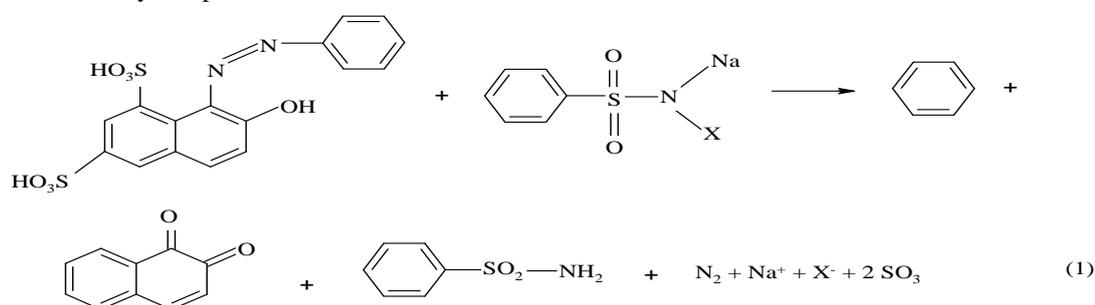
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made at 475 nm (λ_{\max} for AO10) for more than two half-lives. The absorbance readings at $t = 0$ and $t = t$ are D_0 and D_t . Plots of $\log D_0/D_t$ versus time were made to evaluate the pseudo first-order rate constants (k') which were found reproducible within $\pm 4-5\%$.

Reaction stoichiometry

Reaction mixtures containing different ratios of oxidant to AO10 in presence of $2.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ HClO}_4$ were equilibrated at 298 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 FRE consumed one mole of oxidant and the observed reaction stoichiometry is represented as:



Product analysis

In the stoichiometric proportion, the reaction mixtures containing different concentrations of oxidant and substrate in $2.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ HClO}_4$ 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 and chromatographic analysis, which revealed the formation of benzene and naphthaquinone as the oxidation products of AO10 and benzenesulfonamide as the reduction product of the oxidant. The products were confirmed by Mass spectral analysis [Fig. 1 & Fig. 2].

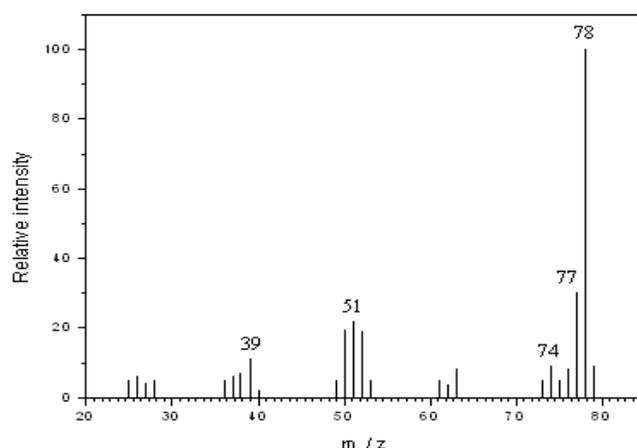


Fig- 1 Mass spectrum of benzene with its molecular ion peak at 78 amu.

The reduction product of the oxidant, benzenesulfonamide, was extracted with ethylacetate and detected by TLC using petroleum ether: CHCl_3 : 1-butanol (2:2:1, v/v) as the solvent system and iodine as spraying agent ($R_f = 0.88$).

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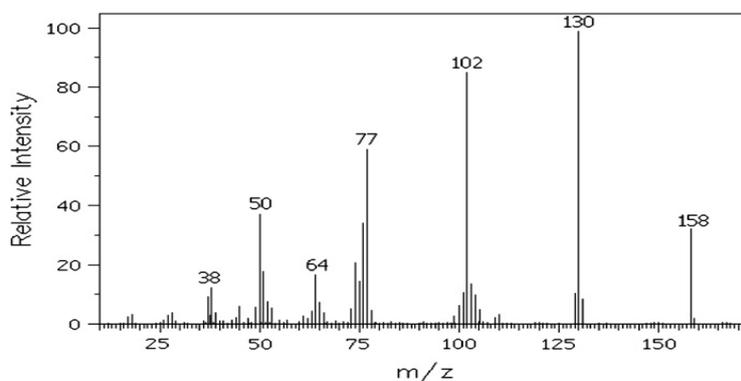


Fig. 2 Mass spectrum of naphthaquinone with its molecular ion peak at 158 amu.

It was further confirmed by GC-MS analysis. Molecular ion peak of 157 amu clearly confirms benzenesulfonamide (Fig. 3). All other peaks observed in MS can be interpreted in accordance with the observed structure. It was also noticed that there was no further oxidation of these products under present kinetic conditions.

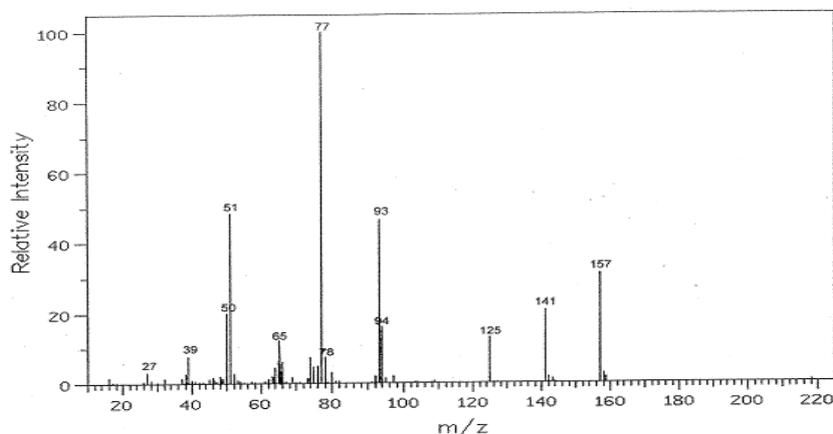


Fig. 3 Mass spectrum of benzenesulfonamide with its molecular ion peak at 157 amu.

III. RESULTS AND DISCUSSION

Effect of reactant concentration on the rate

The kinetics of oxidation of AO10 by CAB and BAB (hereafter condensed as oxidant) have been investigated at several initial concentrations of the reactants, under pseudo first-order conditions of $[\text{oxidant}]_0 \gg [\text{AO10}]_0$, in presence of HClO_4 at 298 K in both cases. The kinetic and mechanistic features for the oxidation of AO10 with the intimately related compounds CAB and BAB in HClO_4 medium are same under identical experimental conditions but the comparative rates of oxidation of AO10 by BAB are about two-fold faster than CAB.

Under the conditions $[\text{oxidant}]_0 \gg [\text{AO10}]_0$ at constant $[\text{oxidant}]_0$, $[\text{HClO}_4]$, temperature, plots of $\log(\text{absorbance})$ versus time were linear ($r > 0.9972$) indicating a first-order dependence of rate on $[\text{AO10}]_0$ in both the cases. The linearity of these plots in both cases, together with the constancy of the slopes obtained at different $[\text{AO10}]_0$, substantiates the first-order dependence of rate on $[\text{AO10}]_0$. The pseudo first-order rate constants (k') obtained are recorded in Table 1.

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Table - 1 Effect of Variation of oxidant, AO10 and HClO₄ concentrations on the reaction rate at 298 K.

| 10 ³ [oxidant] ₀ (mol dm ⁻³) | 10 ⁴ [AO10] ₀ (mol dm ⁻³) | 10 ³ [HClO ₄] (mol dm ⁻³) | 10 ⁴ k' (s ⁻¹) | |
|---|--|---|---------------------------------------|------|
| | | | CAB | BAB |
| 1.0 | 2.0 | 2.0 | 1.52 | 2.66 |
| 2.0 | 2.0 | 2.0 | 2.35 | 5.01 |
| 3.0 | 2.0 | 2.0 | 3.58 | 7.52 |
| 4.0 | 2.0 | 2.0 | 4.65 | 10.2 |
| 5.0 | 2.0 | 2.0 | 6.24 | 16.6 |
| 3.0 | 0.5 | 2.0 | 3.56 | 12.5 |
| 3.0 | 1.0 | 2.0 | 3.65 | 7.83 |
| 3.0 | 2.0 | 2.0 | 3.58 | 7.52 |
| 3.0 | 3.0 | 2.0 | 3.72 | 7.74 |
| 3.0 | 4.0 | 2.0 | 3.30 | 7.40 |
| 3.0 | 2.0 | 0.5 | 1.46 | 3.05 |
| 3.0 | 2.0 | 1.0 | 2.85 | 5.98 |
| 3.0 | 2.0 | 2.0 | 3.58 | 7.52 |
| 3.0 | 2.0 | 3.0 | 5.61 | 11.7 |
| 3.0 | 2.0 | 4.0 | 8.20 | 17.2 |

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 (Fig. 4; r>0.9898) 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>0.9970) passing through the origin corroborate the first-order dependence on [oxidant]₀.

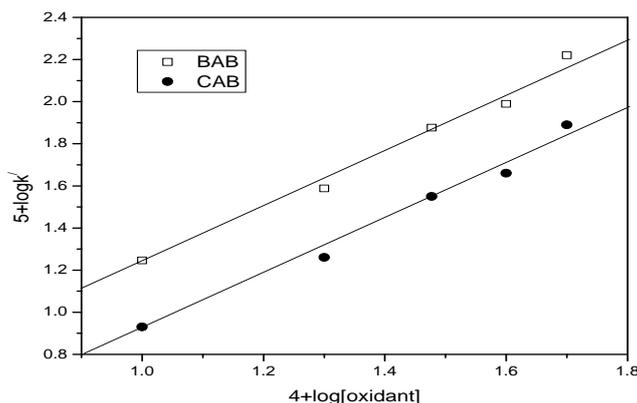


Fig. 4 Plot of log [oxidant] versus log k'.

The rate of reaction augmented with increase in [HClO₄] (Table 1) and plots of log k' versus log [HClO₄] were linear (Fig. 5; r > 0.9788) with slopes of 0.69 and 0.66 for CAB and BAB, showing a fractional-order dependence on [HClO₄].

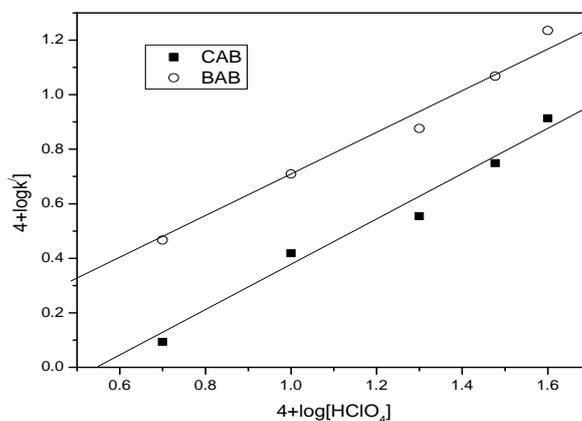


Fig. 5 Plot of $\log [\text{HClO}_4]$ versus $\log k'$.

Effects of halide ions and benzenesulfonamide 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 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 benzenesulfonamide (RNH_2) to the reaction mixture (5.0×10^{-3} mol dm^{-3}) did not influence the rate significantly indicates that RNH_2 is not involved in any step prior to the rate determining step of the proposed scheme.

Effect of dielectric constant of the medium and solvent isotope 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. Since the oxidation of AO10 by CAB and BAB 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 CAB and BAB revealed that $k'(\text{H}_2\text{O})$ was equal to $3.58 \times 10^{-4} \text{ s}^{-1}$ and $7.52 \times 10^{-4} \text{ s}^{-1}$, and $k'(\text{D}_2\text{O})$ was $4.16 \times 10^{-4} \text{ s}^{-1}$ and $10.6 \times 10^{-4} \text{ s}^{-1}$, respectively. Thus, the solvent isotope effect, $k'(\text{H}_2\text{O}) / k'(\text{D}_2\text{O})$ were found to be 0.85 and 0.70 for CAB and BAB.

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. $1/T$ (Fig. 6; $r > 0.9955$), composite activation parameters (E_a , ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger and $\log A$) were computed for the oxidation of AO10 by CAB and BAB. These data are summarized in Table 2.

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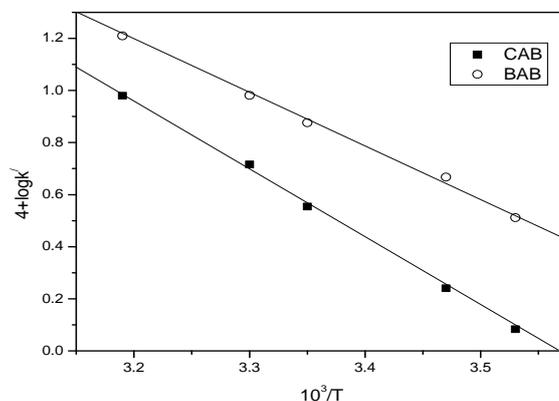


Fig. 5 Plot of $1/T$ versus $\log k'$.

Table - 2 Temperature dependence on the reaction rate and activation parameters for the oxidation of AO10 by CAB and BAB in acid medium.

| Temperature (K) | $10^4 k' (s^{-1})$ | $10^4 k' (s^{-1})$ |
|---|--------------------|--------------------|
| | CAB | BAB |
| 283 | 1.12 | 3.25 |
| 288 | 1.40 | 4.65 |
| 298 | 3.58 | 7.52 |
| 303 | 4.87 | 9.58 |
| 313 | 9.05 | 16.2 |
| E_a (kJ mol ⁻¹) | 52.3 | 41.9 |
| ΔH^\ddagger (kJ mol ⁻¹) | 49.8 | 39.4 |
| ΔG^\ddagger (kJ mol ⁻¹) | 92.5 | 90.6 |
| ΔS^\ddagger (JK ⁻¹ mol ⁻¹) | -143 | -172 |
| Log A | 11.2 | 9.95 |

$[\text{oxidant}]_0 = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{AO10}]_0 = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{HClO}_4] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$.

Polymerization study

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 sodium N-halo-benzenesulfonamides

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 [12, 16]. Since organic N-haloamines have analogous chemical properties, it is predicted that identical equilibria exist in aqueous acidic and basic solutions of these compounds [25-26]. Chloramine-B and bromamine-B act as oxidizing agents in acidic and alkaline media [27-29] with a two electron change per mole giving benzenesulfonamide (BSA) and NaCl or NaBr. The redox potential of CAT-PTS couple is pH dependent [25] 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 N-haloamines, similar redox potential behaviour can be expected for CAB and BAB 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.

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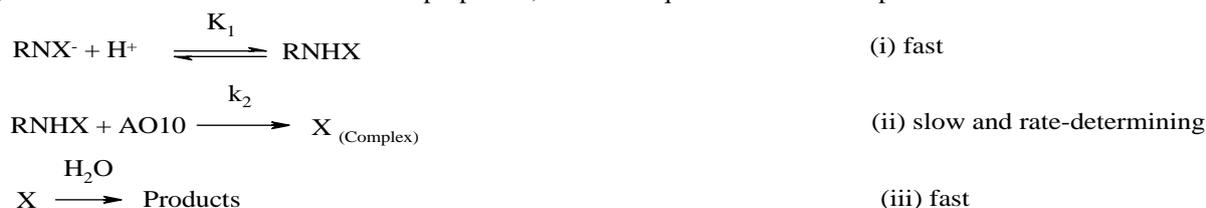
Chloramine-B and bromamine-B (RNXNa) are moderately strong electrolytes [26] in aqueous solutions ($\text{RNXNa} \rightleftharpoons \text{RNX} + \text{Na}^+$), and depending on the pH of the medium, these reagents furnish different types of reactive species in solutions [26, 28-29]. The possible oxidizing species present in acid medium are RNHX, RNX_2 , HOX and also perhaps H_2OX^+ .

Reaction scheme

In the present studies, the first-order dependence of rate on $[\text{oxidant}]_0$ and no effect of rate on $[\text{RNH}_2]$ clearly ruled out the opportunity of both RNX_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 desorption of the [substrate]. Added benzenesulfonamide does not hinder the reaction indicating that HOX is not principally 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.

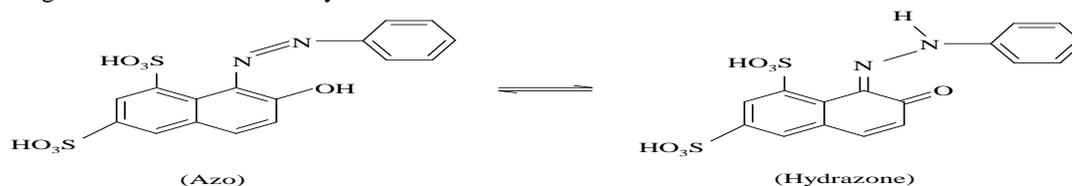


Hence a protonation equilibrium (1) suggesting the anion can be assumed as the reactive oxidizing species. Since organic haloamines have similar chemical properties, the same equilibrium can be expected for CAB and BAB also.



Scheme 1. A general reaction scheme for the oxidation of AO10 by CAB and BAB in acid medium.

In general azo dyes containing hydroxyl groups conjugated to azo group exhibit azo-hydrazone tautomerism. Since AO10 belongs this class of monoazo dyes and hence it exhibits tautomerism as shown below.



In the present case, the azo form of the dye reacts with the conjugate acid of the oxidant to form a AO10-oxidant complex (X) with the elimination of RNH_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 AO10 by CAB and BAB in acid medium is illustrated in Scheme 2, where the structure of the transitional complex X is shown. In a fast initial equilibrium (step (i) of Scheme 1), the anion RNX^- , in acid accelerating step generates the active oxidizing species RNHX. In a slow / rate limiting step (step (ii)), the lone pair of electrons on oxygen of AO10 attacks the positive halogen of RNHX 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 naphthalene as end products.

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

$$[\text{oxidant}]_t = [\text{RN}^-\text{X}] + [\text{RNHX}] \quad (9)$$

By substituting $[\text{RN}^-\text{X}]$ from step (i) of Scheme 1, into Eqn 9 and solving for $[\text{RNHX}]$, one gets,

$$[\text{RNHX}] = \frac{K_1 [\text{oxidant}]_t [\text{H}^+]}{1 + K_1 [\text{H}^+]} \quad (10)$$

From the slow and rate determining step (step (ii) of Scheme 1),

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$$\text{Rate} = k_2 [\text{RNHX}] [\text{AO10}] \quad (11)$$

By substituting for $[\text{RNHX}]$ from Eqn 10 into Eqn 11, the following rate law is obtained:

$$\text{Rate} = \frac{K_1 k_2 [\text{oxidant}]_t [\text{AO10}] [\text{H}^+]}{1 + K_1 [\text{H}^+]} \quad (12)$$

The derived rate law 12 is in good agreement with the experimental results, wherein a first order dependence of rate on each $[\text{oxidant}]_o$ and $[\text{AO10}]_o$ and a fractional-order dependence on $[\text{H}^+]$.

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 [30-34]. For limiting case of zero angle of approach between two dipoles or an ion-dipole system, Amis [33] 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 [33]. Applying the Born equation, Laidler [34] has anticipated the following equation for a dipole-dipole interaction:

$$\ln k' = \ln k_o + 3 / 8kT (2/D - 1) [\mu_A^2 / r_A^3 + \mu_B^2 / r_B^3 - \mu_{\neq}^2 / r_{\neq}^3] \quad (13)$$

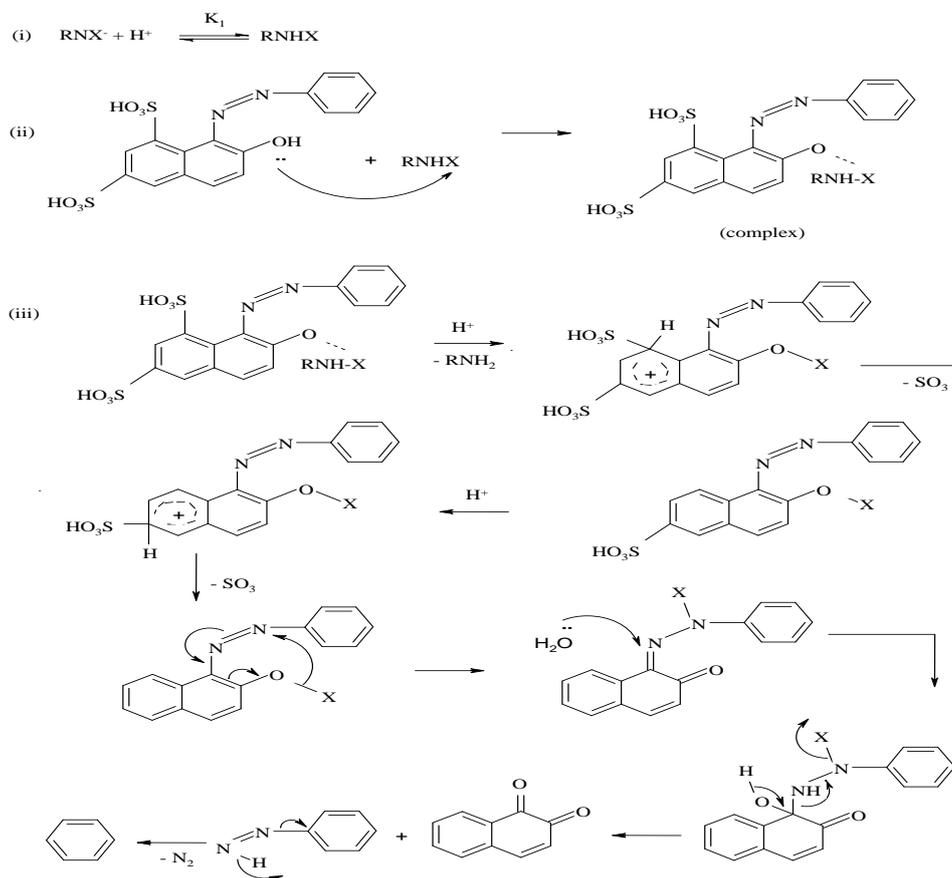
where k_o is the rate constant in a medium of infinite dielectric constant, μ represents the dipole moment and r refers to the radii of the reactants and activated complex. It can be seen from Eq. (13) that the rates should be greater in a medium of lower dielectric constant when $r_{\neq}^3 = r_A^3 + r_B^3$ representing that the extent of charge scattering in the transition state is different. On the other hand, $r_{\neq}^3 \approx r_A^3 + r_B^3$ 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 susceptible 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 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 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 [35-36]. The observed solvent isotope effect of $k'(\text{H}_2\text{O})$ and $k'(\text{D}_2\text{O}) < 1$ 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 $[\text{H}^+]$. Hence, this observation supports the planned mechanism.

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Scheme 2. Detailed mechanistic interpretation for the oxidation of AO10 by CAB and BAB in acid medium.

Relative reactivity of CAB and BAB

A comparison of the rates of reaction of CAB and BAB shows that the oxidation of FRE is about three-fold faster in BAB compared to CAB, under identical set of experimental conditions. This is endorsed by the relative magnitudes of activation energies (Table 2). This trend may be attributed to the difference in electrophilicities 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 electronegativity of 2.7, while chlorine has a higher value of 2.8. As the electronegativity increases the electropositive nature decreases. Since the halo cations are the reactive species in these oxidation reactions, the electropositive nature is in the order: $\text{Br} > \text{Cl}$. Therefore the reactivity of BAB is more compared to CAB. 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 observed in the oxidation of several other substrates using CAB and BAB. The facts furnished in the present research and the literature reports [16,17,20,37-38] lead to conclude that BAB is a stronger oxidant compared to CAB.

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 judicious value of energy of activation and other thermodynamic parameters (Table 2). The fairly high positive values of ΔG^\ddagger and ΔH^\ddagger indicate the transition state is highly solvated while the negative entropy of activation reflects the formation of a compact and ordered transition state. Further, the experimental observation illustrates that there is no effect of benzenesulfonamide, halide ions and ionic strength on the reaction rate which also substantiates the anticipated mechanism.

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In the present redox system the optimum conditions for the controlled oxidation of AO10 by CAB and BAB to naphthalene and 1,2-naphthaquinone in acid medium have been developed. Accordingly, this redox system can be scaled up to industrial operation. Furthermore, AO10 is one of the chief components in the effluents of various industries and is environmentally hazardous and also carcinogenic compound. Hence, the present simple method developed can be adopted for treating the AO10 dye present in industrial effluents to reduce toxicity caused by this dye. Also, this method offers several advantages including short reaction time, cost effective and moderately non-toxic reagents which make the reaction process simple.

IV. CONCLUSION

In the present work, optimum conditions for the oxidative decolorization of AO10 by CAB and BAB in acid medium have been obtained. Chloramine-B decolorizes AO10 almost completely in 55 minutes in acid medium whereas bromamine-B takes hardly 40 minutes. The kinetics of oxidation of AO10 by CAB and BAB in acid medium obeys the rate law $-d[\text{oxidant}] / dt = k [\text{oxidant}]_0 [\text{AO10}]_0 [\text{H}^+]^x$, where $x=0.76$ and 0.65 for CAB and BAB respectively. Hence this method is simple and efficient method including a number of advantages such as cost effective, short time, use of relatively non-toxic reagents. Furthermore, the simple and well-designed method developed in the present research can be implemented with suitable alteration for treating AO10 present in industrial effluents to diminish the toxicity caused by this dye. In addition to this the kinetic and mechanistic picture of AO10-CAB/BAB redox system in acid medium has also been elucidated.

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