Kinetics and Mechanism of Oxidation of P-Methoxyazobenzene by N-Halo-P-Tolunenesulfonamides in Acid Medium

T. Naveen Kumar and T.V. Venkatesha[*]

Alliance College of Engineering and design, Alliance University, Anekal Main Road, Bangalore, Karnataka
[*]Department of Post Graduate Studies and Research in Chemsitry, Kuvempu University, Jnana Sahyadri, Shimoga, Karnataka
Corresponding Author: T. Naveen Kumar

Abstract: *The kinetics of oxidative decolorization of p-methoxyazobenzene (PMAB) by chloramine-T (CAT) and bromamine-T (BAT) in $HClO_4$ medium has been investigated spectrophotometrically (λ_{max} = 347 nm) at 298 K. Kinetic runs were performed under pseudo first-order conditions of $[oxidant]_o$ >> $[PMAB]_o$. The reactions show first-order dependence on $[oxidant]_o$ and [PMAB] 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, p-methoxyazobenzene, oxidation-kinetics, chloramine-T, bromamine-T, 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].
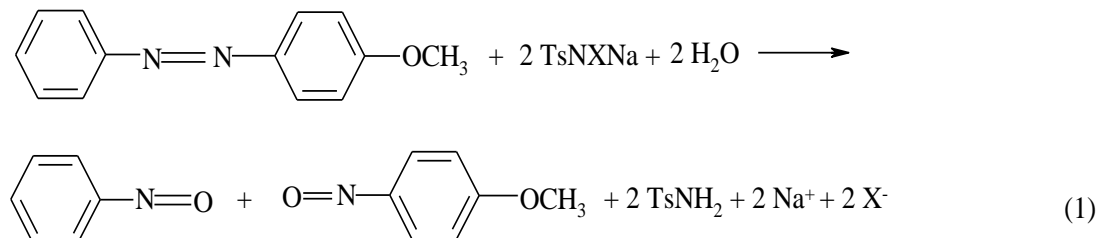
P-methoxyazobenzene (PMAB) is used in textile dyeing [1]. An extensive literature survey reveals that there are no reports on the oxidation of PMAB by any oxidants from the standpoint of the kinetic and mechanistic approach. Hence, it was felt desirable to examine the oxidative decolorization of PMAB with N-haloamines to explore the kinetic and mechanistic aspects of its redox chemistry.

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 [14]. 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 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, BAT is gaining significance as a mild oxidant and is found to be a enhanced oxidizing agent than the chloro derivative [12-14,21-24]. 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

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attention to carry out the detailed kinetic study on the oxidation of PMAB 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.

Stoichiometry and product analysis

Reaction mixtures containing different ratios of oxidant to PMAB in presence of 2.0×10^{-3} mol dm^{-3} 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 PMAB consumed one mole of oxidant and the observed reaction stoichiometry is represented as:

$$\text{PhN=N-C}_6\text{H}_4\text{-OCH}_3 + 2\,\text{TsNXNa} + 2\,\text{H}_2\text{O} \longrightarrow$$

$$\text{PhN=O} + \text{O=N-C}_6\text{H}_4\text{-OCH}_3 + 2\,\text{TsNH}_2 + 2\,\text{Na}^+ + 2\,\text{X}^- \qquad (1)$$

In the stoichiometric proportion, the reaction mixtures containing different concentrations of oxidant and substrate in 2.0×10^{-3} mol dm^{-4} 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 and p-nitrosomethoxybenzenee as the oxidation products and their presence is confirmed by GC–MS analysis. GC–MS data was obtained on a 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer operating in electron-impact mode. The mass spectrum showed a molecular ion peak of 107 amu (Figure 1) and 137 amu (Figure 2) confirming nitosobenzene and p-methoxynitrosobenzene. It was also observed that there was no further oxidation of these products under the prescribed kinetic conditions.

The reduction product of CAT, p-toluenesulfonamide, was detected by paper chromatography (R_f =0.905) and confirmed by mass spectral data (Figure 3).

Kinetic results

The kinetics of oxidation of PMAB by CAT and BAT (hereafter abridged 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 PMAB with the closely related compounds CAB and BAB in HClO$_4$ medium are same under identical experimental conditions but the comparative rates of oxidation of PMAB by BAT are about three-fold faster than CAT.

Under the conditions [oxidant]$_o$ >> [PMAB]$_o$ at constant [oxidant]$_o$, [HClO$_4$], temperature, plots of log (absorbance) versus time were linear (r > 0.9971) indicating a first-order dependence of rate on [PMAB]$_o$ in both the cases. The linearity of these plots in both cases, together with the constancy of the slopes obtained at different [PMAB]$_o$, substantiates the first-order dependence of rate on [PMAB]$_o$. 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]$_o$ (Table 1) and plots of log k' versus log [oxidant] were linear (r > 0.9926) with unit slopes in both the cases. This establishes that the order of the reaction is first-order with respect to [oxidant]$_o$. Further, plots of k' versus [oxidant]$_0$ were linear (r > 0.9955) passing through the origin corroborate the first-order dependence on [oxidant]$_o$.

The rate of reaction augmented with increase in [HClO$_4$] (Table 1) and plots of log k' versus log [HClO$_4$] were linear (r > 0.9982) with slopes of 0.5 and 0.625 for CAT and BAT, showing a fractional-order dependence on [HClO$_4$].

Rate studies were made in water-MeOH mixtures of different compositions (0 – 30% v/v) in order to study the effect of varying dielectric constant (D) of the solvent medium with all other experimental conditions being held constant. The rate was found to decrease with increase in MeOH content (Table 2) and plots of log k' *versus* 1/D were linear (Figure 4; r > 0.9943) with negative slopes. The values of dielectric constant of MeOH - H$_2$O mixtures reported in the literature [26] were used. It was further noticed that no reaction of the dielectric with the oxidant under the experimental conditions used.

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 NaClO₄ solution keeping other experimental conditions constant. It was found that addition of NaClO₄ 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 (RNH₂) to the reaction mixture (5.0×10^{-3} mol dm⁻³) did not influence the rate significantly indicates that RNH₂ is not involved in any step prior to the rate determining step of the proposed scheme.

Since the oxidation of PMAB by CAT and BAT was increased with H⁺ ions, the solvent isotope effect was studied in D₂O as the solvent medium for both the oxidants. The rate constants for CAT and BAT revealed that k' (H₂O) was equal to 9.40×10^{-4} s⁻¹ and 12.80×10^{-4} s⁻¹, and k' (D₂O) was 10.3×10^{-4} s⁻¹ and 13.7×10^{-4} s⁻¹, respectively. Thus, the solvent isotope effect, k' (H₂O) / k' (D₂O) were found to be 0.91 and 0.93 (less than unity) for CAT and BAT.

The effect of temperature on the rate was studied by conducting the kinetic runs at different temperatures (283 – 313 K), keeping other experimental conditions constant. From the linear Arrhenius plots of log k' *versus* 1/T (Figure 5; r > 0.9982), values of activation parameters (E_a, $\Delta H^{\neq}$, $\Delta G^{\neq}$, $\Delta S^{\neq}$ and log A) were computed and these results are summarized in Table 3.

Alkene monomers such as acrylonitrile and freshly prepared 10% acrylamide solutions 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.

II. Discussion

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 [14-17]. Since organic N-haloamines have analogous chemical properties, it is predicted that identical equilibria exist in aqueous acidic and basic solutions of these compounds [30-32]. CAT and BAT act as oxidizing agents in acidic and alkaline media with a two electron change per mole giving PTS 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 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 [30] 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 [28-31]. The possible oxidizing species present in acid medium are TsNHX, TsNX₂, HOX and also perhaps H₂OX⁺.

In the present studies, the first-order dependence of rate on [oxidant]ₒ and no effect of rate on [TsNH₂] clearly ruled out the opportunity of both TsNX₂ 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 principally involved in the rate determining step. Further, Bishop and Jennings [27] 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.

$$\text{TsNCl}^- + \text{H}^+ \rightleftharpoons \text{TsNHCl} \tag{2}$$

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 equilibrium can be expected for BAT also.

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

$$\text{TsNHX} + \text{PMAB} \xrightarrow{k_2} X \qquad \text{(ii) slow determining step}$$

$$X \xrightarrow{\text{H}_2\text{O}} \text{Products} \qquad \text{(iii) fast}$$

Scheme 1. A general reaction scheme for the oxidation of PMAB by CAT and BAT in acid medium.

A detailed mode of oxidation of PMAB by CAT and BAT 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 TsNX$^-$, in acid accelerating step generates the active oxidizing species TsNHX. In a slow / rate limiting step (step (ii)), the lone pair of electrons on oxygen of PMAB attacks the positive halogen of TsNHX forming an intermediate species X. This intermediate complex X (step (iii)) undergoes hydrolysis followed by several fast steps leading to the formation of methoxynitrosobenzene and nitrosobenzene as end products.

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

$$[\text{oxidant}]_t = [\text{TsN}^-\text{X}] + [\text{TsNHX}] \qquad (3)$$

By substituting [TsN$^-$X] from step (i) of Scheme 1, into equation (3) and solving for [TsNHX], one gets,

$$[\text{TsNHX}] = \frac{K_1\,[\text{oxidant}]_t\,[\text{H}^+]}{1 + K_1\,[\text{H}^+]} \qquad (4)$$

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

$$\text{Rate} = k_2[\text{TsNHX}]\,[\text{PMAB}] \qquad (5)$$

By substituting for [TsNHX] from equation 4 into equation 5, the following rate law is obtained:

$$\text{Rate} = \frac{K_1\,k_2\,[\text{oxidant}]_t\,[\text{PMAB}]\,[\text{H}^+]}{1 + K_1\,[\text{H}^+]} \qquad (6)$$

The derived rate law 6 is in good agreement with the experimental results, wherein a first order dependence of rate on each [oxidant]$_o$ and [PMAB]$_o$ and a fractional-order dependence on [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 [30-32]. 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 (Figure 4), 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 [36]. Applying the Born equation, Laidler [37] has anticipated the following equation for a dipole-dipole interaction:

$$\ln k^/ = \ln k_o + 3 / 8kT\,(2/D - 1)\,[\mu^2_A / r^3_A + \mu^2_B / r^3_B - \mu^2_{\neq} / r^3_{\neq}] \qquad (7)$$

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 equation (7) 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 susceptible to acid-base catalysis have been studied in heavy water (D$_2$O) 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$_2$O medium. For a reaction involving a fast equilibrium H$^+$ or OH$^-$ ion transfer, the rate increases in D$_2$O medium since D$_3$O$^+$ or OD$^-$ are a stronger acid and a stronger base respectively, than H$_3$O$^+$ and OH$^-$ ions [33-35]. The observed solvent isotope effect of k$^/$ (H$_2$O) and k$^/$ (D$_2$O) < 1 is due to the greater acidity of D$_3$O$^+$ compared to H$_3$O$^+$. However, the magnitude of increase in rate in D$_2$O 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.

A comparison of the rates of reaction of CAT and BAT shows that the oxidation of PMAB is faster in BAT compared to CAT, under identical set of experimental conditions. This is endorsed by the relative magnitudes of activation energies (Table 3). This trend may be attributed to the difference 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 noted [16, 19, 24, 26, 38] in the oxidation of several other

substrates using CAT and BAT. The facts furnished in the present research and the literature reports [23, 35] led to conclude that BAT is a stronger oxidant compared to CAT.

The proposed mechanism is also supported by the moderate values of energy of activation and other thermodynamic parameters. The energy of activation is highest for the slowest reaction and *vice-versa* indicating that the reaction is enthalpy controlled (Table 3). The positive values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$ indicate that the transition state is highly solvated. The negative values of $\Delta S^{\neq}$ suggest the formation of a rigid associative transition state with a few degrees of freedom in both cases. Further, the comparable values of $\Delta G^{\neq}$ signify the same type of the reaction mechanism could be operative for the oxidation of PMAB by CAT and BAT in alkaline medium. The ineffectiveness of the additions of PTS, neutral salts and halide ions on the rate of the reaction are in agreement with the proposed mechanism and the derived rate law.

In the present redox system the optimum conditions for the controlled oxidation of PMAB by CAT and BAT to naphthalene and 1,2-naphthaquinone in acid medium have been developed. Accordingly, this redox system can be scaled up to industrial operation. Furthermore, PMAB 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 PMAB 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.

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

10^3 [oxidant]$_o$ (mol dm^{-3})	10^4 [PMAB]$_o$ (mol dm^{-3})	10^3 [HClO$_4$] (mol dm^{-3})	$10^4 k'$ (s^{-1})	
			CAT	BAT
0.5	2.0	2.0	2.10	4.65
1.0	2.0	2.0	5.24	7.86
2.0	2.0	2.0	9.40	15.8
4.0	2.0	2.0	18.3	22.9
5.0	2.0	2.0	23.9	34.2
2.0	0.5	2.0	9.25	15.2
2.0	1.0	2.0	9.47	14.8
2.0	2.0	2.0	9.40	15.8
2.0	4.0	2.0	9.52	14.7
2.0	5.0	2.0	9.36	15.5
2.0	2.0	0.5	4.57	6.60
2.0	2.0	1.0	6.45	12.5
2.0	2.0	2.0	9.40	15.8
2.0	2.0	4.0	12.5	22.9
2.0	2.0	5.0	14.1	27.5

Table 2 Effect of dielectric constant on the reaction rate at 293 K.

% MeOH (v/v)	D	$10^4 k'$ (s^{-1})	
		CAT	BAT
0	76.73	9.40	15.8
5	74.50	9.05	14.8
10	72.37	8.72	14.3
20	67.48	8.30	13.4
30	62.71	7.44	12.7

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

Table 3 Temperature dependence on the reaction rate and activation parameters for the oxidative decolorization of PMAB by CAT and BAT in acid medium.

Temperature (K)	$10^4 k'$ (s^{-1})	
	CAT	BAT
283	5.37	11.5
288	6.74	12.7
293	9.40	15.8
303	12.8	20.6
313	19.7	26.3
E$_a$ (kJ mol^{-1})	32.1	19.5
$\Delta H^{\neq}$ (kJ mol^{-1})	29.7	17.0
$\Delta G^{\neq}$ (kJ mol^{-1})	66.9	65.5
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	-126	-163

[oxidant]$_o$ = 2.0 x 10^{-3} mol dm^{-3}; [PMAB]$_o$ = 2.0 x 10^{-4} mol dm^{-3}; [HClO$_4$] = 2.0 x 10^{-3} mol dm^{-3}.
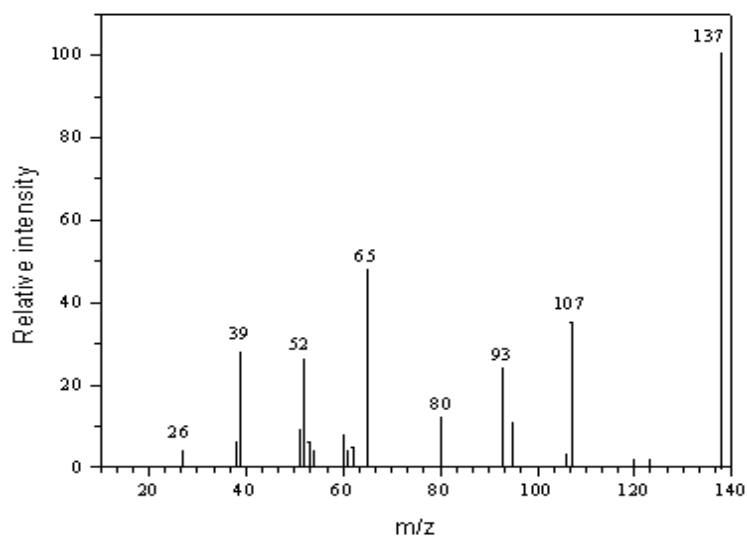
Figure 1 GC-Mass spectrum of p-methoxynitrosobenzene with its molecular ion peak at 137 amu.
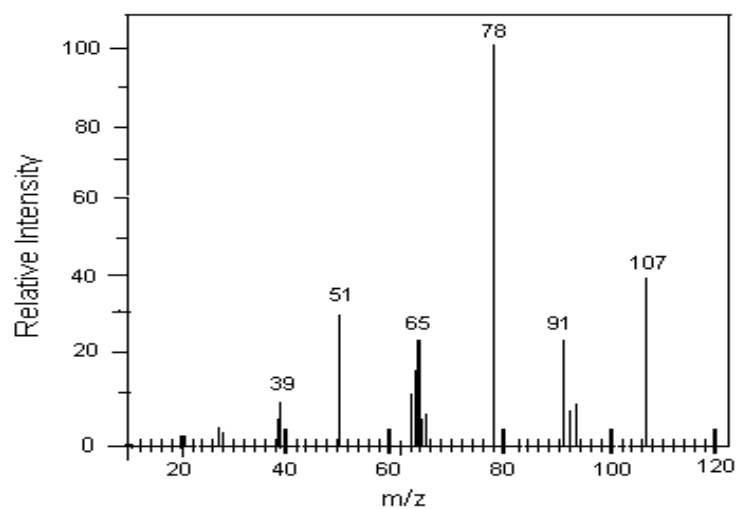
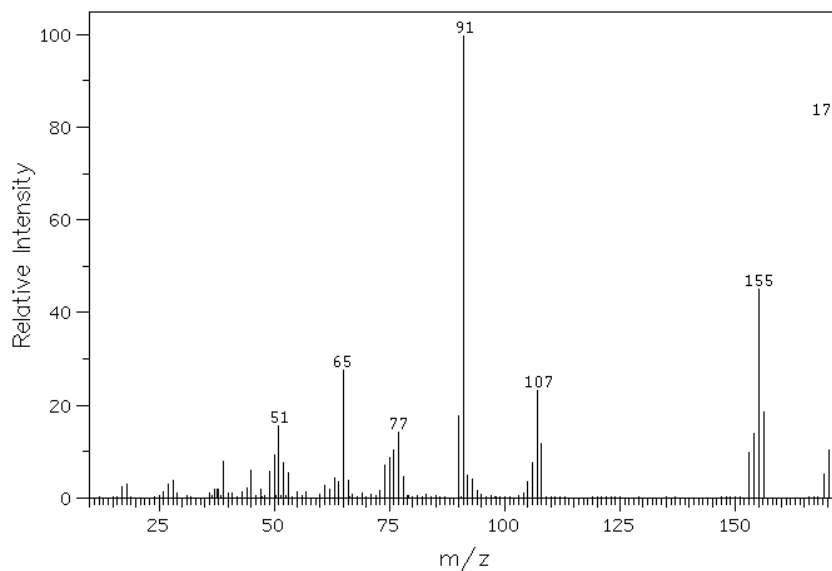**Figure 2** GC-Mass spectrum of nitrosobenzene with its molecular ion peak at 107 amu.

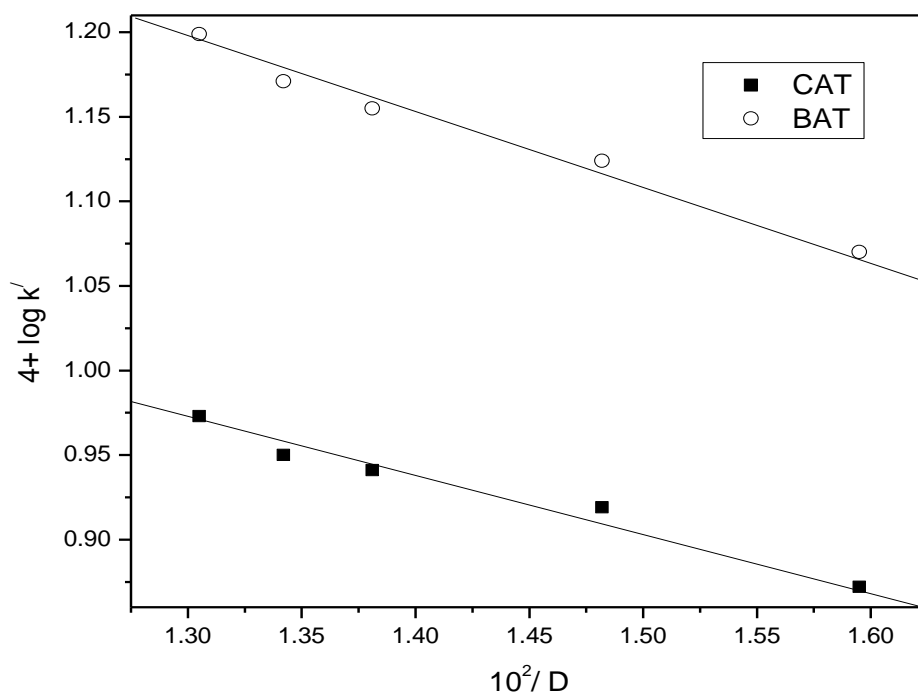**Figure 3** GC-Mass spectrum of p-toluenesulfonamide with its molecular ion peak at 171 amu.
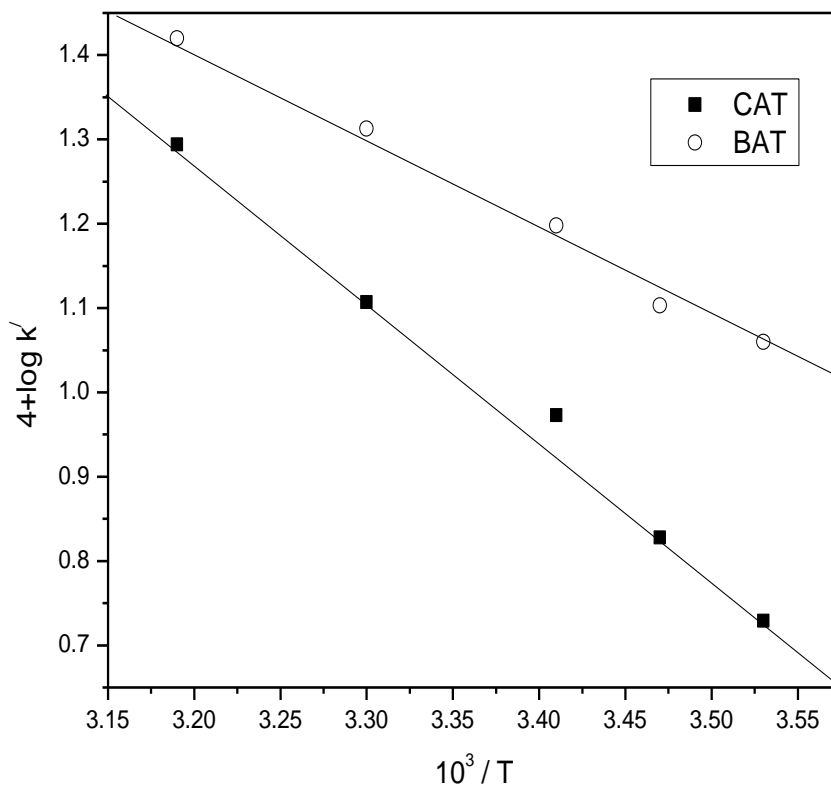
Figure 4 Plots of 1/ D versus log k$^{/}$.

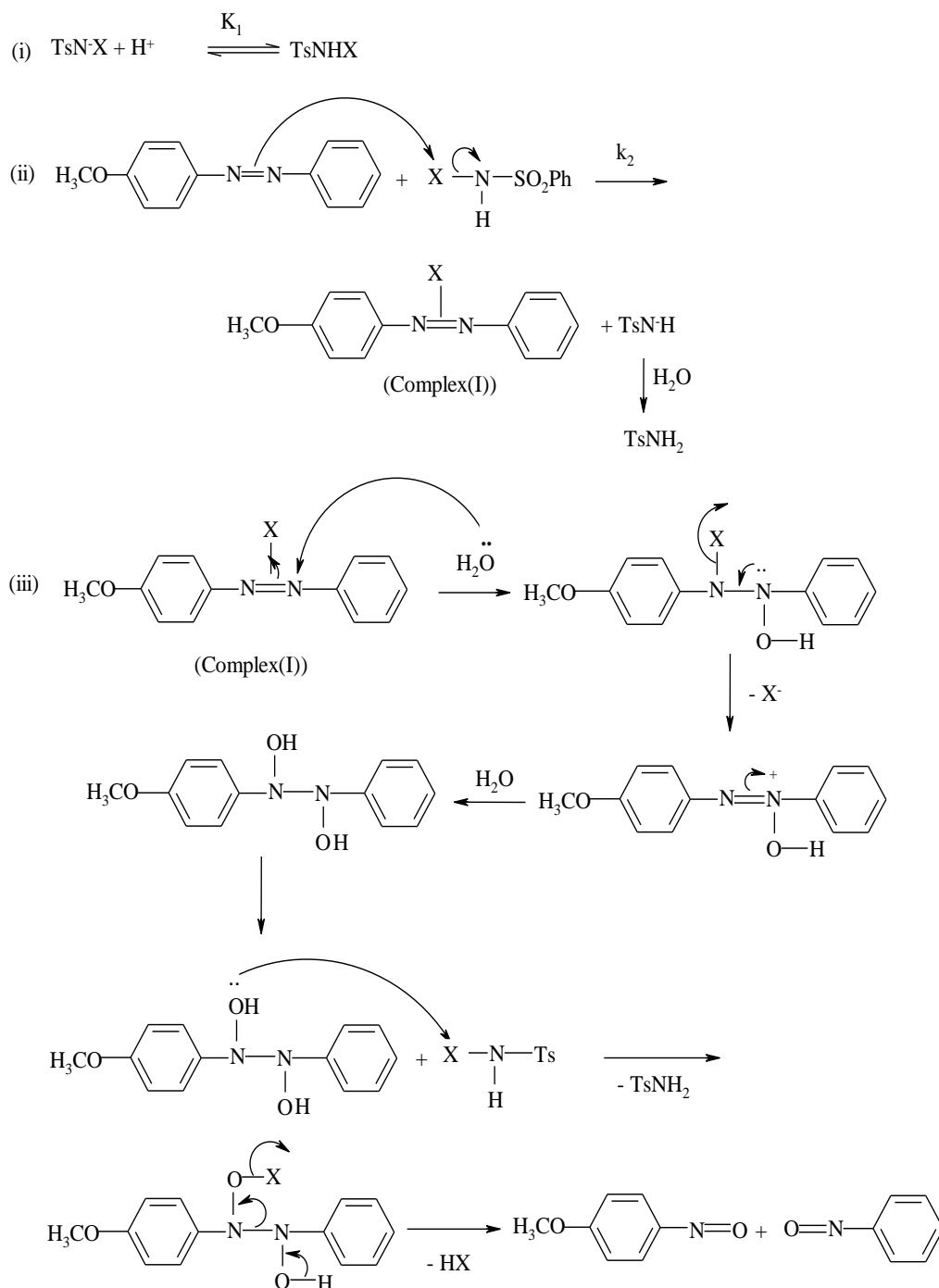**Figure 5** Plots of log k$^{/}$ versus 1/T.

(i) $TsN^-X + H^+ \rightleftharpoons TsNHX$ over K_1

(ii) H_3CO—C$_6$H$_4$—N=N—C$_6$H$_5$ + X—N(H)—SO$_2$Ph $\xrightarrow{k_2}$

H_3CO—C$_6$H$_4$—N=N(X)—C$_6$H$_5$ (Complex(I)) + TsN$^-$H

$\downarrow H_2O$

$TsNH_2$

(iii) (Complex(I)) H_3CO—C$_6$H$_4$—N=N(X)—C$_6$H$_5$ $\xrightarrow{H_2O}$ H_3CO—C$_6$H$_4$—N(X)—N(O—H)—C$_6$H$_5$

$\downarrow -X^-$

H_3CO—C$_6$H$_4$—N(OH)—N(OH)—C$_6$H$_5$ $\xleftarrow{H_2O}$ H_3CO—C$_6$H$_4$—N=N$^+$(O—H)—C$_6$H$_5$

$\downarrow$

H_3CO—C$_6$H$_4$—N(OH)—N(OH)—C$_6$H$_5$ + X—N(H)—Ts $\xrightarrow{-TsNH_2}$

H_3CO—C$_6$H$_4$—N(O—X)—N(O—H)—C$_6$H$_5$ $\xrightarrow{-HX}$ H_3CO—C$_6$H$_4$—N=O + O=N—C$_6$H$_5$

Scheme 2 A detailed mechanistic interpretations for the oxidation of PMAB by CAT and BAT in acid medium

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