

## Oxidative conversion of anilines to azobenzenes with alkaline chloramine-T

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**Abstract**—Anilines are widely used in the manufacture of dyes, medicinals, plastics and perfumes. Anilines are readily oxidized to give products depending on reaction conditions. Conversion of anilines to azobenzenes is important in organic synthesis. In the course of this research, optimum conditions for the facile oxidative conversion of anilines to azobenzenes have been established in very good yields. The kinetics of oxidation of aniline, *p*-methoxyaniline, *p*-methylaniline, *p*-carboxylicaniline and *p*-nitroaniline by chloramine-T (CAT) in NaOH medium shows identical kinetics with a first-order dependence of rate on [CAT]<sub>0</sub>, fractional-order on [Aniline]<sub>0</sub>, and an inverse-fractional order on [OH<sup>-</sup>]. Activation parameters and decomposition constants have been determined. Oxidation products were characterized by NMR spectral studies. Isokinetic temperature is 415 K indicating enthalpy as a controlling factor. The rates increased in the order: *p*-methoxyaniline > *p*-methylaniline > aniline > *p*-carboxylicaniline > *p*-nitroaniline. A Hammett linear free energy relationship is observed for the reaction with  $\rho = -0.52$ . Reaction scheme and kinetic rate law were deduced. We have developed a simple and efficient protocol for the synthesis of azobenzenes by anilines in good yields and hence we believe that this methodology will be a valuable addition to the existing methods.

Keywords: Anilines, Chloramine-T, Oxidation-kinetics, Mechanism, Structure Reactivity

### INTRODUCTION

The oxidation of organic compounds with high selectivity is of extreme importance in synthetic chemistry. Aromatic amines are the derivatives of aromatic hydrocarbons in which a hydrogen of the benzene ring has been replaced by an amino group (-NH<sub>2</sub>). Simple aromatic amines are termed as derivatives of aniline. Anilines are used in the manufacture of dyes, medicinal, polymers, antioxidants and herbicides [1]. The study of the oxidation of anilines is important, as it adds to the body of knowledge on the redox chemistry both from the theoretical as well as practical stand point. For these reasons, anilines have been oxidized by a number of oxidizing agents under various experimental conditions [2-9]. The products of oxidation of anilines depend on the type of oxidant, on the reaction conditions and on the nature of alkyl groups present [10-14]. The oxidation of anilines to the corresponding azobenzenes stage is important transformation in organic synthesis, particularly in aromatic amine chemistry. The azobenzenes are important reagents in organic synthesis and are widely used in the synthesis of organic dyes, food additives, indicators and also in drugs. Our preliminary experiments have shown that chloramine-T (CAT) is an excellent oxidant which allows controlled conversion of selected anilines to the corresponding azobenzenes in an alkaline medium. In the present investigations, the para-substituted anilines were selected for the oxidation by CAT because all are expected similar

behavior with high electron densities compared to meta and ortho positions. Optimum conditions for the facile oxidation of five anilines to the corresponding azobenzenes were established. Because of significant applications of azobenzenes, this method has great scenario in industrial applications.

*N*-metallo *N*-arylhalosulfonamides, generally known as organic *N*-haloamines, contain halogen in +1 oxidation state and are well known mild oxidants [15]. The diverse chemical behavior of *N*-haloamines is attributed to their ability to act as halonium cations, hypohalites, *N*-anions which act both as bases and nucleophiles, and nitrenoids in limited cases [15]. As a result, these compounds react with a wide range of functional groups and effect a variety of molecular changes [16-22]. Generally mono-haloamines undergo two electron change, while di-haloamines are four-electron oxidants. Prominent member of this class of compounds, sodium *N*-chloro-4-methylbenzenesulfonamide or commonly called chloramine-T (hereafter abbreviated as CAT) is a byproduct of saccharin manufacture. It behaves both as a chlorinating and an oxidizing agent in acidic and alkaline media. Generally, CAT undergoes a two-electron change in its reaction, the products being *p*-toluenesulfonamide (PTS) and NaCl [23]. The redox potential of CAT-PTS couple is pH dependent and decreases with an increase in the pH of the medium [24]. The values of redox potential of CAT-PTS system are 1.138, 0.778, 0.614 and 0.5 V at pH 0.65, 7.0, 9.7 and 12, respectively. Chloramine-T has been extensively used for the oxidation of a variety of organic substrates, and the oxidation mechanisms of these reactions have been kinetically investigated [15-22,25-33]. Moreover, CAT is commercially available, inexpensive, water-tolerant, non-toxic and easy to handle [20]. Therefore, we

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have chosen CAT as an oxidant for the present oxidation-kinetic studies.

On the background of the available information, we have twin main aims: (i) to establish optimum conditions for the facile oxidative conversion of anilines to the corresponding azobenzenes with CAT in alkaline medium, and (ii) to explore the kinetic and mechanistic picture of these redox systems. Hence, a systematic kinetic study of the oxidation of aniline and *p*-substituted anilines viz., *p*-methoxyaniline, *p*-methylaniline, *p*-carboxylicaniline and *p*-nitroaniline with chloramine-T in alkaline medium has been made. An attempt has also been made to arrive at a linear free energy relationship to correlate structure and reactivity using a Hammett plot. The remarkable advantage of this protocol is mild reaction conditions, excellent yields of products, operational and experimental simplicity.

## EXPERIMENTAL

### 1. Materials

Thomas Baker sample of chloramine-T was purified by the method of Morris et al. [34]. An aqueous solution of CAT was prepared afresh, standardized by iodometric method and preserved in brown bottles to prevent its photochemical deterioration. The concentration of stock solution of CAT was periodically checked by iodometric method. All the anilines used are acceptable grade purity. Aniline (Spectrochem) was used after distillation. Solid anilines viz., *p*-methoxyaniline (SRL), *p*-methylaniline (SRL), *p*-carboxylicaniline (Loba) and *p*-nitroaniline (SD Fine Chem. Ltd.) were used

as received. Aqueous solutions of anilines were prepared and employed. Reagent grade chemicals and double distilled water were used throughout the work.

### 2. Kinetic Methodology

Detailed kinetic runs were performed under pseudo-first-order conditions of  $[\text{Aniline}]_0 \gg [\text{CAT}]_0$  at 303 K in alkaline medium. A Raaga ultra cold chamber with digital temperature control (Chennai, India) was used to maintain the desired temperature constant with an accuracy of  $\pm 0.1^\circ\text{C}$ . The kinetic run followed to study the progress of the reaction was according to a literature procedure [35]. Reactions were carried out in stoppered Pyrex glass boiling tubes whose outer surfaces were coated black to eliminate photochemical effects. The oxidant as well as the requisite amounts of aniline, NaOH solutions and water (to keep the total volume constant for all kinetic runs) taken in separate tubes were thermostated for about 30 min at 303 K. A measured amount of CAT solution was rapidly added to the reaction mixture, which was shaken intermittently. The progress of the reaction was monitored by the iodometric determination of unreacted CAT in aliquots (5 ml each) of the reaction mixture at different intervals of time. The course of the reaction was studied for at least two half-lives. The pseudo-first-order rate constants ( $k' \text{ s}^{-1}$ ) were calculated from the linear plots of  $\log [\text{CAT}]$  versus time. Duplicate kinetic runs revealed that the rate constants were reproducible within  $\pm 6\%$  error. Regression coefficients ( $R^2$ ) were calculated by using an fx-100 W scientific calculator.

### 3. Stoichiometry

Different sets of reaction mixtures containing different proportions of CAT and aniline with  $1.2 \times 10^{-3} \text{ mol dm}^{-3}$  NaOH were allowed

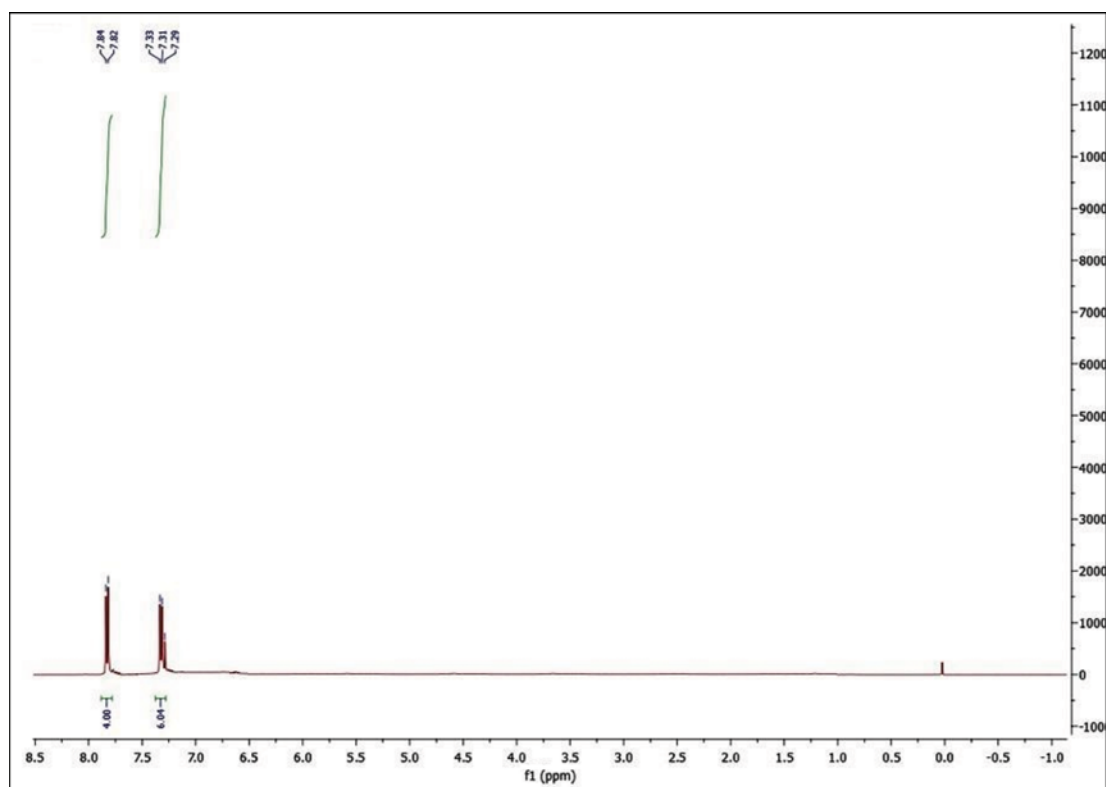


Fig. 1. <sup>1</sup>H NMR spectrum of azobenzene. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.84\text{--}7.82$  (d, 4H),  $7.33\text{--}7.29$  (M, 6H).

to react for 24 h at 303 K and then analyzed iodometrically. Determination of unreacted CAT in the reaction mixture showed that

two moles of the aniline consumed two moles of CAT, confirming the following stoichiometry.

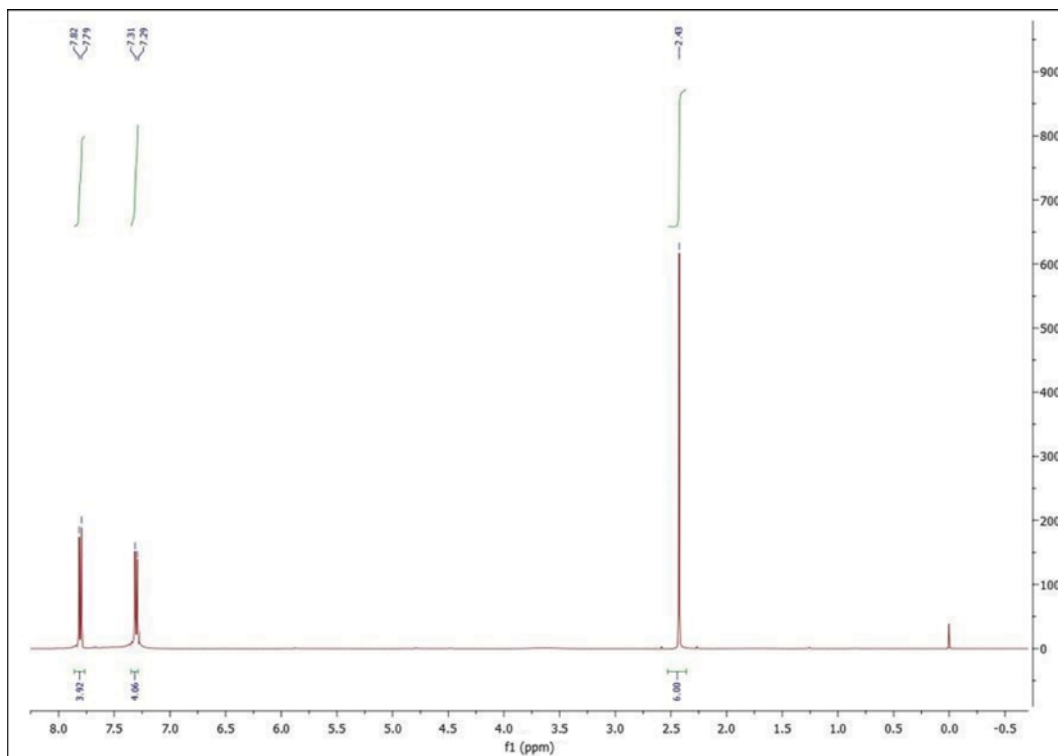


Fig. 2.  $^1\text{H}$  NMR spectrum of 1,2-dip-tolyldiazene.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=7.82\text{--}7.79$  (d, 4H),  $7.31\text{--}7.29$  (d, 4H),  $2.43$  (s, 6H).

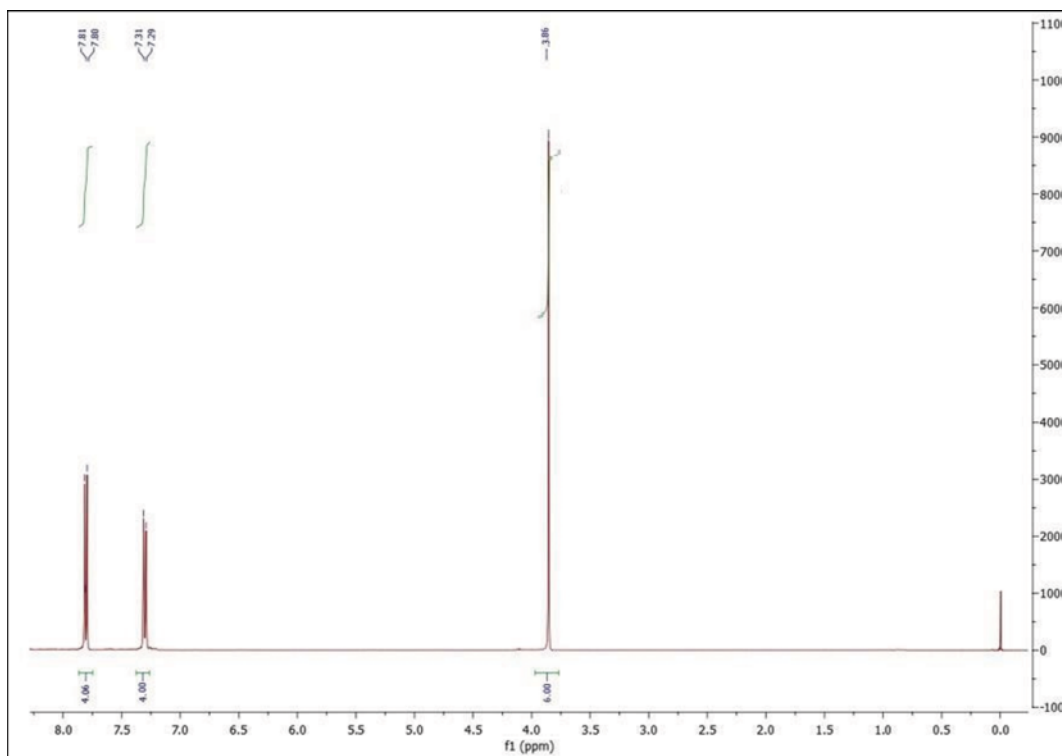
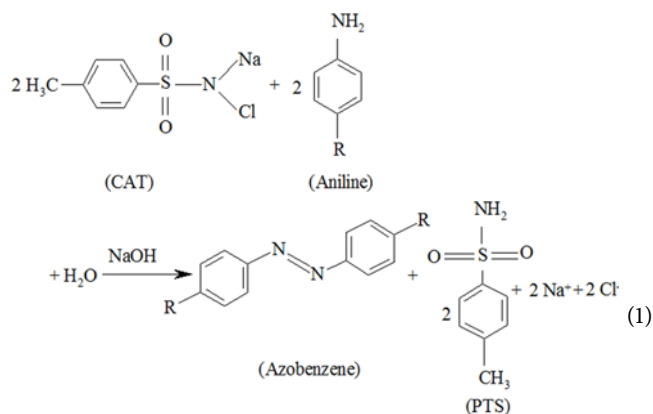


Fig. 3.  $^1\text{H}$  NMR spectrum of 1,2-bis(4-methoxyphenyl)diazene.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=7.81\text{--}7.80$  (d, 4H),  $7.31\text{--}7.29$  (d, 4H),  $3.86$  (s, 6H).



here R = -OCH<sub>3</sub> for *p*-methoxyaniline, -CH<sub>3</sub> for *p*-methylaniline, -H for aniline, -COOH for *p*-carboxylicaniline and -NO<sub>2</sub> for *p*-nitroaniline.

#### 4. Product Analysis

The reactions of all the five anilines with CAT, separately on the stoichiometric ratio under stirred condition in presence of  $1.2 \times 10^{-3}$  mol dm<sup>-3</sup> NaOH, were allowed to progress for 24 h at 303 K. After completion of the reaction (monitored by TLC), the reaction products were neutralized with acid and extracted with ether. The organic products were subjected to spot tests and chromatographic analysis (TLC technique). The reaction mixture was then extracted with ethyl acetate and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure to obtain crude products. The crude products were purified on silica gel column by using pet. ether and ethyl acetate as solvent to get the pure products. Above analysis revealed the formation of corresponding azobenzenes as the oxidation prod-

ucts of anilines. 2-bis(4-methoxyphenyl)diazene, 1,2-dip-tolyldiazene, azobenzene, 2-bis(4-carboxylicphenyl)diazene and 2-bis(4-nitrophenyl)diazene are the oxidation products of *p*-methoxyaniline, *p*-methylaniline, aniline, *p*-carboxylicaniline and *p*-nitroaniline, respectively. Azobenzene, 1,2-dip-tolyldiazene and 1,2-bis(4-methoxyphenyl)diazene were confirmed by NMR spectral studies (Fig. 1-3). NMR spectra were obtained on a Bruker WH 400-MHz Nuclear magnetic resonance spectrometer. No reaction was noticed between all these five oxidation products with CAT under the present set of experimental conditions. We succeeded in estimating the products, azobenzenes, in case of all the five anilines. In some typical experiments, the weight of azobenzenes and their percentage yield obtained are recorded in Table 1. The recovery of azobenzenes was 85-93% yields. *p*-toluenesulfonamide, a reduction product of CAT, was also extracted with ethyl acetate and identified [35] by TLC and confirmed by NMR spectral studies (Fig. 4).

## RESULTS AND DISCUSSION

The kinetics of oxidation of aniline and *p*-substituted anilines--*p*-methoxyaniline, *p*-methylaniline, *p*-carboxylicaniline and *p*-nitroaniline--was investigated at several initial concentrations of the reactants in NaOH medium at 303 K. The kinetic runs were performed under pseudo-first-order conditions of [Aniline]<sub>0</sub> >> [CAT]<sub>0</sub> in all cases. Under comparable experimental conditions, the similar oxidation-kinetic behavior was observed for all the five aforesaid anilines.

### 1. Effect of Varying Reactant Concentrations on the Reaction Rate

Under the conditions [Aniline]<sub>0</sub> >> [CAT]<sub>0</sub>, at constant [Aniline]<sub>0</sub>,

Table 1. Estimation of azobenzenes from oxidation of anilines with CAT in alkaline medium

| Aniline | Azobenzene | Weight of azobenzene (found in gram) | Weight of azobenzene (expected in gram) | Yield of azobenzene (%) |
|---------|------------|--------------------------------------|---|-------------------------|
|         |            | 1.75                                 | 1.96                                    | 89                      |
|         |            | 1.83                                 | 1.95                                    | 91                      |
|         |            | 1.89                                 | 1.95                                    | 93                      |
|         |            | 1.73                                 | 1.97                                    | 87                      |
|         |            | 1.68                                 | 1.97                                    | 85                      |

**Experimental conditions:** Equimolar quantities of CAT and Aniline were taken for the estimation of azobenzenes

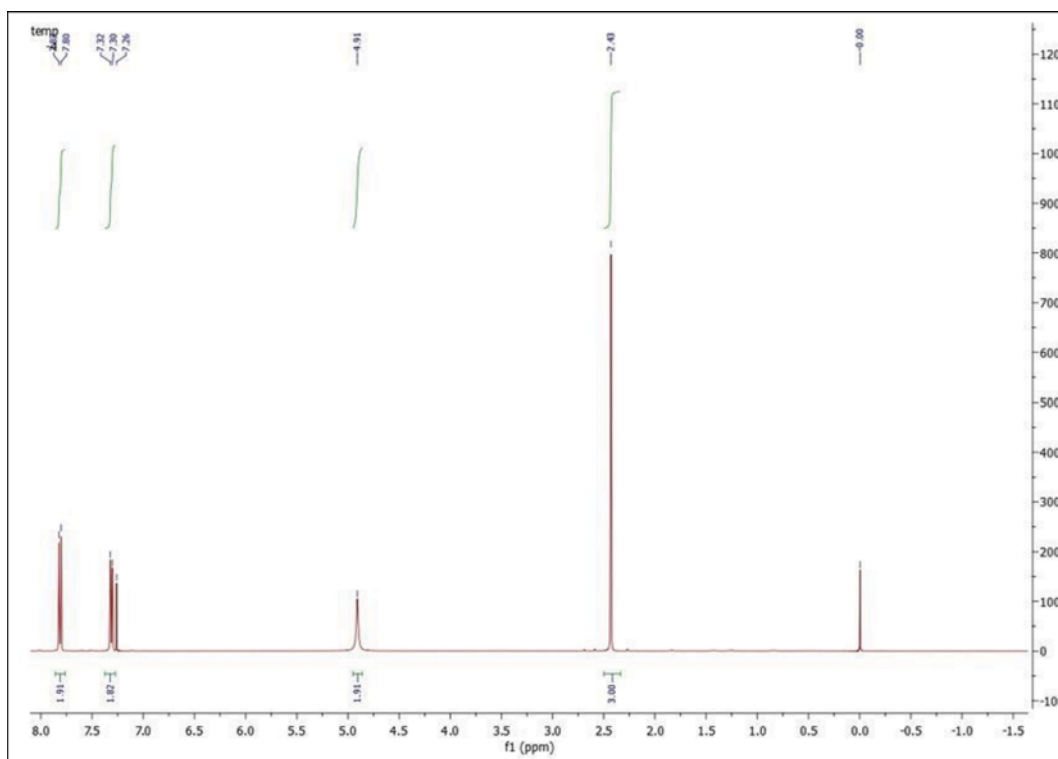


Fig. 4.  $^1\text{H}$  NMR spectrum of *p*-toluenesulfonamide.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.82-7.80 (d, 2H), 7.32-7.30 (d, 2H), 4.91 (s, 2H), 2.43 (s, 3H).

[NaOH] and temperature, the plots of  $\log k'$  versus time were linear ( $R^2 > 0.9901$ ), indicating a first-order dependence of the reaction rate on  $[\text{CAT}]_0$  for all the anilines. The pseudo-first-order rate constants ( $k' \text{ s}^{-1}$ ) calculated from these plots remained unchanged with the variation of  $[\text{CAT}]_0$  (Table 2), confirming first-order dependence of the rate on  $[\text{CAT}]_0$ . Under the same experimental conditions, the rate of the reaction increased with  $[\text{Aniline}]_0$  (Table 2)

and plots of  $\log k'$  versus  $\log [\text{Aniline}]$  were linear ( $R^2 > 0.9910$ ) with fractional slopes (0.53 to 0.91), showing a fractional-order dependence of rate on  $[\text{Aniline}]_0$ .

## 2. Effect of Varying NaOH Concentration on the Reaction Rate

The rate of the reaction decreased with increasing [NaOH] in all the cases (Table 2). The plots of  $\log k'$  versus  $\log [\text{NaOH}]$  were linear ( $R^2 > 0.9956$ ) with negative-fractional-slopes ( $-0.49$  to  $-0.86$ ),

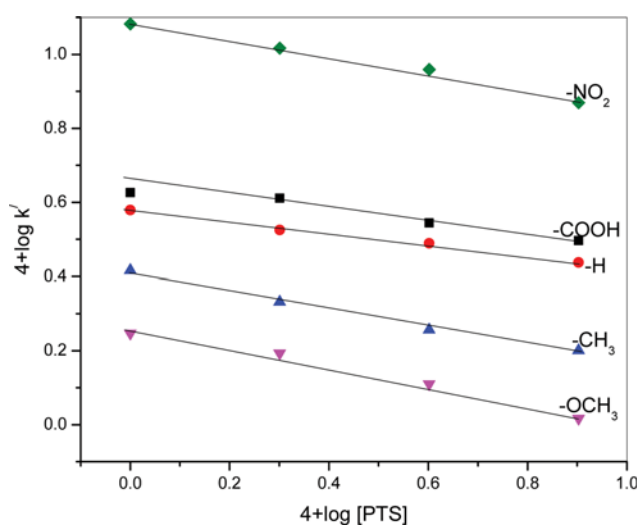
Table 2. Effects of varying reactant concentrations on the reaction rate at 303 K

| $10^4 [\text{CAT}]_0$<br>( $\text{mol dm}^{-3}$ ) | $10^3 [\text{Aniline}]$<br>( $\text{mol dm}^{-3}$ ) | $10^3 [\text{NaOH}]$<br>( $\text{mol dm}^{-3}$ ) | $10^4 k' (\text{s}^{-1})$  |                           |      |                |                           |
|---|---|--|----------------------------|---------------------------|------|----------------|---------------------------|
|   |   |  | <i>p</i> -OCH <sub>3</sub> | <i>p</i> -CH <sub>3</sub> | -H   | <i>p</i> -COOH | <i>p</i> -NO <sub>2</sub> |
| 0.20  | 1.20  | 1.20   | 4.22                       | 3.81                      | 2.63 | 1.76           | 1.22                      |
| 0.40  | 1.20  | 1.20   | 4.21                       | 3.82                      | 2.60 | 1.72           | 1.20                      |
| 0.80  | 1.20  | 1.20   | 4.23                       | 3.80                      | 2.61 | 1.77           | 1.21                      |
| 1.60  | 1.00  | 1.20   | 4.25                       | 3.84                      | 2.62 | 1.79           | 1.24                      |
| 2.20  | 1.20  | 1.20   | 4.20                       | 3.83                      | 2.61 | 1.75           | 1.23                      |
| 0.80  | 0.30  | 1.20   | 2.76                       | 1.47                      | 0.71 | 0.58           | 0.34                      |
| 0.80  | 0.60  | 1.20   | 3.11                       | 2.49                      | 0.95 | 0.72           | 0.56                      |
| 0.80  | 1.20  | 1.20   | 4.23                       | 3.80                      | 2.61 | 1.77           | 1.21                      |
| 0.80  | 1.80  | 1.20   | 7.24                       | 4.95                      | 3.95 | 2.84           | 2.14                      |
| 0.80  | 2.40  | 1.20   | 9.55                       | 6.32                      | 5.51 | 3.35           | 3.09                      |
| 0.80  | 1.20  | 0.30   | 9.21                       | 7.21                      | 5.12 | 4.35           | 3.78                      |
| 0.80  | 1.20  | 0.60   | 6.49                       | 4.95                      | 3.62 | 2.91           | 2.15                      |
| 0.80  | 1.20  | 1.20   | 4.23                       | 3.80                      | 2.61 | 1.77           | 1.21                      |
| 0.80  | 1.20  | 1.80   | 3.25                       | 3.00                      | 2.00 | 1.30           | 0.72                      |
| 0.80  | 1.20  | 2.40   | 2.86                       | 2.50                      | 1.60 | 1.00           | 0.53                      |

**Table 3. Effect of varying *p*-toluenesulfonamide concentration on the reaction rate at 303 K**

| $10^4$ [PTS]<br>(mol dm <sup>-3</sup> ) | $10^4$ $k'$ (s <sup>-1</sup> ) |                           |      |                |                           |
|---|--------------------------------|---------------------------|------|----------------|---------------------------|
|   | <i>p</i> -OCH <sub>3</sub>     | <i>p</i> -CH <sub>3</sub> | -H   | <i>p</i> -COOH | <i>p</i> -NO <sub>2</sub> |
| 0                                       | 4.23                           | 3.84                      | 2.61 | 1.77           | 1.21                      |
| 2.0                                     | 4.09                           | 3.35                      | 2.15 | 1.56           | 1.04                      |
| 4.0                                     | 3.50                           | 3.09                      | 1.81 | 1.29           | 0.91                      |
| 8.0                                     | 3.14                           | 2.74                      | 1.59 | 1.04           | 0.74                      |

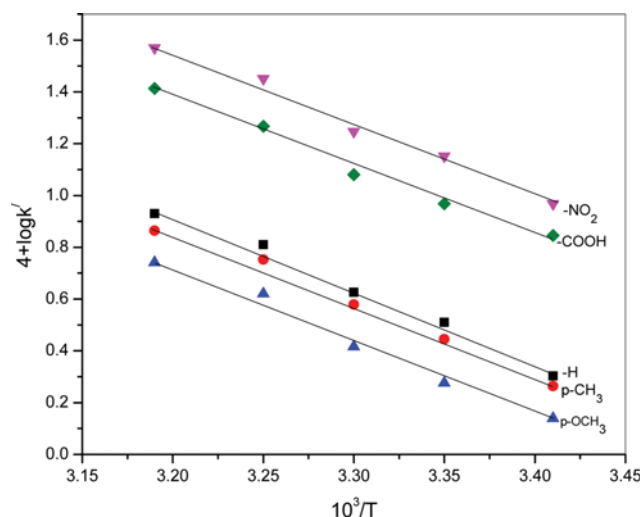
**Experimental conditions:** [CAT]<sub>0</sub>=0.8×10<sup>-4</sup> mol dm<sup>-3</sup>; [Aniline]<sub>0</sub>=1.2×10<sup>-3</sup> mol dm<sup>-3</sup>; [NaOH]=1.2×10<sup>-3</sup> mol dm<sup>-3</sup>

**Fig. 5. Plots of log  $k'$  versus log [PTS].**

indicating a negative-fractional-order dependence of rate on [NaOH].

### 3. Effect of Varying *p*-Toluenesulfonamide Concentration on the Reaction Rate

Addition of *p*-toluenesulfonamide (PTS), retards the reaction rate for all the five anilines. The log-log plots of rate versus [PTS] were linear ( $R^2 > 0.9934$ ) with negative fractional slopes ( $-0.16$  to  $-0.29$ ), signifying the negative-fractional-order dependence of the rate on

**Fig. 6. Plots of log  $k'$  versus  $1/T$ .**

[PTS]. The results are reported in Table 3 and graphically represented in Fig. 5. It indicates that PTS is involved in a fast pre-equilibrium to the rate-determining-step in the proposed scheme.

### 4. Effect of Varying Ionic Strength of the Medium on the Reaction Rate

The effect of ionic strength of the reaction medium on the reaction rate was determined by adding 0.2 mol dm<sup>-3</sup> NaClO<sub>4</sub> to the reaction mixture, with other experimental conditions constant. Variation of ionic strength of the medium did not bring any significant change in the rate of the reaction in all cases, indicating involvement of non-ionic species or neutral molecule(s) in the rate-determining step of the proposed scheme. Subsequently, the ionic strength of the reaction system was not fixed constant for all the kinetic runs.

### 5. Effect of Varying Temperature on the Reaction Rate

To obtain activation parameters, the reaction rates were determined at 293, 298, 303, 308 and 313 K temperatures, keeping other experimental conditions the same. From the linear Arrhenius plots of log  $k'$  versus  $1/T$  (Fig. 6;  $R^2 > 0.9900$ ), values of activation parameters ( $E_a$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ ,  $\Delta G^\ddagger$  and log A) were computed for all the five

**Table 4. Effect of temperature on the reaction rate and activation parameters for the oxidation of anilines by CAT in alkaline medium**

| Temperature (K)   | $10^4$ $k'$ (s <sup>-1</sup> ) |                           |             |                |                           |
|---|--------------------------------|---------------------------|-------------|----------------|---------------------------|
|   | <i>p</i> -OCH <sub>3</sub>     | <i>p</i> -CH <sub>3</sub> | -H          | <i>p</i> -COOH | <i>p</i> -NO <sub>2</sub> |
| 293   | 2.01                           | 1.84                      | 1.38        | 0.93           | 0.70                      |
| 298   | 3.24                           | 2.79                      | 1.89        | 1.42           | 0.93                      |
| 303   | 4.23                           | 3.80                      | 2.61        | 1.77           | 1.21                      |
| 308   | 6.47                           | 5.66                      | 4.18        | 2.83           | 1.85                      |
| 313   | 8.52                           | 7.32                      | 5.52        | 3.72           | 2.59                      |
| $E_a$ (kJ mol <sup>-1</sup> )                             | 50.2                           | 53.6                      | 59.6        | 65.5           | 71.0                      |
| $\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )               | 47.6(±0.08)                    | 51.1(±0.01)               | 57.0(±0.01) | 62.9(±0.01)    | 68.5(±0.02)               |
| $\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )               | 93.8(±0.23)                    | 94.1(±0.24)               | 95.0(±0.24) | 95.8(±0.21)    | 96.8(±0.28)               |
| $\Delta S^\ddagger$ (JK <sup>-1</sup> mol <sup>-1</sup> ) | -152(±0.07)                    | -142(±0.06)               | -125(±0.06) | -108(±0.05)    | -93(±0.04)                |
| log A   | 5.03                           | 6.69                      | 7.01        | 7.91           | 8.51                      |

**Experimental conditions:** [CAT]<sub>0</sub>=0.8×10<sup>-4</sup> mol dm<sup>-3</sup>; [Aniline]<sub>0</sub>=1.2×10<sup>-3</sup> mol dm<sup>-3</sup>; [NaOH]=1.2×10<sup>-3</sup> mol dm<sup>-3</sup>

anilines. The variation of rate constants with temperature and activation parameters are shown in Table 4.

### 6. Effect of Varying Chloride Ions on the Reaction Rate

The effect of  $\text{Cl}^-$  ions on the rates of the reaction were studied with  $0.2 \text{ mol dm}^{-3}$  NaCl solution. There was no significant effect of rates on  $\text{Cl}^-$  ions, suggesting no interhalogen or free chlorine was formed during the reaction sequence.

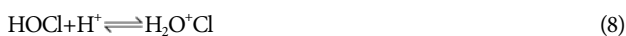
### 7. Test for Free Radicals

The addition of the reaction mixtures to an aqueous acrylamide monomer solution did not initiate polymerization. This indicates the absence of formation of free radical species *in situ* in the reaction sequence. Controlled experiments were also performed under the same reaction conditions in absence of CAT.

Chloramine-T ( $\text{TsNClNa}$ , here  $\text{Ts}=\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2^-$ ) behaves like a strong electrolyte in aqueous solution [36].

### 8. Reactive Species of CAT

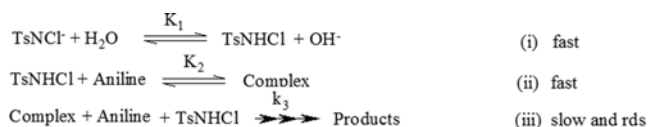
The reactive species responsible for the oxidizing character may depend on the pH of the medium. Bishop and Jennings [36], Hardy and Johnston [37], Morris et al. [34] and Pryde and Soper [38], and Higuchi et al. [39] have formulated the following equilibria for CAT in aqueous solution.



In acid solutions, the probable oxidizing species of CAT are  $\text{TsNHCl}$ ,  $\text{TsNCl}_2$ ,  $\text{HOCl}$  and possibly  $\text{H}_2\text{O}^+\text{Cl}$ . In alkaline medium, where  $\text{TsNCl}_2$  does not exist, the expected reactive species are  $\text{TsNHCl}$ ,  $\text{TsNCl}^-$ ,  $\text{HOCl}$  and  $\text{OCl}^-$ . Amongst the aforesaid four possible oxidizing species of CAT in alkaline medium, the most reactive possible oxidizing species in the present case will be determined based on the observed experimental results. Bishop and Jennings [36] calculated the concentrations of different species in  $0.05 \text{ mol dm}^{-3}$  CAT solutions at different pH. Further, Hardy and Johnston [37] also reported the existence of the following equilibria in alkaline solutions of CAT:



According to Eq. (9), if  $\text{TsNHCl}$  were the reactive species, a retardation of the rate by  $[\text{OH}^-]$  would be expected, which is true in the present investigations. Hardy and Johnston [37] also reported that there could be considerable concentration of  $\text{TsNHCl}$  even in alkaline CAT solutions. Furthermore, several workers observed the retarding influence of  $\text{OH}^-$  ions on the rate of CAT reactions with a number of substrates and suggested that the reactivity of weakly alkaline solutions of CAT is due to the formation of the conjugate acid ( $\text{TsNHCl}$ ) from  $\text{TsNCl}^-$  in a  $\text{OH}^-$  retarding step [40-45]. Based



**Scheme 1. A general reaction scheme for the oxidation of anilines with CAT in alkaline medium.**

on the above argument, it is reasonable to assume that  $\text{TsNHCl}$  as the reactive oxidizing species in the present case.

### 9. Reaction Scheme

In view of the preceding discussion and experimental results, Scheme 1 can be formulated for the oxidation of aniline and *p*-substituted anilines with CAT in alkaline medium.

The detailed mode of oxidation of anilines with CAT and the structure of the intermediate complex can be seen in Scheme 2. In the fast pre-equilibrium step (step(i)) of Scheme 2, the anionic form of CAT,  $\text{TsNCl}^-$ , undergoes hydrolysis in an alkali retarding step, generating the conjugate acid  $\text{TsNHCl}$  as the reactive oxidizing species. In the subsequent fast step (step(ii)), the lone pair of electrons present on the nitrogen of the aniline attacks the chlorine of  $\text{TsNHCl}$  gives an intermediate complex with the elimination of  $\text{TsNH}_2$ . In the next slow and rds (step(iii)), another molecule of aniline attacks the complex to give an intermediate hydrazobenzene. In the subsequent fast steps this intermediate hydrazobenzene reacts with another molecule of oxidant to yield the azobenzene as shown in Scheme 2.

### 10. Deduction of Kinetic Rate Law

The rate law for Scheme 1 can be derived as follows:

$$\text{If } [\text{CAT}]_t = [\text{TsNCl}^-] + [\text{TsNHCl}] + [\text{Complex}] \quad (11)$$

From steps (i) and (ii) of Scheme 1,

$$[\text{TsNCl}^-] = \frac{[\text{Complex}][\text{OH}^-][\text{TsNH}_2]}{K_1 K_2 [\text{Aniline}][\text{H}_2\text{O}]} \quad (12)$$

$$[\text{TsNHCl}] = \frac{[\text{Complex}][\text{TsNH}_2]}{K_2 [\text{Aniline}]} \quad (13)$$

By substituting for  $[\text{TsNCl}^-]$  and  $[\text{TsNHCl}]$  from Eqs. (12) and (13), respectively into Eq. (11) and solving for complex, we obtain,

$$[\text{Complex}] = \frac{K_1 K_2 [\text{CAT}]_t [\text{Aniline}][\text{H}_2\text{O}]}{[\text{OH}^-][\text{TsNH}_2] + K_1 [\text{TsNH}_2][\text{H}_2\text{O}] + K_1 K_2 [\text{Aniline}][\text{H}_2\text{O}]} \quad (14)$$

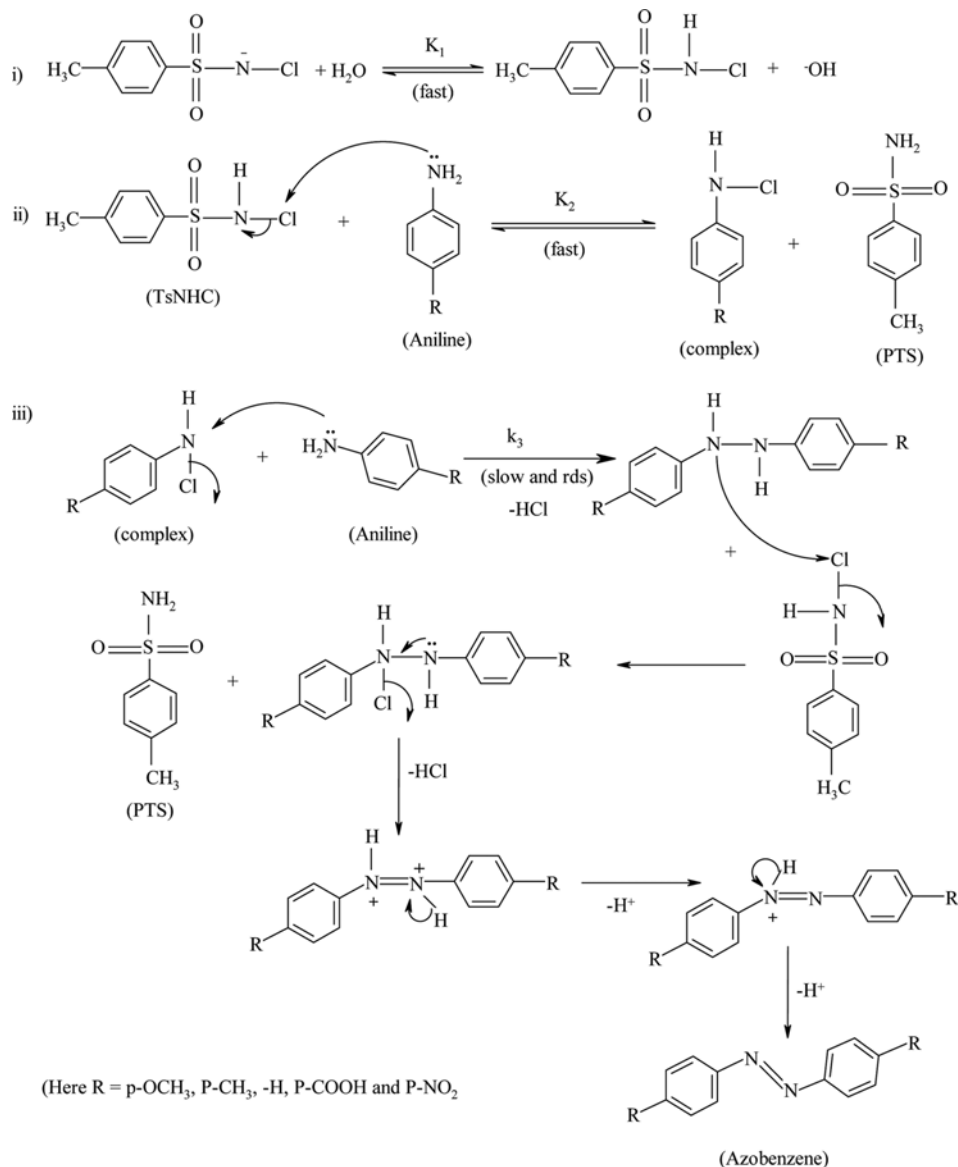
From the slow and rds (step(iii)) of Scheme 1,

$$\text{Rate} = k_3 [\text{Complex}] [\text{Aniline}] \quad (15)$$

By substituting for  $[\text{Complex}]$  from Eq. (14) into Eq. (15), the following rate law is obtained:

$$\text{rate} = \frac{K_1 K_2 k_3 [\text{CAT}]_t [\text{Aniline}]^2 [\text{H}_2\text{O}]}{[\text{OH}^-][\text{TsNH}_2] + K_1 [\text{TsNH}_2][\text{H}_2\text{O}] + K_1 K_2 [\text{Aniline}][\text{H}_2\text{O}]} \quad (16)$$

Rate law (16) is in complete agreement with the experimental kinetic data wherein a first-order dependence of rate on  $[\text{CAT}]_t$ , fractional-order on  $[\text{Aniline}]$  and inverse-fractional-order each on  $[\text{OH}^-]$  and



Scheme 2. A detailed proposed mechanism for the oxidation of anilines with CAT in alkaline medium.

[TsNH<sub>2</sub>] was observed.

### 11. Evaluation of Decomposition Constants

Since rate =  $k'[\text{CAT}]_0$ , under pseudo-first-order conditions of  $[\text{Aniline}]_0 \gg [\text{CAT}]_0$ , rate Eq. (16) can be transformed as:

$$k' = \frac{K_1 K_2 k_3 [\text{Aniline}]^2 [\text{H}_2\text{O}]}{[\text{OH}^-][\text{TsNH}_2] + K_1 [\text{TsNH}_2][\text{H}_2\text{O}] + K_1 K_2 [\text{Aniline}][\text{H}_2\text{O}]} \quad (17)$$

$$\frac{1}{k'} = \frac{[\text{OH}^-][\text{TsNH}_2]}{K_1 K_2 k_3 [\text{Aniline}]^2 [\text{H}_2\text{O}]} + \frac{[\text{TsNH}_2]}{K_2 k_3 [\text{Aniline}]^2} + \frac{1}{k_3 [\text{Aniline}]} \quad (18)$$

$$\frac{1}{k'} = [\text{TsNH}_2] \left\{ \frac{[\text{OH}^-]}{K_1 K_2 k_3 [\text{Aniline}]^2 [\text{H}_2\text{O}]} + \frac{1}{K_2 k_3 [\text{Aniline}]^2} \right\}$$

$$+ \frac{1}{k_3 [\text{Aniline}]} \quad (19)$$

Plots of  $1/k'$  versus  $[\text{TsNH}_2]$  from Eq. (19) were linear ( $R^2 > 0.9764$ ) and yields a

$$\text{slope} = \left\{ \frac{[\text{OH}^-]}{K_1 K_2 k_3 [\text{Aniline}]^2 [\text{H}_2\text{O}]} + \frac{1}{K_2 k_3 [\text{Aniline}]^2} \right\}$$

$$\text{and an intercept} = \frac{1}{k_3 [\text{Aniline}]}$$

Therefore, from the intercepts, the values of decomposition constants of  $k_3$  were calculated for all the five anilines for the standard run with  $[\text{CAT}]_0 = 0.8 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{Aniline}] = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{NaOH}] = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$  and  $T = 303 \text{ K}$ . The  $k_3$  values obtained are 0.378, 0.326, 0.245, 0.148 and  $0.101 \text{ s}^{-1}$  for *p*-methoxyaniline, *p*-methylaniline, aniline, *p*-carboxylicaniline and *p*-nitroaniline,



respectively. The proposed reaction Scheme 1 and rate law (16) are also substantiated by the experimental results discussed below.

## 12. Effect of Ionic Strength

The study of an ionic strength effect on the rate of the reaction provides information about the charges involved in the reaction. According to Brønsted and Bjerrum concept [46], the effect of ionic strength ( $\mu$ ) on the rate of a reaction ( $k$ ) involving two ions ( $Z_A$  and  $Z_B$ ) is given by the equation,

$$\log k' = \log k_0 + 1.018 Z_A Z_B \mu^{1/2} \quad (20)$$

Here,  $k_0$  is the rate constant at infinite dilute concentration. According to this equation, a plot of  $\log k'$  versus  $\mu^{1/2}$  is a straight line with a slope of  $1.018 Z_A Z_B$  and an intercept  $= \log k_0$ . The sign  $Z_A Z_B$  determines the direction of the slope. When the reacting species are of the same sign, an increase in ionic strength increases the rate. When ions of opposite signs react, there is decrease in rate with increasing ionic strength. When one of the reactants is a neutral molecule, the rate constant is expected to be independent of ionic strength of the medium. In the present investigations, addition of  $0.2 \text{ mol dm}^{-3}$   $\text{NaClO}_4$  solution to the reaction mixture did not affect the rate significantly in case of all the five anilines studied. It clearly signifies that one of the reacting species is a neutral molecule, as can be seen in step (iii) of Scheme 2, which is in accordance with the Brønsted-Bjerrum concept [46].

## 13. Isokinetic Relationship

The isokinetic relationship is important for deciding the nature of a mechanism [47]. As can be seen in Table 4, the activation energy is highest for the slowest reaction and *vice-versa*, establishing that the reaction is enthalpy controlled. This is verified by calculating the isokinetic temperature ( $\beta$ ) by two plots. In the present case, the enthalpies and entropies of activation for the oxidation of all the five anilines are linearly related by plotting  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  (Fig. 7;  $R^2=0.9995$ ). The slope of this plot is the isokinetic temperature, which was found to be 415 K. Further, the isokinetic relationship was verified by the Exner criterion [48] by plotting  $\log k'_{(313\text{K})}$  versus  $\log k'_{(303\text{K})}$  (Fig. 7;  $R^2=0.9986$ ). The value of  $\beta$  was calculated from the equation  $\beta = T_1(1-q)/(T_1 - T_2) - q$ , where  $q$  is the slope of

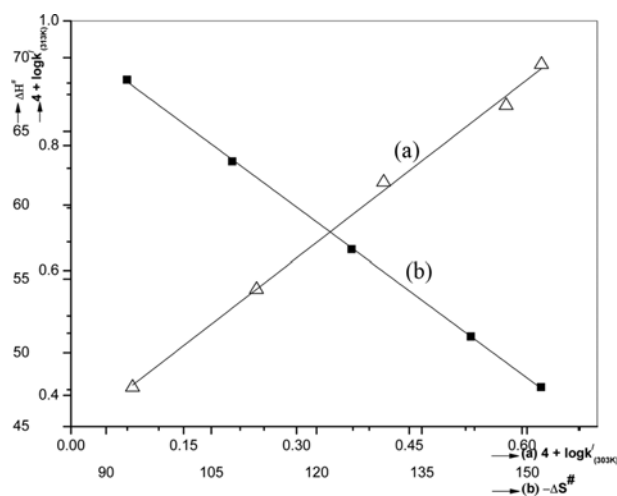


Fig. 7. Isokinetic plots of (a)  $\log k'_{(313\text{K})}$  versus  $\log k'_{(303\text{K})}$  (b)  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$ .

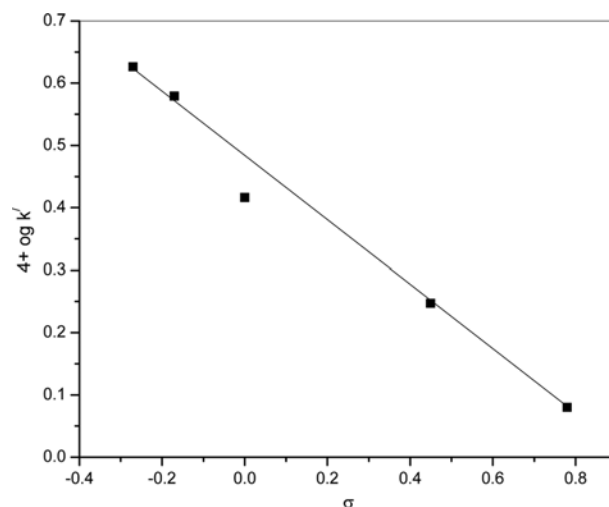


Fig. 8. Hammett plot of  $\log k'$  versus  $\sigma$ .

the Exner plot and the value of  $\beta$  was found to be 416 K, which is in very good agreement with the  $\beta$  calculated from  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  plot. The values of  $\beta$  calculated from both plots are much higher than the experimental temperature range (293-313 K) employed in the present study, indicating enthalpy as a controlling factor.

## 14. Structure Reactivity Correlation

Structural modification on the reactant molecule may influence the rate or equilibrium constant of a reaction [49]. Hammett linear free energy relationship [50,51] describes the correlation between structure and reactivity. In the present case, attempts were made to correlate rates of oxidation of anilines with substituent constants ( $\sigma$ ). A fairly good correlation between  $\log k'$  versus  $\sigma$  with a slope of  $-0.52$  (Fig. 8;  $R^2=0.9905$ ) was observed, which is the reaction constant ( $\rho$ ). The negative sign of  $\rho$  signifies that electron donating substituents ( $-\text{OCH}_3$  and  $-\text{CH}_3$ ) accelerates the reaction rates and electron withdrawing substituents ( $-\text{COOH}$  and  $-\text{NO}_2$ ) retard them, conforms to the Hammett LFER. From an inspection of rate data (Table 4), the rate of oxidation of anilines follows the order: *p*-methoxyaniline > *p*-methylaniline > aniline > *p*-carboxylicaniline > *p*-nitroaniline, signifying the dominance of the inductive effect of the alkyl groups on the reaction.

## 15. Activation Parameters

The proposed reaction mechanism and the derived rate law are also supported by the moderate values of energy of activation and thermodynamic parameters (Table 4). The values of  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  indicate that the transition state is highly solvated. The large negative values of  $\Delta S^\ddagger$  suggest the formation of a rigid associative transition state with a reduction in the number of degrees of freedom of molecules in each case. The near constancy of  $\Delta G^\ddagger$  and a linear plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  (Fig. 7) indicate that a common mechanism operates in the oxidation of anilines studied with CAT in alkaline medium. The values of frequency factors ( $A$ ) specify the frequency of collisions and the orientation of reacting molecules.

## CONCLUSION

Optimum conditions for the efficient oxidative conversion of

anilines to azobenzenes by chloramine-T in alkaline medium have been established. The oxidation reaction follows identical kinetic behavior for all the five anilines studied and obeys the rate law:  $\text{rate} = k [\text{CAT}]^1 [\text{Aniline}]^x [\text{OH}]^{-y} [\text{TsNH}_2]^{-z}$  where  $x$ ,  $y$  and  $z$  are less than unity. Oxidation products were characterized by NMR spectral studies. Composition activation parameters and decomposition constants were deduced. An isokinetic relation is obtained with  $\beta = 415 \text{ K}$ . The rate of oxidation of anilines follows the order: *p*-methoxyaniline > *p*-methylaniline > aniline > *p*-carboxylic aniline > *p*-nitroaniline. The rates correlated well with the Hammett's substituent constants, and the value of reaction constant ( $\rho$ ) obtained from this plot is  $-0.52$ , which indicates that the electron donating groups increase the rate while electron withdrawing groups decrease the rate of reaction. The mechanistic pathways and kinetic modeling for this redox system have been computed. The remarkable advantage of this protocol is mild reaction conditions, excellent yields of products, operational and experimental simplicity and hence great prospects in industrial applications.

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