



## **Kinetics and Thermodynamics of Oxidation of Some *meta*-substituted Anilines by Tetrabutylammonium Bromochromate in Aqueous Acetic Acid Medium**

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<http://dx.doi.org/10.13005/ojc/330134>

(Received: November 30, 2016; Accepted: December 12, 2016)

### **ABSTRACT**

The tetrabutylammonium bromochromate (TBABC) oxidation of anilines, in an aqueous acetic acid medium in the presence of perchloric acid is described. The reaction is first order with respect to aniline, TBABC and acid. The reaction rate has been determined at different temperatures and activation parameters calculated. The TBABC oxidation of *meta*-substituted anilines obeys Hammett relationships.

**Keywords:** Tetrabutylammonium bromochromate; Aniline; Thermodynamic parameters; Kinetics.

### **INTRODUCTION**

Aniline is known to be carcinogenic and also reacts easily in the blood to convert haemoglobin into methaemoglobin, preventing oxygen uptake. Aniline and its derivatives are used as intermediates for the manufacturing of various organic compounds such as colorants, agrochemicals and pharmaceutical

agents. Therefore, a serious effect on human health over a long period of time is possible, even if aniline is in low concentrations<sup>1</sup>.

Aniline can enter the body either by inhalation of air containing aniline, ingestion of food or water containing aniline, or by dermal contact with aniline. Inhalation of air containing aniline can

cause respiratory tract irritation. Exposure to high levels can cause a number of adverse health effects including breathing difficulties, dizziness, headache, irregular heart-beat, methaemoglobinaemia (blood disorder), blue colour to the skin, convulsions and in extreme cases coma and death. Ingestion of aniline can lead to gastrointestinal irritation, nausea, vomiting and diarrhea. Exposure to high levels may lead to effects similar to those for inhalation. Dermal contact with aniline can cause skin irritation and sensitization. Absorption of large quantities of aniline through the skin may cause effects similar to those for inhalation. There is an increased risk in young infants of developing methaemoglobinaemia due to aniline exposure<sup>2</sup>.

Oxidation is an essential reaction for different organic synthesis. Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic

compounds. Chromium compounds especially Cr(VI) reagents have been versatile reagents and capable of oxidizing almost all the oxidisable organic functional groups. The development of newer chromium (VI) reagents for the oxidation of organic substrates continues to be of interest<sup>3</sup>. In recent years, many such reagents have been developed with some success. Some new Cr(VI) based reagents like tetraheptylammonium bromochromate<sup>4</sup>, tripropyl ammonium fluorochromate<sup>5</sup>, isoquinolinium bromochromate<sup>6</sup>, tetrahexylammonium bromochromate<sup>7</sup>, benzimidazolium fluorochromate<sup>8</sup> and tetrabutylammonium bromochromate<sup>9</sup> have been used to study the oxidation of various organic compounds.

The oxidation kinetics of anilines by various oxidizing agents have been extensively studied<sup>10-14</sup>. Since anilines are very harmful to human health and the environment, removal of aniline from the

**Table 1: Effect of variation of [S], [TBABC] and [H<sup>+</sup>] on the rate of reaction at 303 K<sup>a</sup>**

10 <sup>3</sup> [TBABC] (mol dm <sup>-3</sup> )	10 <sup>2</sup> [S] (mol dm <sup>-3</sup> )	[H <sup>+</sup> ] (mol dm <sup>-3</sup> )	10 <sup>4</sup> k <sub>r</sub> (s <sup>-1</sup> ) <sup>b</sup>						
			H	<i>m</i> -OCH <sub>3</sub>	<i>m</i> -OC <sub>2</sub> H <sub>5</sub>	<i>m</i> -CH <sub>3</sub>	<i>m</i> -F	<i>m</i> -Cl	<i>m</i> -NO <sub>2</sub>
0.6	2.0	0.16	10.08	8.04	9.80	11.50	5.52	5.10	2.76
1.0	2.0	0.16	10.16	8.08	9.88	11.52	5.56	5.14	2.78
1.6	2.0	0.16	10.18	8.14	9.84	11.60	5.58	5.18	2.74
2.0	2.0	0.16	10.06	8.10	9.90	11.56	5.50	5.16	2.72
2.6	2.0	0.16	10.20	8.06	9.86	11.54	5.60	5.20	2.80
1.0	1.0	0.16	5.04	4.12	4.88	5.78	2.82	2.54	1.42
1.0	1.5	0.16	7.30	6.14	7.40	8.66	4.14	3.88	2.12
1.0	2.5	0.16	12.60	10.18	12.42	14.32	6.92	6.44	3.48
1.0	3.0	0.16	15.16	12.20	14.78	17.22	8.38	7.78	4.18
1.0	2.0	0.10	6.40	5.08	6.22	7.22	3.44	3.22	1.76
1.0	2.0	0.20	12.60	10.16	12.38	14.36	6.98	6.38	3.48
1.0	2.0	0.26	16.48	13.22	16.10	18.80	9.08	8.36	4.52
1.0	2.0	0.30	19.00	15.20	18.48	21.64	10.46	9.66	5.22
1.0	2.0	0.16	10.10 <sup>c</sup>	8.00 <sup>c</sup>	9.80 <sup>c</sup>	11.58 <sup>c</sup>	5.50 <sup>c</sup>	5.18 <sup>c</sup>	2.72 <sup>c</sup>
1.0	2.0	0.16	7.62 <sup>d</sup>	6.08 <sup>d</sup>	7.42 <sup>d</sup>	8.64 <sup>d</sup>	4.22 <sup>d</sup>	3.86 <sup>d</sup>	2.08 <sup>d</sup>

<sup>a</sup>As determined by spectrophotometrically following the disappearance of Cr(VI) at 362 nm;

<sup>b</sup>Estimated from pseudo first order plots

<sup>c</sup>In the presence of 0.001 mol dm<sup>-3</sup> acrylonitrile;

<sup>d</sup>In the presence of 0.003 mol dm<sup>-3</sup> Mn (II);

Solvent composition = 50% AcOH- 50% H<sub>2</sub>O (v/v)

environment is the ultimate goal of research today. For this a deep understanding of the mechanism of the oxidation process of aniline is needed. Furthermore, one of the important tools in deciding the mechanism of reactions is the study of substituent effects and thermodynamic parameters. The Hammett equation, also known as Linear Free Energy Relationships (LFER) have been found useful for correlating reaction rates and equilibrium constants for *meta*- and *para*-substituted derivatives of benzene. The isokinetic relationship is also an important tool for deciding the nature of a mechanism<sup>14</sup>. Keeping this in view, we report the kinetic features of the oxidation of a series of *meta*-substituted anilines by TBABC in an aqueous acetic acid medium to propose a suitable mechanism.

## EXPERIMENTAL

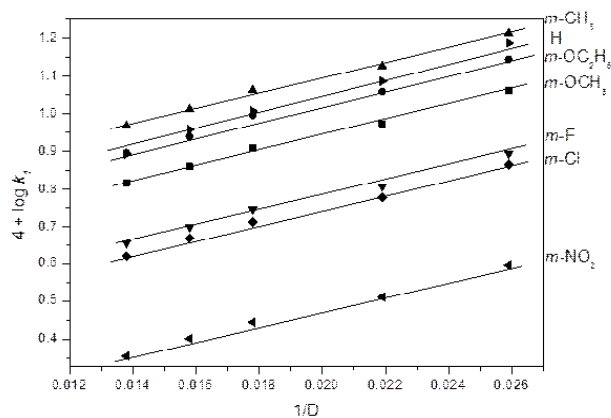
### Materials and reagents

All the employed chemicals and solvents were of analytical grade. Anilines were used with substituents H, *m*-OCH<sub>3</sub>, *m*-OC<sub>2</sub>H<sub>5</sub>, *m*-CH<sub>3</sub>, *m*-F, *m*-Cl and *m*-NO<sub>2</sub>. Tetrabutylammonium bromochromate (TBABC) was prepared by a reported method<sup>9</sup> and its purity was checked by the iodometric method. Doubly distilled water was used for all purposes. The solid anilines were used as such and the liquid anilines were used after vacuum distillation. Acetic acid was purified by standard method and the fraction distilling at 118 °C was collected.

**Table 2: Effect of varying solvent polarity on the rate of reaction of aniline *m*-OCH<sub>3</sub>, *m*-OC<sub>2</sub>H<sub>5</sub>, *m*-CH<sub>3</sub>, *m*-F, *m*-Cl and *m*-NO<sub>2</sub> anilines by TBABC at 303 K**

%AcOH- H <sub>2</sub> O (v/v)	Dielectric constant	$10^4 k_f, (s^{-1})$						
		H	<i>m</i> -OCH <sub>3</sub>	<i>m</i> -OC <sub>2</sub> H <sub>5</sub>	<i>m</i> -CH <sub>3</sub>	<i>m</i> -F	<i>m</i> -Cl	<i>m</i> -NO <sub>2</sub>
30-70	72.0	7.80	6.56	7.86	9.26	4.52	4.16	2.26
40-60	63.3	9.06	7.24	8.68	10.26	5.00	4.66	2.52
50-50	56.0	10.16	8.08	9.88	11.52	5.56	5.14	2.78
60-40	45.5	12.20	9.38	11.42	13.38	6.42	5.98	3.24
70-30	38.5	15.40	11.46	13.94	13.94	16.30	7.84	7.32

$10^2 [S] = 2.0 \text{ mol dm}^{-3}$ ;  $10^3 [\text{TBABC}] = 1.0 \text{ mol dm}^{-3}$ ;  $10 [H^+] = 1.6 \text{ mol dm}^{-3}$



**Fig. 1: Showing plot of 1/D against  $\log k_f$ , showing effect of solvent polarity at various temperatures in the presence of oxalic acid**

**Kinetic measurements**

The pseudo – first-order conditions were attained by maintaining a large excess ( x 15 or more) of aniline over TBABC. The solvent was 50% acetic acid – 50% water (v/v), unless specified otherwise. The reactions were followed, at constant temperatures ( $\pm 0.01$  K), by monitoring the decrease in [TBABC] spectrophotometrically at 362 nm using UV–Vis spectrophotometer, Shimadzu UV-1800 model.

**Data analysis**

Correlation analysis were carried out using Microcal Origin (Version 6.1) computer software. The goodness of the fit is discussed using the correlation coefficients and standard deviations.

**Stoichiometry and Product analysis**

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of TBABC largely in excess over aniline. The estimation of unreacted

**Table 3: Pseudo-first order rate constants for the oxidation of aniline, *m*-OCH<sub>3</sub>, *m*-OC<sub>2</sub>H<sub>5</sub>, *m*-CH<sub>3</sub>, *m*-F, *m*-Cl and *m*-NO<sub>2</sub> anilines by TBABC at various temperatures in aqueous acetic acid medium**

Substrate	10 <sup>4</sup> <i>k</i> <sub>1</sub> (s <sup>-1</sup> )			
	298 K	303 K	308 K	313 K
<i>m</i> -H	7.08	10.16	14.50	20.40
<i>m</i> -OCH <sub>3</sub>	5.52	8.08	11.80	17.24
<i>m</i> -OC <sub>2</sub> H <sub>5</sub>	6.86	9.88	14.24	20.48
<i>m</i> -CH <sub>3</sub>	8.24	11.52	16.12	22.58
<i>m</i> -F	3.74	5.56	8.28	12.34
<i>m</i> -Cl	3.40	5.14	7.76	11.72
<i>m</i> -NO <sub>2</sub>	1.82	2.78	4.24	6.52

10<sup>2</sup> [S] = 2.0 mol dm<sup>-3</sup>; 10<sup>3</sup> [TBABC] = 1.0 mol dm<sup>-3</sup>; 10 [H<sup>+</sup>] = 1.6 mol dm<sup>-3</sup>  
Solvent composition = 50% AcOH - 50% H<sub>2</sub>O (v/v)

**Table 4: Activation parameters and second order rate constants for the oxidation of aniline, *m*-OCH<sub>3</sub>, *m*-OC<sub>2</sub>H<sub>5</sub>, *m*-CH<sub>3</sub>, *m*-F, *m*-Cl and *m*-NO<sub>2</sub> anilines by TBABC in aqueous acetic acid medium**

Substrate	10 <sup>2</sup> <i>k</i> <sub>2</sub> (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )				<i>E</i> <sub>a</sub> kJmol <sup>-1</sup>	$\Delta$ H <sup>#</sup> kJmol <sup>-1</sup>	- $\Delta$ S <sup>#</sup> JK <sup>-1</sup> mol	$\Delta$ G <sup>#</sup> kJmol <sup>-1</sup> (at 303 K)
	298K	303K	308K	313K				
H	3.54	5.08	7.25	10.20	54.94	52.30±0.2	96.86±0.6	81.63±0.4
<i>m</i> -OCH <sub>3</sub>	2.76	4.04	5.90	8.62	58.96	56.48±0.6	85.18±1.8	82.28±1.2
<i>m</i> -OC <sub>2</sub> H <sub>5</sub>	3.43	4.94	7.12	10.24	56.67	54.18±0.4	91.12±1.2	81.78±0.8
<i>m</i> -CH <sub>3</sub>	4.12	5.76	8.06	11.29	52.26	49.78±0.2	104.32±0.6	81.38±0.4
<i>m</i> -F	1.87	2.78	4.14	6.17	61.84	59.35±0.4	78.86±1.2	83.24±0.8
<i>m</i> -Cl	1.70	2.57	3.88	5.86	62.22	61.65±0.6	71.96±1.8	83.45±1.2
<i>m</i> -NO <sub>2</sub>	0.91	1.39	2.12	3.26	64.05	63.56±0.3	70.82±0.9	85.02±0.6

10<sup>2</sup> [S] = 2.0 mol dm<sup>-3</sup>; 10<sup>3</sup> [TBABC] = 1.0 mol dm<sup>-3</sup>; 10 [H<sup>+</sup>] = 1.6 mol dm<sup>-3</sup>  
Solvent composition = 50% AcOH - 50% H<sub>2</sub>O (v/v)

TBABC showed that 1 mol of TBABC reacts with 1 mol of aniline. The oxidative products were analysed using preparative TLC on silica gel, which yields azobenzene m.p 66 °C (Lit 68 °C) and UV Abs.(EtOH) at  $\lambda_{max}$  320 nm.

## RESULTS AND DISCUSSION

The oxidation of anilines by TBABC has been conducted in 50% acetic acid and 50% water

**Table 5: Reaction constant values for the oxidation of aniline, *m*-OCH<sub>3</sub>, *m*-OC<sub>2</sub>H<sub>5</sub>, *m*-CH<sub>3</sub>, *m*-F, *m*-Cl and *m*-NO<sub>2</sub> anilines by TBABC in aqueous acetic acid medium at different temperatures**

Temp.	Reaction constant, $\rho$	Correlation coefficient	Standard deviation
298K	-0.8088	0.990	0.12
303K	-0.7648	0.988	0.14
308K	-0.7214	0.991	0.09
313K	-0.6696	0.992	0.16

$10^2 [S] = 2.0 \text{ mol dm}^{-3}$ ;  $10^3 [\text{TBABC}] = 1.0 \text{ mol dm}^{-3}$ ;  
 $10 [\text{H}^+] = 1.6 \text{ mol dm}^{-3}$

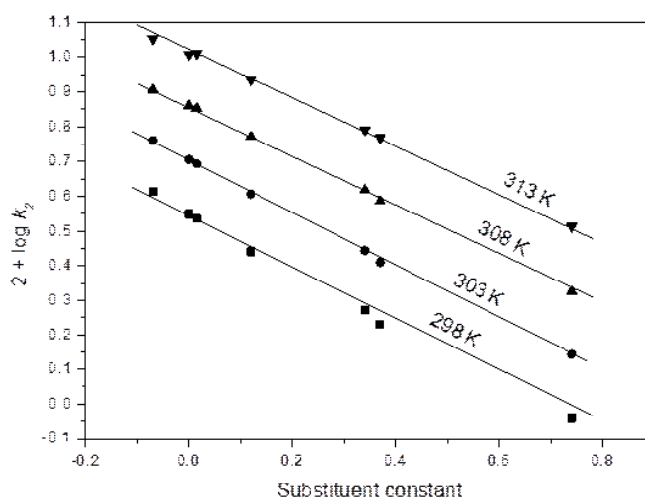
Solvent composition = 50% AcOH - 50% H<sub>2</sub>O (v/v)

medium at 303 K, under pseudo first order conditions and the result obtained were discussed in the following paragraphs.

The values of  $k_1$  were independent of the initial concentration of TBABC (Table 1) suggesting the reactions were of first order with respect to TBABC. The reaction was catalysed by hydrogen ions and the order with respect to [H<sup>+</sup>] was one. Linear plots of  $\log k_1$  versus  $\log [\text{Substrate}]$  with unit slope demonstrate the first-order dependence of the rate on [Aniline].

The oxidation of aniline in a nitrogen atmosphere failed to induce the polymerization of acrylonitrile. Furthermore, the rate of oxidation decreased with the addition of Mn(II), indicating the involvement of a two-electron reduction of Cr(VI) to Cr(IV) (Table 1). Therefore, a one-electron oxidation, giving rise to free radicals, is unlikely.

The oxidation of aniline has been studied in the binary mixture of acetic acid and water as the solvent medium. The concentration of acetic acid was varied from 30% to 70% and the rate were measured. The reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium (Table - 2). Positive slope of



**Fig. 2: Showing Hammett plot of  $\log k_2$  versus substituent constant  $\sigma_p$  for the oxidation of aniline, *m*-OCH<sub>3</sub>, *m*-OC<sub>2</sub>H<sub>5</sub>, *m*-CH<sub>3</sub>, *m*-F, *m*-Cl and *m*-NO<sub>2</sub> anilines by TBABC in aqueous acetic acid medium at different temperatures**

$\log k_1$  versus  $1/D$  plot indicates that the reaction involves a cation-dipole type of interaction in the rate determining step<sup>15</sup> (Fig. 1).

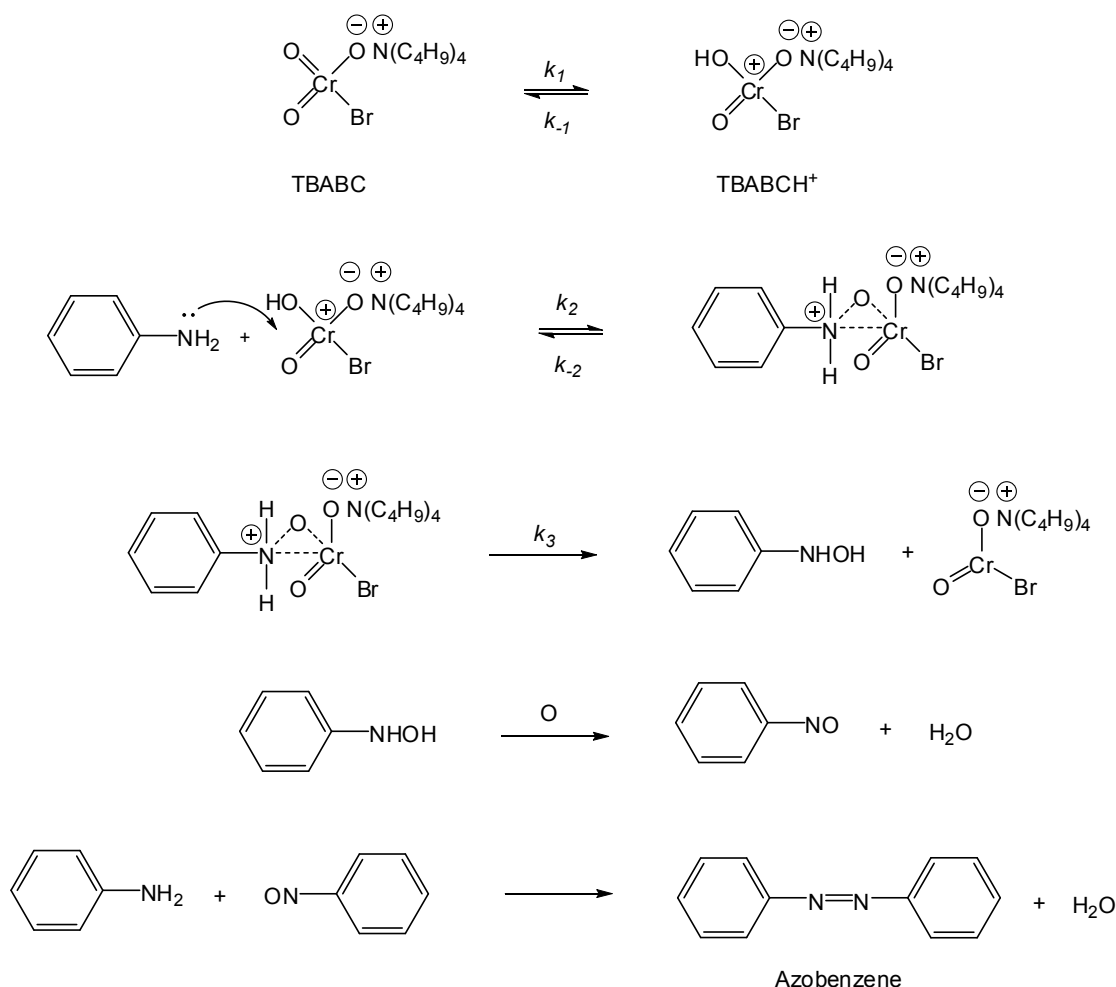
Solvent variations may affect the kinetics and the energy of the electron transfer processes in a complex manner, particularly in mixed solvent media as the physico-chemical properties of mixed solvent media are often quite different from those of the pure solvents or of their ideal mixtures<sup>16</sup>. The dependence of the kinetic parameters for reactions on the composition of mixed aqueous solvents often affords complicated patterns.

Rates of oxidation of anilines were determined at different temperatures between 298 and 313 K in 50% – 50% (v/v) acetic acid – water

medium in presence of perchloric acid and the pseudo-first order rate constants were determined (Table – 3). Various activation parameters were calculated and the values were presented in Table – 4. The entropy of activation is negative for anilines.

The effect of structure on reactivity of *meta*-substituted anilines were studied. It is interesting to note that the reactivity decreases in the order  $m\text{-CH}_3 > \text{H} > m\text{-OC}_2\text{H}_5 > m\text{-OCH}_3 > m\text{-F} > m\text{-Cl} > m\text{-NO}_2$  for the substituents.

A linear Hammett's plot is obtained when substituent constant ( $\delta$ ) for different substituents were plotted against  $\log k_2$  for the oxidation of anilines by TEABC at various temperatures. The value of slope of Hammett plot is known as reaction constant ( $\rho$ ). A



**Scheme 1: Mechanism of oxidation of aniline by TBABC**

linear Hammett's plot is given in Figure 2. Reaction constant values at different temperatures are given in Table 5. According to Hammett, the reaction with positive  $\rho$  values are accelerated by electron withdrawal from benzene ring, whereas those with negative  $\rho$  values are retarded by electron withdrawal from benzene ring<sup>17</sup>. In this oxidation reactions, the electron withdrawing groups decreases the rate and the electron donating groups increases the rate. These observations supporting the negative  $\rho$  values obtained from the Hammett Plot. The negative  $\rho$  values further confirms the formation of a positively charged transition state.

#### Mechanism of oxidation

The sequence of reactions for the oxidation of anilines by TBABC in perchloric acid is shown in Scheme 1. The oxidation of anilines by TBABC in acetic acid water medium is remarkably slow, but is catalyzed in the presence of perchloric acid, and the reaction proceeds at a comfortable rate. Catalysis by perchloric acid suggests protonation of TBABC species rather than the aniline molecule, which would have resulted in retardation. The reaction did not promote polymerization of acrylonitrile indicating absence of free radicals. However, the addition of Mn (II), in the form of  $MnSO_4$ , retards the rate of oxidation. This indicates the involvement of Cr(IV) intermediate in the oxidation of anilines by Cr(VI) reagent.

The reaction proceeds with the formation of a complex followed by the loss of hydride ion. The complex is formed likely by concerted transfer of oxygen from the oxidant to N-atom and electron pair from N-atom to Cr (VI). The negative  $\rho$  value is indicative of the presence of a positive nitrogen center, which would mean depletion of lone-pair electron density, and this can be facilitated only when the oxidant forms a complex with the substrate in which the nitrogen lone-pair can be used up in coordinating with an electron-deficient center, preferably a metal ion. The above mechanism leads to the following rate law:

$$-d[TBABC] / dt = k_1 k_2 k_3 [Aniline] [TBABC] [H^+]$$

#### CONCLUSIONS

In this paper we have reported the detailed mechanism of oxidation of aniline and some *para*-*meta* substituted anilines by TBABC. The reaction is first order each in [Aniline], [TBABC] and [H<sup>+</sup>]. The oxidation of *meta*-substituted anilines yield the corresponding azo benzenes. The negative  $\rho$  values obtained from the Hammett plot reveals that a positively charged reactive intermediate is formed during the oxidation process. Similarly the negative value of "S" provided support for the formation of activated complex in the slow step.

#### REFERENCES

- Bhuvaneshwari, D.S.; Elango, K.P. *Z. Naturforsch.* **2006**, *61b*, 1254 – 1260.
- Jin, Q.; Hu, Z.; Jin, Z.; Qiu, L.; Zhong, W.; Pan, Z. *Bioresour. Technol.* **2012**, *117*, 148-154.
- Wiberg, W. B. *Oxidation in Organic Chemistry*, Academic Press, New York, **1995**
- Ghammamy, G.; Mehrani, K.; Afrand, H.; Javanshir, Z.; Rezaeibehbahani, G. R.; Moghimi, A.; Aghbolagh, Z. S. *J. Chil. Chem. Soc.* **2009**, *54*, 491 - 494.
- Yogananth, A.; Mansoor, S. S. *Oriental J. Chem.* **2015**, *31*, 17-23
- Vibhute, A. Y.; Patwari, S. B.; Khansole, S. V.; Vibhute, Y. B. *Chin. Chem. Lett.* **2009**, *20*, 256 – 260
- Mansoor, S. S.; Asghar, B. H. *J. Indian. Chem. Soc.* **2013**, *90*, 1395 - 1401.
- Malik, V. S.; Vannamuthu, I.; Shafi, S. S.; Mansoor, S. S. *Oriental J. Chem.* **2015**, *31*, 77-83
- Ghammamy, G.; Mehrani, K.; Afrand, H.; Hajjighrammani, M. *Afr. J. Pure Appl. Chem.* **2007**, *1*, 8 -10.
- Patwari, S. B.; Khansole, S. V.; Vibhute, Y. B. *J. Iran. Chem. Soc.* **2009**, *6*, 399-404.
- Gupta, V. K. *React. Catal. Lett.* **1985**, *27*, 207-211
- Mansoor, S. S.; Shafi, S. S. *Arab. J. Chem.* **2014**, *7*, 171–176
- Bhuvaneshwari, D. S.; Elango, K. P. *Int. J. Chem.*

- Kinet.* **2006**, *38*, 657–665
14. Bhuvaneshwari, D.S.; Elango, K. P. Z. *Naturforsch.* **2005**, *60b*, 1105 – 1111
15. Amis, E. S. Solvent Effects on Reaction Rates and Mechanisms. Academic Press, New York, **1967**, 42
16. Bhuvaneshwari, D. S.; Elango, K. P. *J. Serb. Chem. Soc.* **2008**, *73* (7), 735–744
17. Hammett, L.P. Physical Organic Chemistry, First Ed. McGraw-Hill, New York, **1940**