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CHAPTER - IV

DISCUSSION

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DISCUSSION

The mechanism of a chemical reaction is a mental model based on the experimental facts. Now a days knowledge of mechanism of chemical reaction has so advanced that, it is possible to explain the formation of final product which takes place through the number of intermediate steps in the reaction. The most rational approach of Arrhenius<sup>61</sup> for explaining the occurrence of a chemical reaction is the concept of molecular activation as a pre-requisite to a chemical reaction. This concept of activation is now universally accepted and forms the basis of all subsequent theories of chemical reaction.

Oxidation of aromatic amines namely m-Toluidine, p-Toluidine and o-Toluidine was studied here. The reaction was studied in strong acidic medium i.e. 1.25 M H<sub>2</sub>SO<sub>4</sub>. The concentration range of oxidant was 0.625 x 10<sup>-3</sup> M to 3.125 x 10<sup>-3</sup> M. The concentration range of substrate was 0.625 x 10<sup>-2</sup> M to 3.125 x 10<sup>-2</sup> M for m-Toluidine and o-Toluidine, and 1 x 10<sup>-2</sup> M to 2.5 x 10<sup>-2</sup> M for p-Toluidine. The concentration range for sulphuric acid was 1.0 to 2.0 M. The reaction was studied iodometrically upto 75 % completion. The temperature range selected was 298<sup>o</sup>K to 318<sup>o</sup>K.

Pseudo first order is found with respect to oxidant. The order with respect to substrate and acid is also found to be one, for the three amines.

It is also found that for all the three cases, the absence of free radical during the reaction has been confirmed by acrylonitrile test. The effect of salt was also studied, but it is observed that there is no increase or decrease in specific reaction rate with salt concentration. This shows that effect of salt concentration is negligible. The salts used were  $K_2SO_4$ ,  $CdSO_4$  and  $ZnSO_4$ .

The mole ratio for all three reaction is also seen to be 1:1 for Bromate : substrate.

The values of k are nearly constant in case of all three amines for a particular experiment as time passes.

The thermodynamic parameters studied are temperature coefficient, energy of activation, enthalpy of activation, frequency factor, entropy of activation and free energy of activation. The Table No. 4:1 shows all thermodynamic parameters which have been studied.

It is found that the values of specific reaction rate constant seem to increase in order as o-Toluidine < p-Toluidine < m-Toluidine. This indicates that m-Toluidine is more reactive than p-Toluidine and o-Toluidine. The values of pseudo first order rate constants for the three amines under identical conditions of temperature and concentrations as follow,

m-Toluidine	$k_1 = 1.1810 \times 10^{-2} \text{min}^{-1}$	Table No.3.2.13
p-Toluidine	$k_1 = 1.1083 \times 10^{-2} \text{min}^{-1}$	Table No.3.3.5
o-Toluidine	$k_1 = 1.0476 \times 10^{-2} \text{min}^{-1}$	Table No.3.1.13

The order of reactivity seems to be o-Toluidine < p-Toluidine < m-Toluidine. Further it is observed that the thermodynamic parameters for the three compounds are nearly identical. However, it must be mentioned that enthalpy of activation seems to follow the same order as observed for reactivity of the three compounds.

In order to discuss the possible mechanism for the oxidation of Toluidines by potassium bromate, it is necessary to summarise the results obtained, the investigations are summarized as under :

- 1) The oxidation of Toluidines is first order with respect to oxidant, substrate as well as sulphuric acid.
- 2) Absence of free radical has been detected during the course of the reaction.
- 3) The stoichiometry was found to be 1:1 for oxidant to reactant.
- 4) The product analysis shows the presence of O-Benzoquinone.
- 5) The reaction is accelerated by electron-donating substituent and retarded by electron-withdrawing groups. The order of reactivity has been found to be  $m\text{-CH}_3 > p\text{-CH}_3 > o\text{-CH}_3$ . The similar observation has been reported by Vijayalaxmi and Sundaram E.V.<sup>12</sup>

- 6) The effect of added salt on reaction rate is negligible. This indicates that there is no participation of neutral species in the rate determining step.
- 7) The various thermodynamic parameters determined are as follows :

TABLE 4.1

Toluidine	Ea K.cal. mole <sup>-1</sup>	$\Delta H^\ddagger$ K.cal. mole <sup>-1</sup>	A sec <sup>-1</sup>	$\Delta S^\ddagger$ e.u.	$\Delta G^\ddagger$ K. cal. mole <sup>-1</sup>
o-Toluidine	13.384	12.698	$7.65 \times 10^5$	- 31.68	22.455
p-Toluidine	11.668	11.767	$3.49 \times 10^4$	- 37.81	23.415
m-Toluidine	12.202	11.440	$1.25 \times 10^5$	- 35.28	22.30

The fairly high positive value of free energy of activation  $\Delta G^\ddagger$  and enthalpy of activation  $\Delta H^\ddagger$  indicate that the transition state is highly solvated, while the large negative value of entropy of activation  $\Delta S^\ddagger$  suggests the formation of a rigid transition state.

Oxidation of anilines has been studied by P.S. Radha-krishnamurthi and Rama-Krishna Panda<sup>41</sup> using alkaline hexacyanoferrate. Radha-krisnnamurthi and Pati<sup>42</sup> have studied the oxidation of anilines by uncatalysed and Ru(III) catalysed Ti (III) ions in acetic acid medium. It has been shown by them that oxidation follows a free radical mechanism

for both the oxidants. Azo-benzene have been shown to be the end products. But, the oxidation of aniline and substituted aniline has been studied by Vijayalaxmi and E.V. Sundaram<sup>24</sup> using potassium bromate in acid medium in the presence of mercuric acetate in binary solvent mixture of acetic acid and water. It has been shown that oxidation did not follows a free radical mechanism, and Azobenzene have been shown to be the end product.

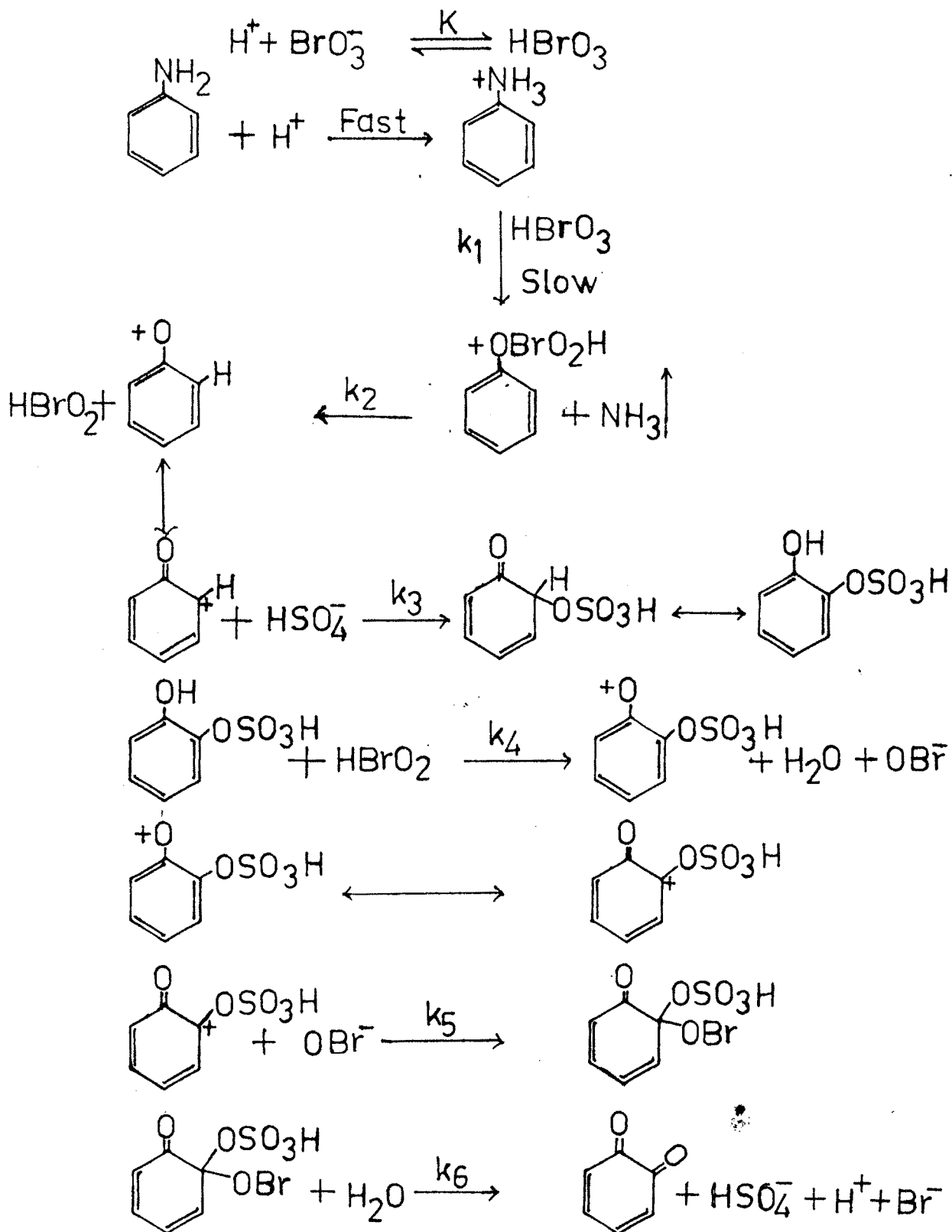
As the free radical has not been detected in the present investigation and the end product of oxidation is found to be O-Benzoquinone, the mechanism suggested by these authors does not seem to apply for the present case.

However, the oxidation of phenol has been studied by Vijayalaxmi and E.V. sundaram,<sup>12</sup> who have used  $\text{KBrO}_3$  as an oxidant in acetic acid medium. They have shown that the reaction is first order with respect to oxidant as well as reactant but second order with respect to  $[\text{H}^+]$ . They have obtained O-quinone as the end product and also they could not detect any free radical during the reaction. It seems, therefore, probable that Toluidines are oxidized to O-Benzoquinones by a similar mechanism which has been suggested for oxidation of phenols by Vijayalaxmi and E.V. Sundaram.<sup>12</sup>

However, the fact that order of the reaction with respect to  $[\text{H}^+]$  is one in the present study and not two as observed for phenols, suggests that the oxidizing species is not  $\text{H}_2\text{BrO}_3^+$  as suggested by them but simply  $\text{HBrO}_3$ .

It seems probable that Toluidine is first oxidized by  $\text{BrO}_3^-$  to corresponding substituted phenol which undergoes a similar course of reaction as suggested for phenol to give O-Benzoquinone as end product of the reaction. Therefore, we suggest the following mechanism for the oxidation of Toluidines by  $\text{BrO}_3^-$  ion in presence of  $\text{H}_2\text{SO}_4$ .

REACTION MECHANISM





In the original mechanism suggested by Vijayalaxmi and E.V. Sundaram,<sup>12</sup> substitution of acetate ion is assumed because they have used acetic acid as the medium. Since we have used sulphuric acid as the medium we have suggested the substitution of  $\text{HSO}_4^-$  ion.

In the mechanism second step is assumed to be the rate determining step. The velocity constant for phenol oxidation as reported by Vijayalaxmi and Sundaram are nearly 100 times smaller than the velocity constants observed by us. This clearly indicates that attack of  $\text{H BrO}_3$  species on the  $-\text{NH}_2$  group of Toluidine must be a rate determining step. The detection of ammonia during the course of the reaction also supports this view.

Further from table No. 3.1.5, 3.2.5, 3.3.5, it is clear that although  $k$  observed are proportional to  $[\text{Amine}]$  indicating first order with respect to Amine. The values of  $k$  at higher concentrations fall short of the proportionality indicating that the rate expression should be of the form

$$\frac{k_2 k_3 [\text{Amine}]}{1 + k_3 [\text{Amine}]}$$

It is according to William H. Richardson, Oxidation in organic chemistry, edited by Kenneth B. Wiberg,<sup>63</sup> Acad. Press N-1 (London) 1965.247.

Hence the overall rate equation should be of the final form.

$$-\frac{d[\text{BrO}_3^-]}{dt} = \frac{k_1 k_2 k_3 [\text{H}^+] [\text{BrO}_3^-] [\text{Amine}]}{1 + k_3 [\text{Amine}]}$$

The mechanism suggested above also fits this rate equation and is in accordance with the observations as order with respect to  $[\text{H}^+]$  is one, mole ratio of the reaction is 1:1. End product of the reaction is o-Benzoquinone, and free radical mechanism is absent.

Inductive effect of the substituents :

From the values of the rate constants at 303°K the order of the reactivity for the three amines is found to be O-Toluidine < p-Toluidine < m-Toluidine. It is clear that reaction is accelerated by an electron donating substituents and retarded by electron withdrawing groups, as the reaction proceeds via formation of a cations. However, substitution at m-position plays more inductive effect than at p-position. This is because proportion of  $\text{NH}_2$  group is hindered by electron donating group probably through delocalization of lone pair of electron on nitrogen atom. Such delocalization should be more at m-position. Thus stabilizing the activated complex. However, these effects are not very prominent as indicated by very close values of  $E_a$ ,  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  for the three compounds.