

CHAPTER VI

Discussion:

Oxidation of anilines namely aniline ($C_6H_5NH_2$) O-chloro aniline ($C_6H_4ClNH_2$) and P-Chloro-aniline ($C_6H_4ClNH_2$) is studied here. The reaction is studied in strong acidic medium i.e. 5N H_2SO_4 . The concentration range of oxidant ($KBrO_3$) was $2.5 \times 10^{-3}M$ to $12.5 \times 10^{-3}M$. The concentration range of substrate was $2.5 \times 10^{-3}M$ to 12.5×10^{-3} for aniline and $4 \times 10^{-2}M$ - $7 \times 10^{-2}M$ for ortho and para Chloroaniline. The concentration range for sulphuric acid was 4 N to 8 N. The reaction was studied iodometrically upto 90 % completion. The temperature range selected was $298^{\circ}K$ to $318^{\circ}K$.

Pseudo-first order is found with respect to oxidant ($KBrO_3$). 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 is also studied, but it is observed that there is no increase or decrease in specific reaction rate with salt concentration. This shows that there is no salt effect. The salts used were Na_2SO_4 , K_2SO_4 and $MgSO_4$.

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

The values of K are nearly constant in case of aniline for a particular experiment. In case of O-chloroaniline and P-chloroaniline the values of K slightly decreases as the time passes.

The thermodynamic parameters studied are temperature coefficient, energy of activation, enthalpy of activation, frequency factor, entropy of

activation, frequency factor, entropy of activation and free energy of activation. The table No. 6.1 shows all thermodynamic parameters which have been studied.

It is found that the values of specific reaction rate seem to increase in order as aniline < P-chloroaniline < O-chloroaniline. This indicates O-chloroaniline is more reactive than P-chloroaniline and aniline.

The values of Pseudo-first order rate constants for the three anilines under identical conditions of temperature and concentrations are,

$$K_1 \text{ (aniline)} 7.67 \times 10^{-3} \text{ (Table No. 3.1.2)}$$

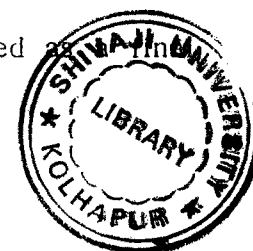
$$K_1 \text{ (O-chloroaniline)} 2.303 \times 10^{-2} \text{ (Table No. 4.2.2)}$$

$$K_1 \text{ (P-chloro aniline)} 1.228 \times 10^{-2} \text{ (Table No. 5.3.2)}$$

The order of reactivity seems to be aniline < P-chloro-aniline < O-chloro-aniline. Further it is observed that the thermodynamic parameters for the three compounds are nearly identical. However, it must be mentioned that free energy of activation seems to follow the same order as observed for reactivity of the three compounds.

While discussing the mechanism of these reactions we must consider the following observations

1. Reaction is first order w.r.t. to the oxidant as well as substrate. The reaction is also first order w.r.to H_2SO_4 . The reaction seems to follow the rate equation $-\frac{de}{dt} = K_1 [\text{BrO}_3^-] [\text{Aniline}] [\text{H}^+]$ in its simplest form.
2. No free radical has been detected during the course of the reaction.
3. End product analysis has shown that O-quinone is formed as product.



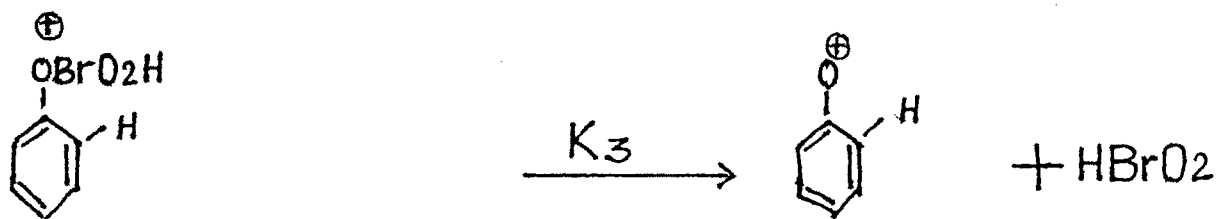
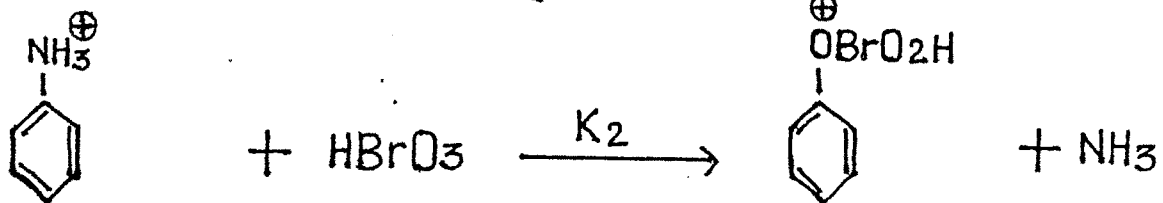
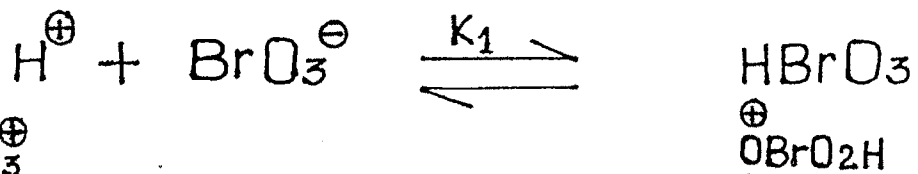
4. The mole ratio is found to be 1:1 for oxidant to reactant proportion.

Oxidation of anilines has been studied by P.S. Ratha-Krishnamurthi and Rama Krishna Panda⁴¹ using alkaline hexacyanoferrate. Similarly Ratha-Krishnamurthi and Pati⁴² have studied the oxidation of anilines by uncatalysed and Ru (III) catalysed Tl (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. As the free radical has not been detected in the present investigation and the end product is found to be O-quinone, the mechanism suggested by these authors does not seem to apply for the present case.

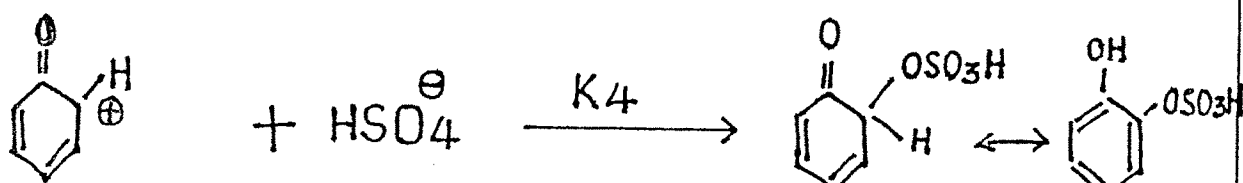
However, the oxidation of phenols has been studied by Vijaylaxmi and E.V.Sundaram¹⁰, who have used KBrO_3 as an oxidant in acetic acid medium. They have shown that the reaction is first order w.r. to oxidant as well as reductant but second order w.r. to (II^+) . They have obtained O-quinone as the end product and also they could not detect any free radical during the reaction. It seems, therefore, probable that anilines are oxidized to O-quinones by a similar mechanism which has been suggested for oxidation of phenols of Vijaylaxmi and E.V. Sundaram¹⁰. They have given the course of the reaction.

However, the fact that order of the reaction with respect to $[H^+]$ is one in the present studies and not two as observed for phenols, suggests that the oxidizing species is not $H_2BrO_3^+$ as suggested by them but simply $HBrO_3$.

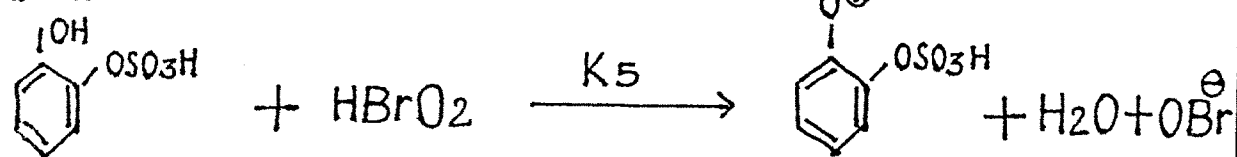
It seems probable that aniline is first oxidized by BrO_3 to corresponding phenol which undergoes a similar course of reaction as suggested above to give O-quinone as end product of the reaction. Therefore we suggest the following mechanism for the oxidation of anilines by BrO_3 ion in presence of H_2SO_4 .



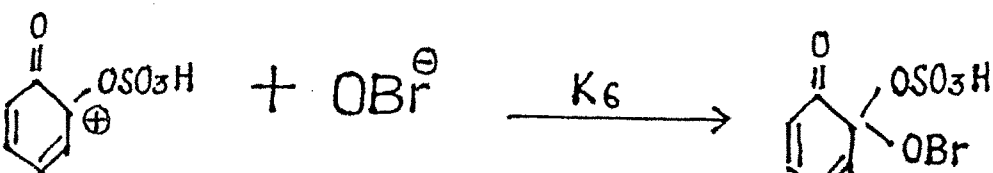
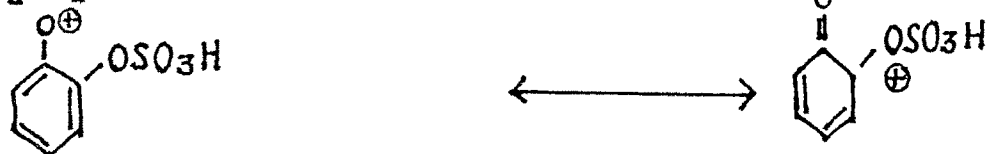
[A]



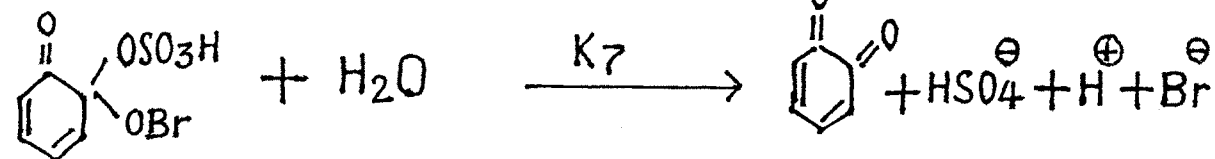
[B]



[C]



[D]



[F]

In the original mechanism suggested by Vijaylaxmi and Sundaram¹⁰, 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 HSO_4 ion instead.

In this mechanism step 2 is assumed to be the rate determining step. The velocity constant for phenol oxidation as reported by Vijaylaxmi and Sundaram¹⁰ are nearly 100 times greater than the velocity constants observed by us. This clearly indicates that attach of HBrO_3 species on the $-\text{NH}_2$ group of aniline must a rate determining step. The detection of ammoni NH_4^+ during the course of the reaction also supports this view.

Further from table No. 3.1.2, 4.2.2 and 5.3.2, it is clear that although K observed are propertional of $[\text{Amine}]$ indicating first order w.r. to $[\text{Amine}]$. 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 Willian H. Richardson in oxidation in organic chemistry edited by Knneht B. Wiberg⁶⁷ (Acad press N.I & London) 1966, 247.

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

$$\frac{d[\text{BrC}_3^-]}{dt} = \frac{K_1 K_2 K_3 [\text{H}^+] [\text{BrO}_3^-] [\text{Amine}]}{1 + K_3 [\text{Amine}]}$$

The mechanism suggested above also fits this rate equation and is in accordance with the following observations-

1. Order with respect to $[\text{H}^+]$ is one.
2. Mole ratio of the reaction is 1:1

3. End products of the reaction is O-quinone.
4. Free radical mechanism is absent.

Inductive effects 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 aniline < P-chloroaniline < O-chloroaniline. It is clear that reaction is accelerated by an electron withdrawing group (Cl⁻) as the reaction proceeds via formation of cation (A, B and D from mechanism).

However substitution of o-position plays more inductive effect than at P. position. This is because protonation of NH₂ group is hindered by electron withdrawing group probably through delocalization of lone pair of electrons on nitrogen atom. Such delocalization should be more at o-position thus stabilizing the activated complex (A). However, these effects are not very prominent as indicated by very close values of ΔE^\ddagger , ΔF^\ddagger and ΔS^\ddagger values for the three compounds. (Table No. 6.1) However it must be pointed out that the reactivity pattern of the three compounds aniline < P-chloro < O-chloroaniline is also related in the values of three thermodynamic parameters.

TABLE No. 6.1

| Temperature T ^o K | K Premium | Tempera- ture co- efficient | Energy of activation Ea KCal | Enthalpy of activa- tion ΔH^\ddagger | Frequency factor Λ Sec ⁻¹ | Entropy of activation ΔS^\ddagger e.u. | Free energy of activation ΔG^\ddagger KCal mol ⁻¹ |
|---------------------------------|------------------------|-----------------------------------|------------------------------------|--|---|--|--|
| 303 | 1.535×10^{-2} | | 12.948 | 12.4184 | 3.184×10^7 | - 28.254 | 21.1759 |
| ANILINE | 2.215×10^{-2} | 1.8755 | | | | | |
| 308 | 2.879×10^{-2} | 1.9571 | | | | | |
| 313 | 4.335×10^{-2} | | | | | | |
| 318 | 1.783×10^{-2} | | | | | | |
| 298 | 2.40×10^{-2} | 1.9495 | 13.71 | 12.1562 | 5.445×10^7 | - 27.1653 | 20.450 |
| 303 | 3.476×10^{-2} | 2.0963 | | | | | |
| O-CHLORO- ANILINE | 5.046×10^{-2} | | | | | | |
| 303 | 1.152×10^{-2} | | 13.2945 | 12.377 | 6.0394×10^7 | - 27.0093 | 20.763 |
| 308 | 1.706×10^{-2} | 2.06335 | | | | | |
| P-CHLORO ANILINE | 2.377×10^{-2} | 1.9636 | | | | | |
| 313 | 3.350×10^{-2} | | | | | | |
| 318 | | | | | | | |