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## Effect of ionic strength

The impact of ionic strength on the rate of oxidation of 2-aminophenol was studied by using various concentrations of KCl in the range of 0.30 to 0.45 M. The linear increase in rate with the ionic strength shows the primary salt effect i.e. involvement of same type of species in reaction mechanism.

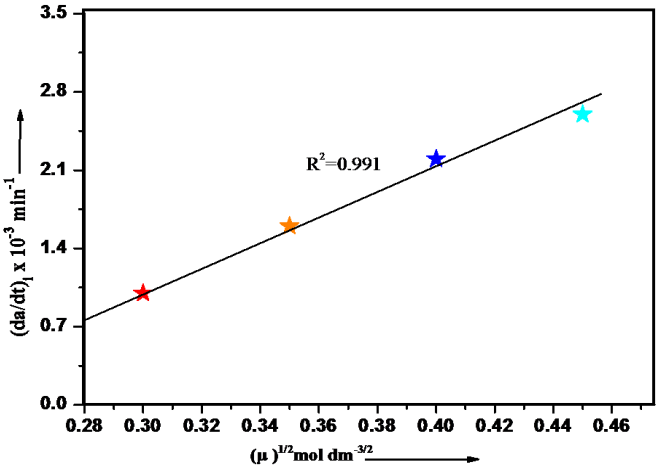


**Fig. 4.** Effect of ionic strength on the rate of oxidation of 2- Aminophenol. Temp. 25 °C, λmax 417.8nm, [HCF(III)] $3x10^{-4}$ mol/$dm^3$, [2-AP] $3x10^{-5}$ mol/$dm^3$.

## Thermodynamic parameters

The calculation of thermodynamic parameters was performed after investigating the impact of temperature on reaction rates at 25, 30, 35, and 40 °C.

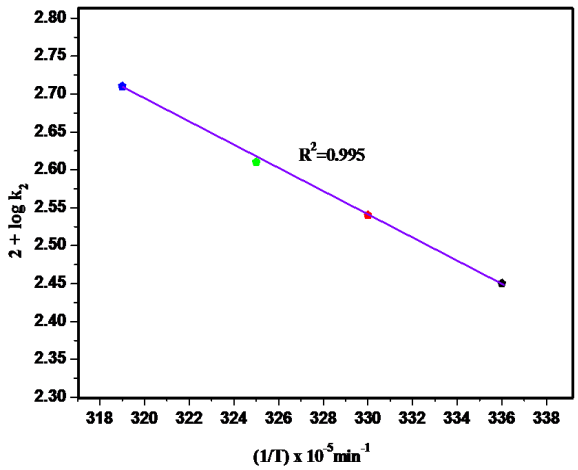


**Fig. 5.** Impact of temperature on the oxidation of 2- Aminophenol. pH 9, λmax 417.8, [HCF(III)] $3x10^{-4}$ mol/$dm^3$, [2-AP] $3x10^{-5}$ mol/$dm^3$.

Thermodynamic parameters including enthalpy of activation ($\Delta H^{\#}$), pre-exponential factor ($A$), activation energy ($E$a), energy of formation ($\Delta F$#) and entropy of activation ($\Delta S$#) for the oxidation of 2-

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aminophenol by HCF(III) ions have been evaluated using Arrhenius equation and plot (Fig. 4). The data represents that the reaction was characterized by a more negative value of entropy ($S^{\#}$) of activation shows the formation of polar species during the reaction. Positive value of enthalpy of activation ($\Delta H^{\#}$) shows reaction is endothermic because the enthalpy of product is greater than enthalpy of reactant. The Arrhenius equation is mentioned as follows:

$$K = A.e^{Ea/RT}$$

**Table 2.** Calculated values of thermodynamic parameters.

| S. No | Thermodynamic Parameter | Values |
|---|---|---|
| **1** | $E_a$ (kcal/mol) | 8.24 |
| **2** | A (L $mol^{-1}$ $s^{-1}$) | $29.74x10^5$ |
| **3** | $\Delta S^{\#}$ (e.u.) | -31.5 |
| **4** | $\Delta H^{\#}$ (kcal/mol) | 7.63 |
| **5** | $\Delta F^{\#}$ (kcal/mol) | 17.2 |

## Separation and identification of product

The product is extracted from reaction mixture by dichloromethane [20] after about 24 hours of reaction and then the extraction had been run in column of silica gel to obtain product. The red crystals separated were analyzed by preliminary test as melting point, element detection and functional group test. After separation the yield of product was about 60 %. The melting point 253 °C and functional groups -$NH_2$ and >CO group indicates the formation of 2-AHP [21]. The product is further characterized by FTIR and GC-MS methods of analysis.

## FT-IR (Fourier transform infrared) spectroscopy

The product is analyzed by FT-IR technique to find the existences of the functional groups in it. The IR spectra of product show bands in the region 3321.22, 2922.77, 2855.24, 1744.38, 1581.22, 1350.68 and 1207.73$cm^{-1}$. The comparison of data with the literature data [22] suggests the presence of ether group (1207.73$cm^{-1}$), amine group (1350.68 and stretching at 3321.22$cm^{-1}$). The band frequency at 1581.22, 1744.38 and 2855.24 $cm^{-1}$ correspond to =N-H, >CO and aromatic groups [23] respectively.

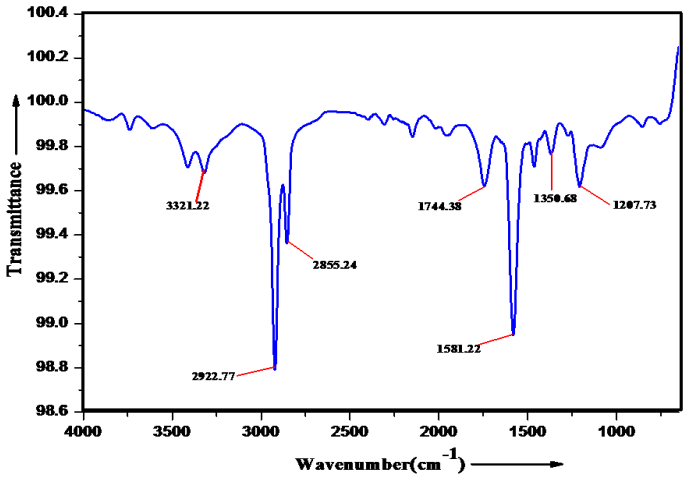


**Fig. 7.** FTIR spectra of product (2-AHP).

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## GC-MS

Gas chromatography-mass spectroscopy (GCMS) is a technique that merges the physical separation capabilities of gas chromatography with the mass analysis. Hence, in the present study m/z values have been used to investigate the product of the reaction. Single peak with retention time 3.0 min and m/z value 212 confirm the formation of 2-AHP as the main oxidation product.

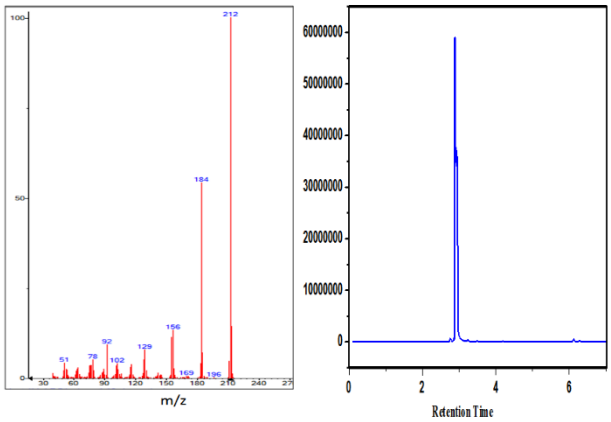


**Fig. 8.** GC-MS spectra of extracted product showing **(A)** m/z value and **(B)** Retention time.

## Antibacterial Activity: Agar well diffusion method

The gram positive (*Staphylococcus aureus*) and gram negative (*E. Coli*) bacteria are used to examine the antibacterial activity of 2-AHP. Activity of 2-AHP was evaluated qualitatively by agar well diffusion method in Muller Hinton agar medium. The concentration of 2-AHP was 100 (sample **(A)**) and 50 (sample **(B)**) µg/mL. The wells of diameter 6 mm were puncture with a sterile cork borer. The solution of product (2-AP) was used in two concentrations (**(A)** and **(B)**) and DMSO used as a solvent **(D)** and a positive control **(C)**. A control of vancomycin was also used for positive control **(C)**. After incubation of petriplate for 24 hours at 37 °C, then the zone inhibition was measured. The Fig. 9 inform that vancomycin (sample **(C)**) gives 17 mm, 100 µg/mL (sample **(A)**) 15 mm and 50 µg/mL (sample **(B)**) 8 mm zone of inhibition with *S. aureus*. In *E. coli* again vancomycin shows 17 mm, sample A 9 mm and sample B 7 mm zone of inhibition.

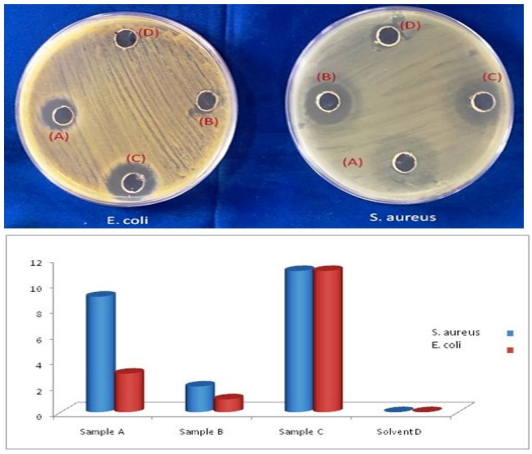


**Fig. 9.** Antimicrobial activity of 2-AHP in two concentrations **(A)** and **(B)** on *E. coli* and *S. aureus*. Positive control **(C)** and solvent **(D)**.

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**Mechanism**

Taking the above observation in view at lower concentration of reactants, the following rate expression may be suggested

$$r = k_{obs}\,[S][Fe(CN)_6^{3-}] \quad (1)$$

Where $k_{obs}$ is observed rate constant. The observed k value was found to be 2.34 $mol^{-1}dm^3s^{-1}$ and [S] represents concentration of substrate 2-AP.

Thus, in order to explain the above said results, the following reaction mechanism can be proposed in alkaline medium

$$\text{(i)}\ S + OH^- \underset{}{\overset{K}{\rightleftharpoons}} S^- + H_2O$$

$$\text{(ii)}\ S^- + [Fe(CN)_6]^{3-} \xrightarrow[slow]{k_1} \text{Complex } (C_1)$$

$$\text{(iii)}\ C_1 + \text{2-AP} \xrightarrow{fast} \text{Product} + Fe(CN)_6^{4-}$$

**Scheme 1.** In the above scheme it is based on the results and reported work [24]. It is assumed that in alkaline medium 2AP(S) forms anion $[S^-]$with $OH^-$.

This anion forms a labile complex ($C_1$) with ferricyanide ion (Scheme 1). The complex $C_1$ dissociates into the final product and ferrocyanide ion through the fast step.

Now from the step (ii), the rate of reaction would be given by:

$$r = k_1\,[S^-][Fe(CN)_6^{3-}] \quad (2)$$

from equation (i), assuming that water is in excess, and its concentration remains constant during the reaction, the concentration of anion $[S^-]$ is:

$$[S^-] = K\,[S][OH^-] \quad (3)$$

From equation 2 and 3:

$$r = k_1\,K\,[S][OH^-][Fe(CN)_6^{3-}] \quad (4)$$

$$r = k_1.k^{I}\,[S][Fe(CN)_6^{3-}] \quad (5)$$

since the concentration of $OH^-$ is constant, so a new constant $k^{I}$ is used at the place of a constant $K[OH^-]$. The derived rate law equation (5) is similar to the experimental rate law (1) verifies the proposed mechanism at lower concentration of reactants.

Based on the experimental work and literature, following oxidation scheme is proposed:

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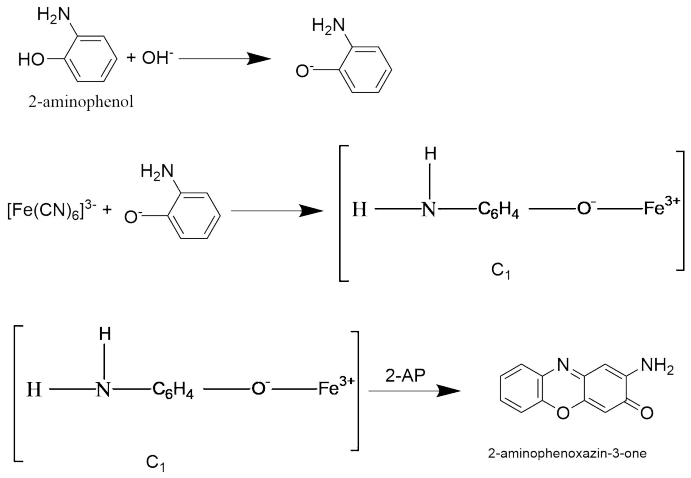


**Scheme 2.** Plausible scheme for oxidation of 2-AP.

The formation of product is confirmed by product analysis using GC-MS and FT-IR methods of analysis.

## Conclusion

The oxidative degradation of 2-aminophenol was observed kinetic-spectrophotometrically by using hexacyanoferrate (III) ions in aqueous alkaline medium. The oxidative kinetics of 2-aminophenol follows 1$^{st}$ order kinetic model with respect to [HCF(III)] and [2-aminophenol].

The oxidized product 2-aminophenoxazin-3-one was identified by the FTIR and GC-MS methods of analysis. The product of oxidation (2-AHP) shows good antibacterial activity for *S. aureus* (gram positive) than *E. coli* (gram negative). The results present in Fig. 8 shows that zone of inhibition of b) < a) i.e. lower the concentration of 2-AHP, lower is its inhibition power. Thus, the present method seems to be green and environmentally friendly for the oxidative conversion of 2-aminophenol to 2-AHP. The method is efficient, simpler, and cheaper due to the need of less amount of oxidant [HCF (III)] as compared to the other reported methods of oxidation (in Table 1). Thus, this study may be helpful for improvement in quality of wastewater of many industries and others.

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