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Mechanistic Aspects of Oxidation of P-Bromoacetophen one by Hexacyanoferrate (III) in Alkaline Medium

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ABSTRACT
The kinetics of oxidation of *p*-bromoacetophenone by hexacyanoferrate (III) has been studied in alkaline medium. The order of reaction with respect of both acetophenone and hexacynoferrate (III) has been found to be unity. The rate of reaction increases with increase in the concentration of sodium hydroxide.On addition of neutral KCl, reaction rate increases. The effects of solvent and temperature have been also studied. The product *p*-bromophenyl glyoxal have been characterized by IR studies.
Keywords:*p*-bromoacetophenone; Hexacyanoferrate; Oxidation; Mechanism;Kinetics

I. INTRODUCTION

Aromatic ketones are widely used in the synthesis of a large number of fine chemicals such as drugs, fragrances, dyes and pesticides [1-3].Friedal-Craft acylation is one of the most important methods for the synthesis of aromatic ketones. Aromatic ketones are mainly prepared by acylation of aromatics with acid chlorides, carboxylic acids and their anhydrides in the presence of acid catalysts. *p*-bromoacetophenone is an aromatic chemical compound with an aroma. *p*-bromoacetophenone was synthesised from bromobenzene via friedal craft acylation [4] The ^{13}NMR spectrum of *p*-bromoacetophenone is very interesting in several point of views .Note particularly that six carbon absorption are observed ,even though the molecule has eight carbon [5] .Various thermodynamics parameters like entropy, enthalpy etc. was studied by Jaspal etal.[6].

Hexacyanoferrate(III) has been proven to be an efficient oxidant for a wide variety of organic substrates, because the CN^- ligands are resistant to substitution reactions and thereby outer-sphere electron transfer is the preferred oxidation pathway [7].Kinetics of oxidation of

ketones [8,9] have been studied in alkaline medium by hexacyanoferrate (III),which isclassified as an oxidising agent in which the oxidising species is a complex electron attracting ion and the reactions are brought to proceed by a radical formation [10,11]. We report here the kinetics and mechanism of oxidation of *p*-bromoacetophenone by hexacyanoferrate(III) in alkaline medium.

II. EXPERIMENTAL

2.1. Materials and Methods

p-bromoacetophenone(Fluka) and all other chemicals of A.R., B.D.H. grade were used. In a 50 ml flask freshly prepared standard solution of acetophenone in methanol-water (w/w) and in another flask desired solution of hexacyanoferrate(III) and NaOH were taken and placed in a thermostat maintained at± 0.1^{o}C accuracy.

After half an hour both the reactants were mixed. At different intervals of time,5 ml aliquot was taken out and poured in a flask containing 5ml of 2N H_2SO_4 and 1 gm of KI. The unreacted $K_3Fe(CN)_6$ was estimated by titrating the liberated iodine against standard sodium thiosulphate solution, using starch as an indicator.

$$2\,Fe(CN)_6^{3-} + 2I^- \longrightarrow 2Fe(CN)_6^{4-} + I_2$$

The result of stoichiometeric runs under conditions,$[K_3Fe(CN)_6]$>>[acetophenone] keeping for 15 to 16 days at room temperature(25-30^{0}C) showed that one mole of acetophenone consumed 36 moles of $K_3Fe(CN)_6$ for its oxidation. The liberation of bromide ion is confirmed by adding $AgNO_3$ solution.

Stoichiometery and product analysis:

However, under experimental conditions [acetophenone]>>$[K_3Fe(CN)_6]$, the product *p*-methoxyphenylglyoxal has been separated by distillation and characterized by preparing its 2,4 dinitrophenylhydrazone derivative [12,13] m.p.132^{0}C (lit. value-130.5^0 C)followed by stretching frequencies at 1630 cm^{-1}for C=O recorded by I.R. spectra (in KBr). Thus stoichiometeric equation can be shown as

$$BrC_6H_4COCH_3 + 4Fe(CN)_6^{3-} + 4O\,H^- \longrightarrow BrCH_3C_6H_4COCHO + 4Fe(CN)_6^{4-} + 3H_2O \ldots (i)$$

This difference in observation indicates that oxidation takes place in stages.

III. RESULT AND DISCUSSION

Underpseudo conditions [substrate]>>$[Fe(CN)_6]^{3-}$, the data collected at

varying concentration of hexacyanoferrate(III) from 1.43 to 3.33x 10^{-3} at 25^0C ; [methanol] 30% (w/w); [NaOH] =0.166 M; [*p*-bromoaceto] =1.25x10^{-2}M and constant ionic strength(μ=0.4M) gave uniform pseudo first order velocity constants k_1= (3.12$^+$-0.035) x 10^{-4} s^{-1}indicating first order dependence of the reaction rate on oxidant. Under similar conditions,k_1 values calculated at varying concentration of *p*-bromoacetophenone from 1.66 x10^{-2} M to 1.11 x 10^{-2} M; gave uniform ratio; k_1/[aceto] =2.58 x10^{-2} $mole^{-1}s^{-1}$ in each set confirming the first order dependence of the reaction rate on substrate concentration.The reaction rate increases proportionality with the increase in concentration of NaOH from 0.11 to 0.25 M. The ratio; k_1/[NaOH] =1.85 x10^{-3} is fairly uniform in each set showing thereby that the reaction is base catalysed in nature.

On addition of KCl from 0.2 to 0.6 M the reaction rate increases from 1.83 to5.32 s^{-1} at 25^0C. The linear plots passing through origin between log k_1/k_0 (where k_0 = 4.17 x10^{-5} s^{-1}) and √μ with unit slope indicate ion-ion interaction [14] in the rate determining step.The data collected at different dielectric constants (D) from 69.99 to 56.28 by varying weight percentage of methanol in methanol-water mixture.(20 to 50% w/W) at 25^0C;[$K_3Fe(CN)_6$] = 2.0 x 10^{-3} M;[NaOH] = 0.166 M; [*p*-bromoacetophenone] =1.25 x 10^{-2} M ; μ=0.4M show that the reaction rate decreases from 5.31 to 0.63 x 10^{-4} s^{-1} with decrease in dielectric constant of the medium . The linear plot between log k_1 and 1/D with negative slope further indicates interaction between simply charged ions[15].

Effect Of Temperature:

The reaction rates are enhanced on enhancing the temperature from 20^0C to 35^0C of the reaction mixture. The energy of activation (E_a) has been determinedfrom the slope of linear plots between log k_1 and 1/T and all others activation parameters have been evaluated at 25^0C as:
K_r= 15.8 x10^{-2} $sec^{-1}l^2mole^{-2}$, E_a=68.9 kJ $mole^{-1}$, $\Delta H^{\#}$=66.5 kJ $mole^{-1}$, $\Delta S^{\#}$=- 39.2kJ $mole^{-1}$ and $\Delta F^{\#}$=78.1 kJ $mole^{-1}$

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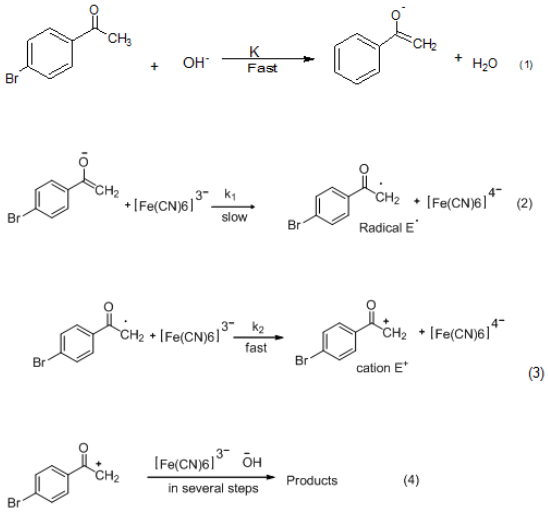
IV. MECHANISM OF REACTION



Kinetically it appears that at first the enolate anion is formed due to interaction between the enolateanion is formed due to interaction between acetophenone and OH^- ion, which interacts slowly with $Fe(CN)_6^{3-}$ and as a result of an electron transfer, it is converted into a radical [16], which is subsequently oxidized into *p*-bromophenylglyoxal in a fast process.

4.1. Rate Law

The rate of disappearance of [Fe $(CN_6)^{3-}$] is given by step 2 as :

$$- d [Fe (CN_6)^{3-}] / dt = k_1 [anion] [Fe (CN_6)^{3-}]$$

From step 1 taking activity of water as unity:

$$[anion] = K_1 [acetophenone] [OH^-]$$

And then final rate law becomes:

$$- d [Fe (CN_6)^{3-}] / dt = K_1.k_1 [acetophenone] [OH^-] [Fe (CN_6)^{3-}]$$

V. CONCLUSION

The derived rate law is fully justified by observed kinetics. The produced free radical is quite weak, as it is ineffective to polymerization of monomer acrylamide.

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