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Mechanistic Aspects of Oxidation of *P*-Methoxy Acetophenones by Hexacyanoferrate [III] in Alkaline Medium

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Abstract

The kinetics of oxidation of *p*-methoxy acetophenone 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*-methoxy phenyl glyoxal have been characterized by IR studies.

Keywords : Hexacyanoferrate; Kinetics; Oxidation; Mechanism; *p*-methoxy acetophenone

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]. Friedel-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-methoxy acetophenone is an aromatic chemical compound with an aroma. P-methoxy acetophenone was prepared by Ghodke et al. under solvent free condition using solid acid catalysts [4-5].

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 [6] . The kinetics of oxidation of aliphatic, aromatic and cyclic ketones have been studied In alkaline medium by hexacyanoferrate (III) and mechanism has been suggested via radical formation [7-10]. In this paper, we report the kinetics and mechanism of oxidation of *p*-methoxy acetophenone by hexacyanoferrate (III) in alkaline medium.

Aim of the Study

Many papers have been published regarding the kinetics of oxidation of acetophenones by several oxidising agents such as chromic acid, Vanadium (V), manganese (III), cerium (IV), Chloramine T and hydrogen Peroxide in acidic medium, but the kinetics of oxidation of acetophenones by different oxidants in alkaline medium is less reported in literature because they are soluble in acids rather than in alkali. The oxidation products also lack proper isolation and characterisation.

Review of Literature

The oxidants potassium permanganate, potassium ferricyanides, copper complexes of citrate and tartarateetc, are most employed in medium .Potassium ferricyanides also known as hexacyanoferrate (III), in which the oxidising species is one electron abstraction ion.

$Fe(CN)_6^{3-} + e^- \dashrightarrow Fe(CN)_6^{4-}$

The redox potential of the system is 0.45 volts.

In alkaline medium the oxidation of aniline and substituted aniline has been studied by hexacyanoferrate (III) at constant ionic strength is reported by Radha krishamurti & Panda1.The oxidation of diols are also studied in alkaline medium by hexacyanoferrate (III)2.

On the other hand, there are several papers dealing with kinetic study of oxidation of acetophenones which are used as hypnotic, in perfumery and a power lachrymator, by different oxidants, such as kinetic study of acetophenones with perbenzoic acid 3, kinetics of cerium (IV) oxidation of acetophenones by Patnaik & others 4 . Singh et al 5 have studied the kinetics of ferricyanide oxidation of acetone and ethyl methyl ketone in alkaline medium at constant ionic strength.

From foregoing studies, it is apparent that the kinetics of oxidation of acetophenones have been studied more in acidic medium by different oxidants than in alkaline medium because acetophenones are highly souluble in acids rather than in alkali or water.In alkaline medium the work has been carried out by using different composition of solvent; water alcohol mixture. It is of interest therefore ,to study the kinetics of oxidation of p-methoxyacetophenones in alkaline medium and to investigate their products.

Experimental

Materials and Methods

p-methoxy acetophenone (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 and in another flask desired solution of hexacyanoferrate (III) and NaOH were taken and placed in a thermostat maintained at± 0.1° C accuracy.

After half an hour both reactants were mixed and progress of the reaction was followed by estimating unreacted hexacyanoferrate (III) iodometrically. From the titre values and first order integrated equation, the k_1 values have been calculated.

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 42 moles of $K_3Fe(CN)_6$ for its oxidation.

Stoichiometery and Product Analysis

However, under experimental conditions [acetophenone]>>$[K_3Fe(CN)_6]$, the product *p*-methoxy phenyl Glyoxal has been separated by distillation and characterized by preparing its 2,4 dinitro phenyl hydrazone derivative [11, 12] m.p.230^{0}C (lit.value-235^{0}C) followed by stretching frequencies at 1630 and 1620cm^{-1}for C=O and C=N respectively, recorded by I.R. spectra (in KBr). Thus stoichiometeric equation can be shown as

$$OCH_3C_6H_4COCH_3+4Fe(CN)_6{}^{3-}+4OH^- \longrightarrow OCH_3C_6H_4COCHO +_4Fe(CN)_6{}^{4-}+3H_2O \text{.......(i)}$$

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

Result and Discussion

Under pseudo conditions [substrate]>> [Fe (CN)6]3-,the data collected at varying concenteration of hexacyanoferrate(III) (Table 1) and acetophenone (Table 2) at constant ionic strength show a first order dependence of the reaction rate on both the oxidant and substrate concenteration (Table 3) showing there by that reaction is base catalysed in nature.

Table 1:Effect of varying [oxidant] on the reaction rate

$[aceto^-]$ = 2X10^{9}M, [NaOH]= 0.20 M, [Methanol] = 20% (v/V), T= 30 ^{0}C

M x 10^3	1.66	2.00	2.50	2.33	5.00	10.00
K_1x10^{4}sec^{-1}	3.44	3.84	3.84	3.84	4.61	4.98

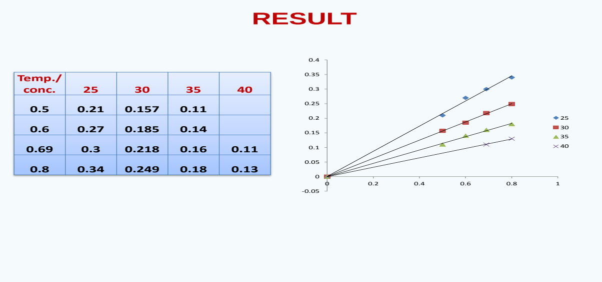
Table 2

Effect of varying [acetophenones] on the reaction rate

$[K_3 Fe(CN)_6]$=2.5x10-^{3}M, [NaOH]=0.20M, [Methanol]=20%v/V,µ=0.5M,Temp.30^{0}C

Acetophenones k1 x 104k1x 102/aceto

Acetophenones	k1 x 104	k1x 102/aceto
	Temp.25^{0}C	
2.00	4.61	2.31
1.66	3.70	2.29
1.43	3.30	2.31
1.25	2.90	2.32
	Temp.30^{0}C	
2.00	6.36	3.18
1.66	5.40	3.24
1.43	4.57	3.19
1.25	4.01	3.20
	Temp.35^{0}C	
2.00	8.43	4.22
1.66	7.10	4.28
1.43	6.10	4.27
1.25	5.41	4.32
	Temp.40^{0}C	
1.43	8.52	5.96
1.25	7.55	6.04



RESULT

Temp./ conc.	25	30	35	40
0.5	0.21	0.157	0.11	
0.6	0.27	0.185	0.14	
0.69	0.3	0.218	0.16	0.11
0.8	0.34	0.249	0.18	0.13

The linear plots between1/k_1 and 1/[aceto] passing through origin indicate that no complex formed between acetophenone and $Fe(CN)_6{}^{3-}$ prior to oxidation step.

Table 3: Effect of varying [NaOH] on the reactionrate [aceto]=2x10^{-2}M,$[K_3Fe(CN)_6]$=2.5x10^{-3}M, Methanol 20% (v/V), µ=0.5M, Temp.30^{0}C

[NaOH](M)	0.143	0.167	0.20	2.26	0.33	0.40
K_1x 10^4 sec^{-1}	3.41	4.43	5.52	6.35	8.16	9.45
K_1x10^3/[NaOH]	2.39	2.66	2.61	2.54	2.45	2.35

Table 4: Effect of varying ionic strength on the reaction rate

[aceto]=2x10-^{2}M, [NaOH]=0.25M, [Methanol] 20% (v/V), [K3Fe(CN)6]=2.5x10-^{3}M,Temp.30^{0}C

µM	k_1x10^4 sec^{-1}
0.3	3.59
0.4	4.31
0.5	6.35
0.6	7.53
0.7	9.01

On addition of KCl from0.3 to 0.7M the reaction rate increases from 3.59 to 9.01 $sec.^{-1}$ (Table 4) indicating positive salt effect. The linear plots between log K_1/K_0 and$\sqrt{\mu}$ (where K_0 is the rate constant at zero ionic strength) passing through origin indicate ion ion interaction [13] in the rate determining step.

Effect of Temperature

The reaction rates are enhanced on enhancing the temperature from 25^0C to 40^0C of the reaction mixture. The energy of activation (E_a) has been determined from the slope of linear plots between log k_1 and 1/T and all others activation parameters have been evaluated at 30^0C as:

K_r= $12.7x10^2$ sec^{-1} $mole^{-1}$, E_a=47.9 kJ $mole^{-1}$, $\Delta H^{\#}$ =45.4 kJ $mole^{-1}$, $\Delta S^{\#}$=- 113.7kJ $mole^{-1}$ and $\Delta F^{\#}$=82.1 kJ $mole^{-1}$

Mechanism of Reaction

Kinetically it appears that at first the enolate anion is formed due to interaction between the enolate [14] anion 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 [15], which is subsequently oxidized into *p*-methoxy phenyl glyoxal in a fast process. The reaction sequence is shown as:

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:

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

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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