

Mechanistic Aspects of Oxidation of m- Hydroxy acetophenones by Hexacyanoferrate [III] in Alkaline Medium.

Abstract

The kinetics of oxidation of *m*-hydroxyacetophenone by hexacyanoferrate (III) has been studied in alkaline medium. The order of reaction with respect of both acetophenone and hexacyano ferrate (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*-hydroxyphenyl glyoxal have been characterized by IR studies. Activation parameters have been calculated and a probable mechanism proposed.

Keywords: *M*-Hydroxy acetophenone, Hexacyanoferrate, Oxidation, Mechanism, Kinetics.

Introduction

Aromatic ketones are widely used in the synthesis of a large number of fine chemicals such as drugs, fragrances, dyes and pesticides¹⁻³. 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. The Kinetics and mechanism of oxidation of acetophenone in acidic medium have been studied⁴⁻⁵ due to high solubility in acids. But the study of oxidation of acetophenone in alkaline medium has little attention. Various thermodynamics parameters like entropy; enthalpy etc. was studied by Jaspal etal.⁶.

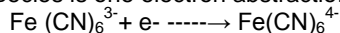
Hexacyanoferrate (III) has been proven to be an efficient oxidant for a wide variety of organic substrates, because the CN⁻ ligands are resistant to substitution reactions and thereby outer-sphere electron transfer is the preferred oxidation pathway⁷. Kinetics of oxidation of ketones⁸⁻⁹ have been studied in alkaline medium by hexacyanoferrate (III), which is classified 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 formation¹⁰⁻¹¹. We report here the kinetics and mechanism of oxidation of *m*-hydroxyacetophenone 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 alkaline isolation and characterisation.

Review of Literature

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



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



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Radha Krishna Murti & Panda¹. The oxidation of diols is also studied in alkaline medium by hexacyanoferrate (III).

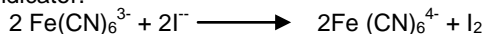
On the other hand, there are several papers dealing with kinetic study of oxidation of acetophenones which are used as hypnotic, in perfumery and a power lachrymator, by different oxidants, such as kinetic study of acetophenones with perbenzoic acid³, kinetics of cerium (IV) oxidation of acetophenones by Patnaik & others⁴. Singh et al⁵ 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 has been studied more in acidic medium by different oxidants than in alkaline medium because acetophenones are highly soluble 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

m-hydroxy 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 (w/w) and in another flask desired solution of hexacyanoferrate (III) and NaOH were taken and placed in thermostat maintained at $\pm 0.1^\circ\text{C}$ 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 5 ml of 2N H_2SO_4 and 1 gm of KI. The unreacted $\text{K}_3\text{Fe}(\text{CN})_6$ was estimated by titrating the liberated iodine against standard sodium thiosulphate solution, using starch as an indicator.



The result of stoichiometric runs under conditions, $[\text{K}_3\text{Fe}(\text{CN})_6] \gg [\text{acetophenone}]$ keeping for 15 to 16 days at room temperature ($25\text{--}30^\circ\text{C}$) showed that one mole of acetophenone consumed 36 moles of $\text{K}_3\text{Fe}(\text{CN})_6$ for its oxidation. The liberation of bromide ion is confirmed by adding AgNO_3 solution.

Stoichiometry and Product Analysis

However, under experimental conditions $[\text{acetophenone}] \gg [\text{K}_3\text{Fe}(\text{CN})_6]$, the product *m*-hydroxyphenylglyoxal has been separated by distillation and characterized by preparing its 2,4 dinitrophenylhydrazone derivative¹²⁻¹³ and characterized by IR Spectra (stretching frequencies at 1630 cm^{-1} for C=O recorded by I.R. spectra (in KBr). Thus stoichiometric equation can be shown as

$$\text{ONaC}_6\text{H}_4\text{COCH}_3 + 4\text{Fe}(\text{CN})_6^{3-} + 4\text{O}^- \longrightarrow \text{ONaCH}_3\text{C}_6\text{H}_4\text{COCHO} + 4\text{Fe}(\text{CN})_6^{4-} + 3\text{H}_2\text{O} \dots (i)$$

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

Result and Discussion

Under pseudo conditions $[\text{substrate}] \gg [\text{Fe}(\text{CN})_6]^{3-}$, the data collected at varying concentration of hexacyanoferrate (III) and [acetophenones] and at

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constant Ionic Strength show first order dependence each an[oxidant] (Table 1) and [substrate] (Table 2).

Table 1

Effect of varying [oxidant] on the reaction rate
 $[\text{M-hydroxy acetophenone}] = 1 \times 10^{-2} \text{ M}$, $[\text{NaOH}] = 0.10 \text{ M}$, $[\text{Methanol}] = 20\% (\text{v/v})$,
 $\mu = 0.5 \text{ M}$, Temp. 30°C

$M \times 10^3$	1.25	1.11	1.00	0.83	0.71
$k_1 \times 10^4 \text{ sec}^{-1}$	2.86	2.88	2.82	2.83	2.88

Table 2

Effect of varying [acetophenone] on the reaction rate
 $[\text{K}_3\text{Fe}(\text{CN})_6] = 1.0 \times 10^{-3} \text{ M}$, $[\text{NaOH}] = 0.1 \text{ M}$,
 $[\text{Methanol}] = 20\% \text{ v/v}$; $\mu = 0.2 \text{ M}$

[<i>m</i> -hydroxy acetophenone] $\times 10^2 \text{ m}$	$k_1 \times 10^4 \text{ s}^{-1}$	$k_1 \times 10^2 / \text{aceto}$
Temp. 25°C		
1.11	2.34	2.11
1.00	2.12	2.12
0.91	1.90	2.09
0.83	1.69	2.03
Temp. 30°C		
1.43	4.06	2.84
1.25	3.59	2.87
1.11	3.17	2.85
1.00	2.82	2.82
Temp. 35°C		
1.11	4.48	4.03
1.00	4.07	4.07
0.91	3.65	4.02
0.83	3.44	4.13
Temp. 40°C		
1.11	6.23	5.61
1.00	5.47	5.47
0.91	5.16	5.68
0.83	4.69	5.63

The reaction rate increases proportionality with an increase in $[\text{OH}^-]$. For example under the conditions; $[\text{K}_3\text{Fe}(\text{CN})_6] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{m-hydroxy acetophenone}] = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $\mu = 0.2 \text{ mol dm}^{-3}$ and Temp. = 30°C , $10^4 \times k_1$ increases from 2.35 to 3.52 s^{-1} when NaOH was increased from 0.083 to $0.125 \text{ mol dm}^{-3}$.

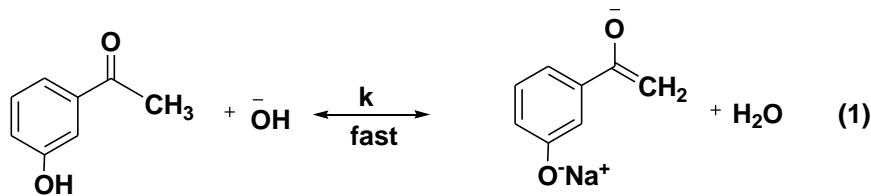
On addition of KCl from 0.1 to 0.3 mol dm^{-3} the reaction rate increases from 1.29 to 6.72 s^{-1} at 25°C . The linear plots passing through origin between $\log k_1/k_0$ (where $k_0 = 1.99 \times 10^{-5} \text{ s}^{-1}$) and $\sqrt{\mu}$ with unit slope indicate ion-ion interaction¹⁴ in the rate determining step. The data collected at different dielectric constants (D) from 70.68 to 57.70 by varying weight percentage of methanol in methanol-water mixture. (10 to 40% w/w) at 25°C ; $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{NaOH}] = 0.25 \text{ mol dm}^{-3}$; $[\text{m-hydroxyacetophenone}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $\mu = 0.5 \text{ mol dm}^{-3}$ show that the reaction rate decreases from 7.89 to $0.63 \times 10^{-4} \text{ s}^{-1}$ 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 ions¹⁵.

Effect of Temperature

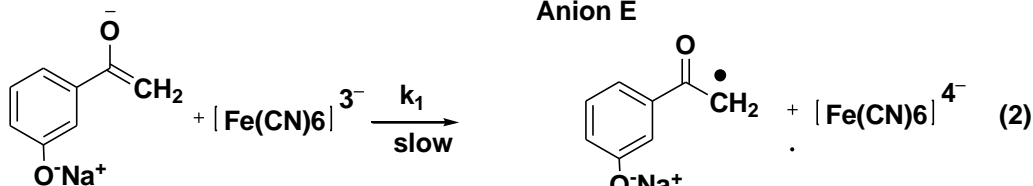
The reaction rates are enhanced on enhancing the temperature from 20°C to 35°C of the reaction mixture. The energy of activation (E_a) has been determined from the slope of linear plots

between $\log k_1$ and $1/T$ and all others activation parameters have been evaluated at 30°C as:

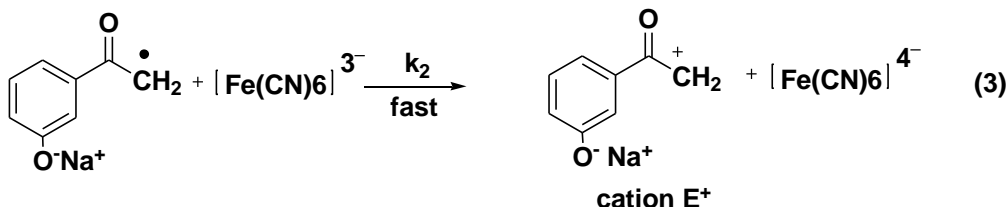
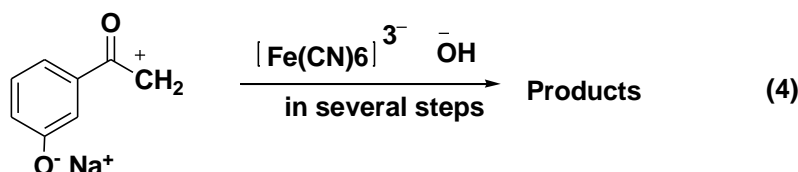
$$K_f = 28.20 \times 10^{-2} \text{ sec}^{-1} \text{ mole}^{-2}, E_a = 51.07 \text{ kJ mole}^{-1}, \\ \Delta H^\ddagger = 48.55 \text{ kJ mole}^{-1}, \Delta S^\ddagger = -95.74 \text{ JK}^{-1} \text{ mole}^{-1} \text{ and} \\ \Delta F^\ddagger = 77.56 \text{ kJ mole}^{-1}.$$

Mechanism of Reaction

Anion E



Radical E

cation E⁺

On the basis of above scheme, the rate of disappearance of $[\text{Fe}(\text{CN})_6]^{3-}$ is given by steps (1) and (2) as:

$$-\frac{d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = 4k_1 [\text{anion}] [\text{Fe}(\text{CN})_6]^{3-}$$

Kinetically it appears that at first the enolate anion is formed due to interaction between the acetophenone and OH^- ion, which interacts slowly with $[\text{Fe}(\text{CN})_6]^{3-}$ and as a result of an electron transfer, it is converted into a radical¹⁶, which is subsequently oxidized into *p*-hydroxyphenylglyoxal in a fast process.

Rate Law

The rate of disappearance of $[\text{Fe}(\text{CN})_6]^{3-}$ is given by step 2 as:

$$-d[\text{Fe}(\text{CN})_6]^{3-} / dt = k_1 [\text{anion}] [\text{Fe}(\text{CN})_6]^{3-}$$

From step 1 taking activity of water as unity:

$$[\text{anion}] = K_1 [\text{acetophenone}] [\text{OH}^-]$$

and then final rate law becomes $-d[\text{Fe}(\text{CN})_6]^{3-} / dt = K_1 k_1 [\text{acetophenone}] [\text{OH}^-] [\text{Fe}(\text{CN})_6]^{3-}$

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. The observed negative entropy is due to solvation of activated complex which becomes more

polar than the reactants leading to a decrease in entropy.

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