International Journal of Chemistry Research
ISSN-0976-5689 **Vol 1, Issue 2, 2010**

Research Article

KINETICS AND MECHANISTIC STUDY OF ACETOPHENONES BY TL (III) PERCHLORATE IN PERCHLORIC ACID

SYED SULTAN*, SYED ASIF, MAZAHAR FAROOQUI

***Post Graduate and Research Center, Maulana Azad College, Aurangabad. Email: mazahar_64@rediffmail.com**

Received: 01 May 2010, Revised and Accepted: 17 Jun 2010

Abstract

Kinetic and mechanistic study of oxidation of 4-Chloroacetophenone 4- Methyl acetophenone and 4-methoxy acetophenone is carried out using Tl (III) perchlorate in perchloric acid media. The effect of variation of substrate, oxidant and perchloric acid was studied under pseudo first order reaction conditions. The order of reaction was found to be zero for oxidant, first order with respective hydrogen ion and acetophenones. A probable mechanism has been suggested on the basis of experimental observations.

Keywords: Kinetics, Acetophenones

INTRODUCTION

In the recent years, kinetic and mechanistic studies of oxidation of aldehydes and ketones by various oxidants such as permanganate[1], N-Bromosuccinimide[2] alkaline hexacyanoferrate[3], Ce(IV) in presence of iridium (III) chloride[4], TiO_2[5], I_2 + Zeolite[6], bromamine-b[7], heamatite[8], etc. have been reported. Ce (IV) in sulphuric acid media is used to oxidation of mannitol[9]. Literature survey reveals that very little work is reported on the oxidation of acetophenones by Tl (III) perchlorate in perchloric acid. Therefore, we investigated the oxidation kinetics of 4-Chloro acetophenone, 4- Methyl acetophenone and 4-methoxy acetophenone using Tl (III) perchlorate.

EXPERIMENTAL

All the chemicals required are of AR grade and of SD fine chemicals Ltd. These were used without further purification. The substituted acetophenones are synthesized by Freidel Craft reaction using respective phenols. The substrate used was 4-Chloro acetophenone, 4- Methyl acetophenone and 4-methoxy acetophenone.

The substrates with known concentrations were taken in a reaction vessel. The Thalium perchlorate (1×10^{-3} M to 5×10^{-3} M) was added to it. The known amount of perchloric acid was added to it. The ionic strength was maintained by adding lithium perchlorate. The oxidation was followed by titrating known amount against stand sodium thiosulphate using ferroin as an indicator at 30^{0}C constant temperature at definite time intervals. Similar kinetic runs were determined by varying oxidant, temperature perchloric acid and lithium perchlorate and temperature.

Product Analysis

Reaction mixture containing overall concentration of Thalium perchlorate to be 0.05 M, acetophenones to be 0.01M and that of perchloric acid 1M in 50 ml was prepared and kept for four to five days. The mixture was equilibrated with ether, extracted and evaporated to dryness. The dry mass was identified. The following conversions are observed.

4- Chloro acetophenone to 4- Chloro benzoic acid (mp 243^{0}C) and formaldehyde

4- Methyl acetophenone to 4- methyl benzoic acid (mp 205^{0}C) and formaldehyde

4- Methoxy acetophenone to 4- Methoxy benzoic acid (mp 184^{0}C) and formaldehyde

Stochiometry

A mixture was prepared by taking 0.05M Tl (III), 0.01M acetophenones and 1M $HClO_4$. It was allowed to stand for overnight and unreacted Tl (III) was determined by titration. It shows that one mole of acetophenone consumes two moles of Tl (III)).

RESULTS AND DISCUSSION

Tl (III)) is a potential oxidizing agent The pseudo first order rate constant for variation in acetophenones, Tl (III)) perchlorate, variation and was determined and represented in table I. It was observed that the reaction if first odder with respect to hydrogen ion concentration. Further it was confirmed that the reaction is zero order with respect to concentration of Tl (III). By varying the concentration of acetophenones it was observed that the rate is first order with respect to the concentration of substrate. Tl (III) is considered to undergo two electron transfers and get converted into Tl (I). In first step Tl (II) is formed which immediately undergo redox reactions with substrate. The oxidation potential of Tl (III) / Tl (I) is less than the redox potential of Tl (II)/Tl (I) couple. This justify that Tl (II) i9s stronger oxidant than Tl (III) Therefore as soon as it is formed in the reaction it get immediately consumed by the substrate therefore there is no evidence of intermediate Tl (II) is observed .It is also established fact that one electron transfer step is more facile than the reaction step in which there are two electron transfer at a time. Tl(I) is the end product of the reaction which is in the presence of iodide ion gives TlI_3 complex Thus the titration of Tl(III) iodometrically is shaken vigorously for each addition of hypo solution and a bright yellow color was obtained as a end point. The concentration of hydrogen ion present also determined by the titrating an aliquot of the reaction mixture against slandered solution of sodium hydroxide in the presence of potassium bromide. The role of bromide ion is to complex Tl (III) so the thallium bromide does not undergo hydrolytic reactions at this pH. The effect of temperature on rate constant is studied at three different temperatures (table II). Assuming that rate constant varies with temperature as per Arrhenius equation energy of activation is calculated. Similarly other thermodynamic parameters like free energy, entropy change and enthalpy change is also calculated and represented in table III.

The entropy of oxidation is negative which indicate favorable conditions. The activation energy is very high which shows that reaction is slow.

It was observed that rate constant is independent of concentration of Tl (III); therefore we can say that oxidant is involved only in fast step of reaction. The rate controlling step is keto-enolisation. Hence, in view of zero order dependence on oxidant, the rate controlling step will be enolisation of acetophenone. The rate constant increases with increase in concentration of hydrogen ion, which indicates that enolisation is a catalyzed reaction. If enolisation step is considered to be the rate determining step, the catalysis of enolisation of acetophenone hydrogen ion should indicate first order dependence with respect to hydrogen ion.

Table 1: Rate constant for first order oxidation process

[Sub] [M]	Tl(III) [M]	[$HClO_4$] [M]	[$LiClO_4$] [M]	K(S^{-1}) (4-Cl ACP)	(4-Me-ACP)	(4-MeoACP)
0.01	0.001	1.0	-	9.91×10^{-3}	2.75×10^{-3}	2.89×10^{-2}
0.025	0.001	1.0	-	9.08×10^{-2}	8.9×10^{-2}	8.1×10^{-2}
0.02	0.002	0.01	-	1.04×10^{-2}	1.09×10^{-2}	9.2×10^{-3}
0.05	0.002	1.0	0.1	8.2×10^{-2}	1.1×10^{-1}	8.8×10^{-2}

Table 2: Effect of temperature on first order rate constant

[sub] = 0.01M, [$HClO_4$] = 1M, [T(III)] = 0.001M

Temp k	Rate constant (s^{-1})		
	(4- Cl ACP)	(4-Me ACP)	(4-Meo ACP)
303	1.05×10^{-2}	9.9×10^{-3}	1.10×10^{-2}
308	1.08×10^{-2}	1.1×10^{-2}	1.24×10^{-2}
313	1.65×10^{-2}	1.15×10^{-2}	1.65×10^{-2}

Table 3: Thermodynamic parameters

[Sub]	ΔH KJ/mol	ΔG KJ/mol	ΔS JK^{-1}	Ea .KJ/mol
4-Cl ACP	52.14	79.59	-90.55	54.66
4-Me ACP	72.02	80.80	-28.80	74.50
4Meo ACP	42.32	98.20	-43.90	63.20

This is exactly the case in our observation. This is further supported by the effect of ionic strength on the rate of reaction as there is no effect of ionic strength, the reaction might be between an ion and molecule. Considering all experimental observations following mechanism has been proposed.

$$\text{Keto} + H^+ \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \text{enol}$$

$$\text{enol} + \text{Tl(III)} \xrightarrow{K_3} \text{complex}$$

$$\text{complex} \longrightarrow \text{oxidation product} + \text{Tl(I)}$$

This lead to the rate law,

$$\frac{-dTl(III)}{dt} = K_2[enol][Tl(III)]$$

$$= \frac{K_1K_2[keto][H^+][Tl(III)]}{K_2 + K_3[Tl(III)]}$$

Assuming enol is the steady state concentration,

$$[enol] = \frac{K_1[keto][H^+]}{K_2 + K_3[Tl(III)]}$$

$$K_2 << K_3[Tl(III)]$$

$$\frac{-dTl(III)}{dt} = \frac{K_1K_2[keto][H^+]}{K_3}$$

Hence this mechanism can be accounted for the experimental observations i.e. first order dependent with respect to ketone and hydrogen ion concentration, independent of concentration of oxidant.

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