

Kinetics and mechanistic study of acetophenones by Mn(III) pyrophosphate in perchloric acid

SYED SULTAN*, SYED UMMUL KHAIR ASEMA,
SYED ASIF and MAZAHAR FAROOQUI

Post Graduate and Research Center, Maulana Azad College, Aurangabad (India).

(Received: June 19, 2010; Accepted: July 26, 2010)

ABSTRACT

Kinetic and mechanistic study of oxidation of 2-hydroxy 4-methyl acetophenone, 2-hydroxy 4-chloro acetophenone and 4-bromo acetophenone is carried out using Mn(III) pyrophosphate 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 respect to hydrogen ion and acetophenones. A probable mechanism has been suggested on the basis of experimental observations.

Key words: Acetophenones, Mn(III) pyrophosphate, perchloric acid.

INTRODUCTION

In the recent years, kinetic and mechanistic studies of oxidation of aldehydes and ketones by various oxidants such as permanganate¹, N-Bromosuccinimide² alkaline hexacyanoferrate³, Ce(IV) in presence of iridium (III) chloride⁴, TiO₂⁵, I₂ + Zeolite⁶, bromamine-b⁷, hematite⁸, etc. have been reported. Literature survey reveals that very little work is reported on the oxidation of substituted acetophenones by Mn(III) pyrophosphate in perchloric acid. Therefore, we investigated the oxidation kinetics of 2-hydroxy 4-methyl acetophenone, 2-hydroxy 4-chloro acetophenone and 4-bromo acetophenone using Mn(III) pyrophosphate.

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 Friedel Craft reaction using respective phenols.

The substrates with known concentrations were taken in a reaction vessel. The Mn(III) pyrophosphate (1×10^{-3} mol/dm³ to 5×10^{-3} mol/dm³) 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 standard sodium thiosulphate using starch as an indicator at 30°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 Mn(III) pyrophosphate to be 0.05 mol/dm³, Substituted acetophenone to be 0.01mol/

dm³ and that of perchloric acid 1 mol/dm³ 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.

Stoichiometry

A mixture was prepared by taking 0.05 mol/dm³ Mn(III), 0.01 mol/dm³ substituted acetophenone and 1 mol/dm³ HClO₄. It was allowed to stand for overnight and unreacted Mn(III) was determined by titration. It shows that one mole of acetophenone consumes four moles of Mn(III).

RESULTS AND DISCUSSION

Mn(III) is a potential oxidizing agent. We can use sulphuric acid or perchloric acid as media to carry oxidation.

The pseudo first order rate constant for variation in acetophenones, Mn(III)pyrophosphate, variation and was determined and represented in table I.. The effect of temperature on rate constant is studied at three different temperatures (table II). Assuming that rate constant varies with temperature

Table 1: Rate Constant for First Order Oxidation Process

[Sub] Mole/dm ³	Mn(III) Mole/dm ³	[HClO ₄] Mole/dm ³	[LiClO ₄] Mole/dm ³	K(S ⁻¹)		
				2-OH4-Me	2-OH 4-Cl	4-Br
0.01	0.001	1.0	-	1.40x10 ⁻²	1.02x 10 ⁻²	1.36x10 ⁻²
0.025	0.01	1.0	-	4.57x10 ⁻²	7.58x 10 ⁻²	8.29x10 ⁻²
0.02	0.002	0.01	-	1.54x10 ⁻²	1.06x10 ⁻²	1.25x10 ⁻²
0.05	0.002	1.0	0.1	8.89x10 ⁻²	5.6x10 ⁻²	9.7x10 ⁻²

Table 2: Effect of temperature on first order rate constant

$$[\text{sub}] = 0.01 \text{ mol/dm}^3, [\text{HClO}_4] = 1 \text{ mol/dm}^3, \\ [\text{CeIV}] = 0.001 \text{ mol/dm}^3$$

Temp k	Rate constnat (s ⁻¹)		
	2-OH4-Me	2-OH 4-Cl	4-Br
303	2.9 x 10 ⁻²	6.21 x 10 ⁻³	4.37 x 10 ⁻³
308	5.1 x 10 ⁻²	1.10 x 10 ⁻²	8.98 x 10 ⁻³
313	9.8 x 10 ⁻²	1.61 x 10 ⁻²	1.00 x 10 ⁻³

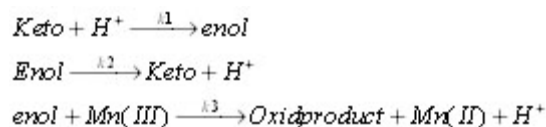
Table 3: Thermodynamic Parameters

[Sub]	DH KJ/mol	DG KJ/mol	DS JK ⁻¹	Ea .KJ/mol
2-OH4-Me	80.3	69.2	-15.3	37.5
2-OH 4-Cl	79.2	71.3	-43.3	47.3
4-Br	81.3	73.2	-23.7	68.2

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 Mn(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. 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.

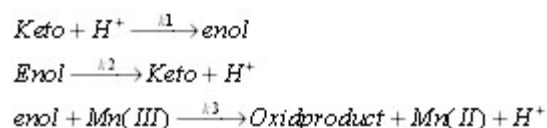


This lead to the rate law,

$$\frac{-d[\text{Mn(III)}]}{dt} = 2k[\text{keto}][\text{H}^+]$$

Where 2K, has been used to account for the stoichiometry of the reaction in which two moles of Mn(III) are required for one mole of acetophenone. The energy of activation ΔE is found to be high, which confirms that the transition state is more compact and hence compare to the oxidation of acetophenones in sulphuric acid, these perchloric acid oxidations are slower.

An alternate mechanism can also be suggested such as,



The rate of reaction can be govern by,

$$\frac{-d[\text{Mn(III)}]}{dt} = K[\text{enol}][\text{Mn(III)}]$$

$$= \frac{k_1 k_3 [\text{keto}][\text{H}^+][\text{Mn(III)}]}{k_2 + k_3[\text{Mn(III)}]}$$

$$k_2 \ll k_3[\text{Mn(III)}]$$

$$\frac{-d[\text{Mn(III)}]}{dt} = k_1[\text{keto}][\text{H}^+]$$

Hence both mechanisms can be accounted for the experimental observations are first order with respect to ketone and hydrogen ion concentration, independent of concentration of oxidant.

REFERENCES

1. Bhagwansing Dobhal, Mazhar Farooqui and Milind Ubale – *Int. J. Chem.Tech. Res.* **2**(1): 443 -446 (2010).
2. Bharat Singh, Laiji Pandey, J. Sharma and S.M. Pandey; *Tetrahedron*; **38**(1): 169-172 (1982).
3. Praveen K. Tandon, Santosh Kumar, Manish Srivastava, Shaista Z. Khanam and Santosh B. Singh; *J. Mol. Cat. A: Chem* **261**(2): 282-287 (2007).
4. Praveen K. Tandon, Sumita Sehgal, Alok K. Singh, Santosh Kumar and Mamta; *J. Mol.*

- Cat A: Chem*; **258**(1-2): 320-326 (2006).
5. C. Raillard, V. Hequet, P. Le. Cloirec and J. Legrand; *J. Photochem Photobiol A: Chem*; **163**(3): 425-431 (2004).
6. Michael J. Zacuto, Dongwai Cai; *Tetrahedron Letters*; **46**(48): 8289-8292 (2005).
7. D.S. Mahadevappa, K. Mohan, S. Ananda *Tetrahedron*, **42**(7): 4857-4866 (1986).