

Kinetics of oxidation of β -isophorone to keto-isophorone catalyzed by manganese Schiff base complex using molecular oxygen

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Abstract

Kinetic investigations were carried out on the oxidation of β -isophorone (β -IP) to keto-isophorone (KIP) catalyzed by [LMn(III)(Cl)], (where, L = bis-salicylaldehydeethylenedi-imine, salen) at temperature in the range 10–27°C and partial pressure 0.2–3 atm of molecular oxygen. β -IP gave mainly KIP as the oxidation product under the reaction conditions studied. Initial rate approach was adopted to evaluate kinetic parameters of the reaction. From the kinetic investigations, it was found that the rate of oxidation of β -IP showed a first-order dependence with respect to catalyst and substrate concentrations, and half-order dependence on the partial pressure of oxygen. The effect of temperature on the rates of oxidation was also investigated and from the Arrhenius plot of $-\ln$ rate vs. $1/T$, the activation energy estimated is 16.12 kcal mol⁻¹. Thermodynamic activation parameters such as enthalpy, entropy and free energy of the reaction were calculated from the known thermodynamic equations. Based on the kinetic investigations, a plausible mechanism for manganese salen complex catalyzed oxidation of β -IP to KIP has been proposed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: β -Isophorone; Keto-isophorone; Manganese; Salen; Oxidation

1. Introduction

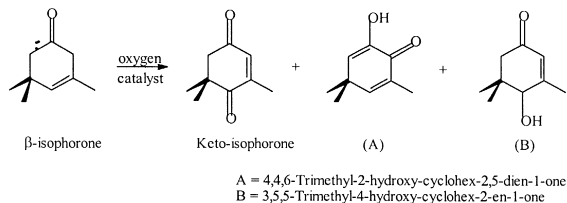
Oxidation of hydrocarbons using molecular oxygen to oxygenated products is an important industrial reaction; since hydrocarbon molecule may possess several potential sites for attack by oxygen, a number of initial products will be formed. There are numerous commercial applications of catalytic liquid phase oxidation reac-

tions of aliphatic, aromatic and cyclic hydrocarbons carried out over the years to give corresponding oxygenated derivatives [1–7]. Transition metal complexes have been found to be effective catalyst systems for the oxidation of hydrocarbons to products of commercial importance [8–11]. However, selective oxidation of cyclic olefins under milder conditions, such as the oxidation of β -isophorone (β -IP) to keto-isophorone (KIP), is an important reaction for application in industries. Oxidation of β -IP gave mainly KIP as the major product along with

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small amounts of side products **A** and **B** and is shown in the following equation.



KIP is used as a building block for the synthesis in terpene chemistry and for producing compounds of vitamin A, E series and carotinoids. Many conventional oxidation routes have been described in literature to prepare KIP via oxidation of α -IP or β -IP [12–18]. However, systematic study involving kinetics of metal complexes catalyzed oxidation of β -IP to KIP under homogeneous conditions has not been reported in the literature. We recently carried out the oxidation of β -IP to KIP catalyzed by manganese salen complex encapsulated in Zeolite-Y at ambient conditions using molecular oxygen as an oxidant, and have filed a patent [18]. In continuation of our work on this subject, we are reporting in this paper the study on the kinetics of manganese salen complex catalyzed oxidation of β -IP to KIP under homogeneous reaction conditions.

2. Experimental

2.1. Materials

[Mn(III)(salen)Cl] complex was prepared by following the procedure described elsewhere [19]. Manganese acetate, ethylenediamine and salicylaldehyde of A.R. grade were used as it is in the preparation of salen ligand. Methyl ethyl ketone (MEK), acetylacetone, triethylamine and water were distilled and used in the experiments. β -IP and KIP of high purity (> 99%) (supplied by M/s Herdillia Mumba) and oxygen gas (high purity) supplied in cylinder were used

in this study. Liquid samples were analyzed by gas chromatography (HP-5890) using FID detector in a capillary column, 0.5 mm, I.D, 30 m long HP-5 and KIP was confirmed by GC-MS and by comparing retention time with its standard. Pressure reactor (M/s Parr Inst. U.S.A) was used for pressure experiments.

2.2. Measurements

Kinetic experiments were conducted in a jacketed glass reactor having provisions for maintaining constant temperature, withdrawal of the samples and dissolution of oxygen gas (filled in balloon). In a sample experiment, a reaction mixture containing known amounts of substrate, catalyst, MEK solvent (excess) consisting of small amounts of acetylacetone, water and triethylamine (added as additives) was placed into the glass reactor. The reactor was flushed twice with oxygen and the temperature of the jacketed glass reactor was maintained by circulating water from the cryostat. Reaction was initiated by stirring the reaction mixture with a magnetic needle and at this stage, a sample was withdrawn. With the progress of the oxidation reaction, samples were withdrawn at regular intervals of time and analyzed for products by gas chromatography. From GC analysis, conversions of β -IP were calculated and initial rates were estimated by graphical method. β -IP (conversion range up to 30%) gave mainly KIP (> 90%) as the major product and the remaining side products **A** and **B** (\approx 10%).

3. Results and discussion

β -IP gave mainly KIP as the oxidation product at lower conversions (< 30%). However, at higher conversions, we found that it forms side products **A** and **B** (see equation), which decreased the selectivity for KIP (\approx 60%) at higher conversions of β -IP (> 90%) and is seen in Fig. 1.

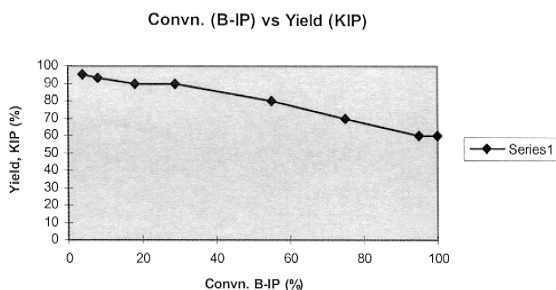


Fig. 1. Conversion of β -IP vs. yield of KIP plot. Conditions: β -IP = 10.08 g, $[\text{Mn(III)(salen)Cl}] = 0.020$ g, methyl ethyl ketone (MEK) = 40.0 g, acetylacetonone = 1.08 g, triethylamine = 0.6 g, water = 4.0 g, $\text{O}_2 = 1$ atm and temperature = 20°C .

The solvent used in the oxidation of β -IP consists of MEK (excess) and small amounts of acetylacetonone, triethylamine and water, which were additives in the reaction. However, the role of these additives in the oxidation reaction has not been established in this study. The total weight of the reaction mixture for kinetic experiments was adjusted to around 10.0 g.

3.1. Kinetics

Kinetic investigations on the oxidation of β -IP to KIP were conducted by varying the concentrations of catalyst, substrate and oxygen partial pressure and temperature. The effect of partial pressure of oxygen was also studied in a 300-ml pressure reactor. Conversions of β -IP estimated at different intervals of time were plotted against the variations made in the concentrations of reactants, and initial rates were calculated by graphical method.

3.1.1. Effect of catalyst concentration

The catalyst concentration was varied from 0.003 to 0.014 mM at 1 atm of molecular oxygen, substrate 0.14 mM and at 20°C . The initial rates of oxidation (β -IP conversions, M min^{-1}) observed at different catalyst concentrations were plotted as shown in Fig. 2, indicating that the rate of β -IP oxidation has a first-order

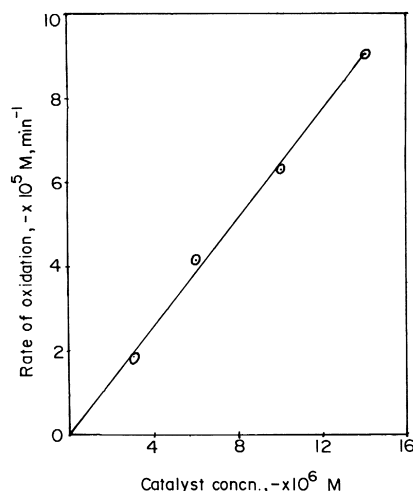


Fig. 2. Effect of catalyst concentration.

dependence with respect to catalyst concentration.

3.1.2. Effect of substrate concentration

β -IP concentration was varied between 8 and 44 mM, keeping other concentrations constant as catalyst, 0.001 mM, oxygen partial pressure, 1 atm and at 20°C . Fig. 3 shows the plot of rate of oxidation vs. β -IP concentration, which indicated that the rate of oxidation has a first-order dependence with respect to substrate concentration.

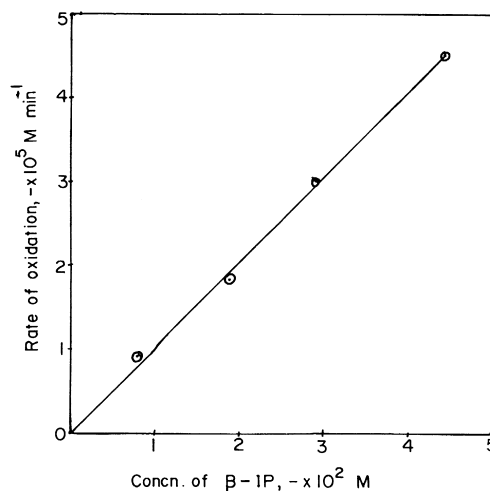


Fig. 3. Effect of β -IP concentration.

3.1.3. Effect of dissolved oxygen concentration (partial pressure)

Partial pressure of molecular oxygen was varied from 0.2 to 3 atm, keeping the catalyst concentration constant as 0.014 mM, β -IP concentration, 14 mM and at 27° C. Dissolved oxygen concentrations in the solvent medium were obtained and computed for the interpretation of kinetic data [20]. The plot of rate of oxidation vs. $1/[O_2]^{1/2}$ shown in Fig. 4, indicated that the rate of β -IP oxidation has half-order dependence with respect to dissolved oxygen concentration.

3.1.4. Effect of temperature

The effect of temperature on the rate of oxidation of β -IP was studied in the temperature range 10–27° C, keeping catalyst concentration at 0.014 mM, β -IP concentration 14 mM, and 1 atm of oxygen. From the graph of $-\ln \text{rate}$ vs. $1/T$ shown in Fig. 5, the activation energy, E_a , was evaluated as 16.12 kcal mol⁻¹, indicating endothermic nature of the oxidation reaction.

3.1.5. Mechanism and rate law

Based on kinetic data on the [Mn(III)-(salen)Cl]-catalyzed oxidation of β -IP to KIP, a probable mechanism is as shown in Scheme 1,

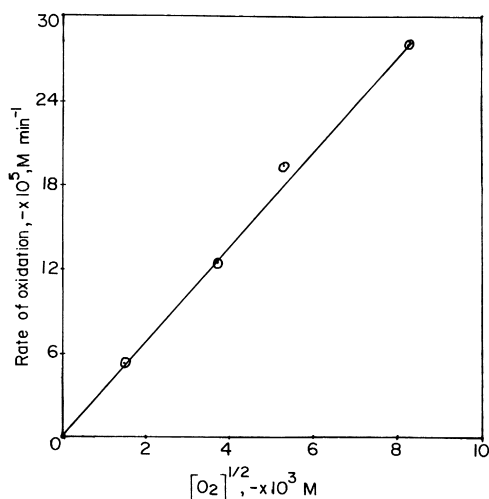


Fig. 4. Effect of dissolved O_2 concentration.

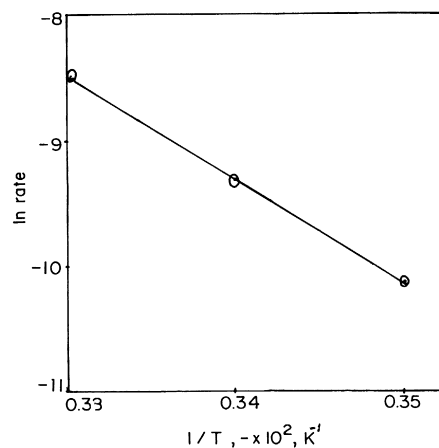
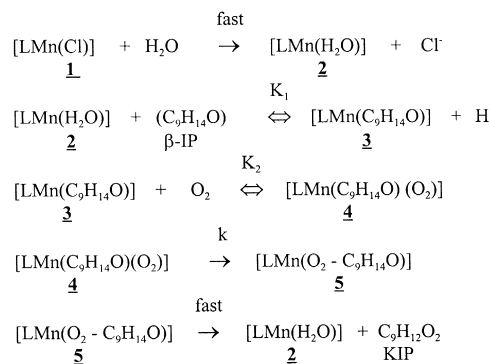


Fig. 5. Effect of temperature.

where, L = -salen (bis-salicylaldehydeethylene-diimine), β -IP = β -isophorone and KIP = keto-isophorone.

In the proposed mechanism, complex **1** in the presence of water (present in the reaction medium) forms an aqua species **2** in a fast step. Species **2**, reacts with a mole of β -IP in a pre-equilibrium step to give mixed ligand intermediate species **3**. Transient species **3** is formed by metal–olefin linkage, a well-established fact in metal complexes catalyzed epoxidation of olefinic substrates. Species **3** takes up a mole of oxygen in another pre-equilibrium step to form a peroxo intermediate **4** which, under a rate-determining step undergoes a cyclic peroxometallation of the olefin coordinated to Mn^V, to give species **5**. Species **5**, in a fast step, undergoes a



Scheme 1.

hetero-elimination of hydrogens followed by intermolecular rearrangement to give KIP and water, while regenerating species **1** in a catalytic cycle. Similar observation with Rh(I) complex catalyzed oxidation of oct-1-ene to octan-2-one has been suggested by Bortolini et al [21] and others [22,23]. However, the mechanism proposed for oxidation of β -IP, is speculative and the role of additives in MEK solvent have not been clearly established. It is believed that the activation of C–H bond of an olefin is favored in the presence of a base (triethylamine), while acetylacetonone stabilizes the intermediate manganese species.

From the proposed mechanism for oxidation of β -IP, the rate equation for the formation of KIP can be written as:

$$\text{rate} = kK_1K_2[\text{Cat}][\beta\text{-IP}][\text{O}_2]^{1/2} \quad (1)$$

where $[\text{Cat}]$ = concentration of complex **1**, $[\beta\text{-IP}]$ = concentration of β -isophorone and $[\text{O}_2]$ = concentration of oxygen, K_1 and K_2 are the pre-equilibrium constants and k = rate constant for the reaction.

By applying steady state conditions, and involving total catalyst concentration $[\text{Cat}]_T$ present in the form of different species (Scheme 1), the final rate law can be written as:

$$\text{rate} = \frac{kK_1K_2[\text{Cat}]_T[\beta\text{-IP}][\text{O}_2]^{1/2}}{1 + K_1[\text{O}_2]^{1/2} + K_1K_2[\beta\text{-IP}][\text{O}_2]^{1/2}} \quad (2)$$

Eq. (2), could be written in a slope and intercept form in two ways as:

$$\frac{[\text{Cat}]_T}{\text{rate}} = \frac{1}{[\beta\text{-IP}]} \left(\frac{1}{kK_1K_2[\text{O}_2]^{1/2}} + \frac{1}{kK_2} \right) + \frac{1}{k} \quad (3)$$

$$\frac{[\text{Cat}]_T}{\text{rate}} = \frac{1}{[\text{O}_2]^{1/2}} \left(\frac{1}{kK_1K_2[\beta\text{-IP}]} \right) + \frac{1}{k} \left(1 + \frac{1}{K_2[\beta\text{-IP}]} \right) \quad (4)$$

From Eq. (3), a plot of $[\text{Cat}]_T/\text{rate}$ vs. $1/[\beta\text{-IP}]$ gives a straight line with an intercept from which the value of k was calculated. Similarly, from Eq. 4 a plot of $[\text{Cat}]_T/\text{rate}$ vs. $1/[\text{O}_2]^{1/2}$ gives a straight line and substituting the value of k , in the slope and intercept values, K_1 and K_2 were obtained. Thus, the values of k , K_1 and K_2 , for the oxidation of β -IP to KIP at 20°C were found to be: $k = 16.7 \text{ min}^{-1}$, $K_1 = 72.9 \text{ M}^{-1}$ and $K_2 = 140 \text{ M}^{-1}$.

From, the Arrhenius plot (Fig. 4), the activation energy, enthalpy, entropy and free energy for the oxidation of β -IP to KIP were calculated, and are: (1) activation energy, $E_a = 16.12 \text{ kcal mol}^{-1}$, (2) enthalpy, $\Delta H^\ddagger = 15.55 \text{ kcal mol}^{-1}$, (3) entropy, $\Delta S^\ddagger = +58.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$ and (4) $\Delta G^\ddagger = -1.5 \text{ kcal mol}^{-1}$. Values of thermodynamic activation parameter indicated that the oxidation of β -IP to KIP is an endothermic reaction involving associative transition state of the metal ion, substrate and molecular oxygen.

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References

- [1] L.I. Simandi (Ed.), Studies in Surface Science and Catalysis Vol. 66 Elsevier, Amsterdam, 1991.
- [2] Activation of Saturated Hydrocarbons by Transition metal Complexes, Reidel, Dordrecht, the Netherlands, 1984.
- [3] J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic, New York, 1978.
- [4] J.T. Groves, R.C. Haushalter, M. Nakamura, T.E. Nemo, B.J. Evans, J. Am. Chem. Soc. 103 (1981) 2884.
- [5] J.T. Groves, Y. Watanabe, J. Am. Chem. Soc. 108 (1986) 507.
- [6] A. Zombeck, D.E. Hamilton, R.S. Drago, J. Am. Chem. Soc. 104 (1982) 6782.
- [7] A. Nishinaga, T. Yamada, H. Fujisawa, K. Ishizaki, H. Ihara, T. Matsuura, J. Mol. Catal. 48 (1988) 249.
- [8] M. Constantini, A. Dromard, M. Jouffret, B. Brossard, J. Varagnat, J. Mol. Catal. 7 (1980) 89.

- [9] M.M. Taqui Khan, D. Chatterji, S. Kumar, A. Prakash Rao, N.H. Khan, *J. Mol. Catal.* 75 (1992) L49.
- [10] M.M. Taqui Khan, D. Chatterji, N.H. Khan, R.I. Kureshy, *J. Mol. Catal.* 77 (1992) 153.
- [11] A. Nishinaga, S. Yamazaki, T. Matsuura, *Tetrahedron Lett.* 27 (1986) 2649.
- [12] Brit. Pat. 1,448, 976 (Sept. 8, 1976) to Hoffmann-LaRoche.
- [13] J.J. Becker, U.P. Hochstrasser, W. Skorianetz, U.S. Pat. 3,944,620 (March 16, 1976) to Firmenich.
- [14] H. Bellut, U.S. Pat. 4,970,347 (Nov. 13, 1990) to Huls.
- [15] J.J. Becker et al., U.S. Pat. 4,026,948 (May 31, 1977) to Firmenich.
- [16] W. Brenner, U.S. Pat 4,046, 813 (Sept. 6, 1977) to Hoffmann-LaRoche.
- [17] G. Ulrich, H. Klaus, H. Frank, K. Steffen, European Patent No. EP 0,808,816 A1.
- [18] S.B. Halligudi, M.P. Degaonkar, S.S. Deshpande, Indian Patent, CSIR, New Delhi, 1999.
- [19] L.T. Boucher, *J. Inorg. Nucl. Chem.* 36 (1974) 531.
- [20] A. Seidel, W.F. Linke, *Solubilities of Inorganic Compounds*, Van Nostrand, New York, 1952.
- [21] O. Bortolini, F.D. Furia, G. Modena, R. Seraglia, *J. Mol. Catal.* 22 (1984) 313.
- [22] H. Mimoun, M.M. Perez Machirant, I. Seree de Roch, *J. Am. Chem. Soc.* 100 (1978) 5437.
- [23] H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, R. Weiss, *J. Am. Chem. Soc.* 102 (1980) 1047.