

OXIDATION OF LACTIC ACID BY CHROMIC ACID IN PRESENCE OF MODERATELY STRONG ACID; A KINETIC AND MECHANISTIC STUDY

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ABSTRACT

Kinetics and mechanism of oxidation of Lactic Acid by Chromic Acid in presence of moderately strong acid⁶ (Monochloroacetic Acid) has been studied with spectrophotometry in the temperature range of 300K-320K. The rate of the reaction increases with the increase in the added concentration of Monochloroacetic Acid. Kinetics of oxidation of Glycolic Acid by Chromic Acid shows first order reaction. Kinetics and spectrophotometric results indicate the formation of intermediate complex. The complex finally decomposes to give reaction product Pyruvic Acid (α - keto acid). A mechanism for the reaction is proposed based on the experimental observations. Kinetic parameters such as catalytic constant, temperature coefficient and pH values are calculated.

I. INTRODUCTION

Chemical kinetics, also known as reaction kinetics, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. In course of study of inversion of Sucrose in presence of acid Wilhelm²⁰ showed the rate of a reaction at any instant was proportional to the amount of Sucrose remaining unchanged at that instant. Pioneer experiments in this field were carried out by Wilhelm²⁰ and therefore he is regarded as the founder father of chemical kinetics. Since the first kinetic studies performed by Westheimer and Novick¹⁰ on the Chromic Acid oxidation of Isopropyl Alcohol, investigations have been carried out on the oxidation of carboxylic acids etc. Chromium exists usually in both trivalent and hexavalent forms in aqueous systems. However, these two oxidation states are characterized by different physical and chemical behavior and toxicity Cr (VI) in many different compounds is a well established carcinogen and mutagen. There is, therefore, appreciable interest in determining the mode of action of Chromium species derived from initial Chromium (VI) compounds taken into the body, epidemiology and animal studies, as well as in vitro mutagenicity assays, indicate that Chromium (VI) compounds pose serious danger to biological systems, where Chromium (III) compounds are relatively nontoxic. Chromium (VI) is one of the most versatile available oxidizing agents for the oxidation of organic

compounds. It can be reduced to lower oxidation states by various biological and chemical reductants. The chemistry of the intermediate oxidation states of Chromium, Cr (V) and Cr (IV), which observed during the oxidation of organic substrates by Chromium (VI) was attracted many researchers because of their implication in the mechanism of Chromium-induced cancers. Oxidation of organic compounds by Chromic Acid has been extensively studied. Westheimer⁹ considered that the oxidation of alcohols by Chromic Acid involves reversible formation of a chromate ester which slowly decomposes by a process catalyzed by base. Bakore et al. have studied the oxidation of a number of α -hydroxy acids¹³ and explained the mechanism on the basis of the Kwart-Francis¹¹ scheme which is a minor variation of the well known Westheimer's⁹ mechanism. Seikichi et al, have studied an aerobic oxidation mechanism of α -hydroxy acid¹⁷.

Lactic Acid is an important biochemical and industrial molecule. It is a useful feedstock used in the generation of aldehydes and ketones via oxidative methods. In its solid state, it is white and water-soluble. In its liquid state, it is clear. It is produced both naturally and synthetically. With a hydroxyl group adjacent to the carboxyl group.

Lactic Acid is classified as a α -hydroxy acid. In the form of its conjugate base called lactate, it plays a role in several biochemical processes. In solutions, it can ionize a proton from the carboxyl group, producing the lactate ion. Compared to Acetic Acid, its pK_a is 1 unit less, meaning Lactic Acid deprotonates ten times more easily than Acetic Acid. This higher acidity is the consequence of the intra molecular hydrogen bonding between the α -hydroxyl and the carboxylate group.

Lactic Acid is chiral, consisting of two optical isomers. One is known as L-(+)-Lactic Acid or (S)-Lactic Acid and the other, its mirror image, is D-(-)-Lactic Acid or (R)-Lactic Acid. A mixture of the two in equal amounts is called DL-Lactic Acid, or racemic Lactic Acid. Lactic Acid is hygroscopic. DL-Lactic Acid is miscible with water and with ethanol above its melting point which is around 17 or 18 °C. D-Lactic Acid and L-Lactic Acid have a higher melting point. In industry, Lactic Acid fermentation is performed by Lactic Acid bacteria, which convert simple carbohydrates such as Glucose, Sucrose, or Galactose to Lactic Acid. These bacteria can also grow in the mouth, the acid they produce is responsible for the tooth decay known as caries. In medicine, Lactate is one of the main components of lactated Ringer's solution and Hartmann's solution. These intravenous fluids consist of Na and K cations along with lactate and chloride anions in solution with distilled water, generally in concentrations isotonic with human blood. Lactic Acid is most commonly used for fluid resuscitation after blood loss due to trauma, surgery, or burns.

Kinetics study of oxidation of this acid helps to understand more about the compounds

II. MATERIALS AND METHOD

All the chemicals were of AnalaR grade Lactic Acid (Merck), Chromium Trioxide (Qualigens), Monochloroacetic Acid (Merck) and others all chemicals were used throughout the work of highest purity available commercially. Solutions were prepared in double distilled water. Solutions of oxidant and reaction mixtures containing known quantities of substrates, Lactic Acid, Monochloroacetic Acid, Chromic Acid and other necessary solutions were separately thermo stated. The reaction was initiated by mixing the requisite

amounts of the oxidant with the reaction mixture. Progress of the reaction was monitored by following the rate disappearance of Cr (VI) by spectrophotometer.

II. PRODUCT ANALYSIS

In order to study the overall oxidation product(s) of Lactic Acid by Chromic Acid reaction, all reactants were mixed in equimolar amounts. The reaction mixture was kept for 24 hours at 300K temperature. It was observed that initial light yellow colour changed to light blue colour in course of reaction. This clearly indicates the reduction of hexavalent Chromium to trivalent Chromium through different stages. Under the kinetics conditions, the results show that Glycolic Acid react with Chromic Acid to form an intermediate compound. Intermediate compound finally decompose to give reaction product Pyruvic Acid (α - keto acid) .

In the oxidation of Lactic Acid by Chromic Acid in presence of moderately strong acid i.e. Monochloroacetic Acid some of the kinetic runs performed by keeping the concentration of Chromic Acid and Lactic Acid constant at 4.25×10^{-3} M and 2.25×10^{-2} M respectively while the concentration of Monochloroacetic Acid had varied from 1.25×10^{-2} M to 6.25×10^{-2} M respectively. The average value of catalytic constant is determined and found to be order of the 1.8161×10^{-1} . Values of rate constant and catalytic constants of various reaction mixtures are given below;

Table No-01

Values of rate constant, pH, Hydrogen ion and catalytic constant

S. No	Concentration of Monochloroacetic Acid (M)	Rate Constant $K \times 10^{-3} \text{ min}^{-1}$	pH values at 300K	Hydrogen ion concentration $\times 10^{-2}$ at 300K	Catalytic Constant $\times 10^{-1}$
1.	0.00×10^{-2}	1.4535	2.03	0.933	-
2.	1.25×10^{-2}	4.6125	1.67	2.138	1.4775
3.	2.50×10^{-2}	5.3002	1.66	2.188	1.7581
4.	3.75×10^{-2}	5.7313	1.62	2.399	1.7832
5.	5.00×10^{-2}	6.5768	1.59	2.570	1.9935
6.	6.25×10^{-2}	7.1492	1.56	2.754	2.0682

Table No.02

Values of rate constants at different temperatures

S. No	Concentration of Monochloroacetic Acid (M)	Rate constants $K \times 10^{-3}$ at 300K	Rate constants $K \times 10^{-3}$ at 310K	Rate constants $K \times 10^{-3}$ at 320K	Temperature Coefficient	
					k_{310}/k_{300}	k_{320}/k_{310}
1.	0.00×10^{-2}	1.4535	2.8489	5.6407	1.96	1.98
2.	1.25×10^{-2}	4.6125	8.9944	17.7190	1.95	1.97
3.	2.50×10^{-2}	5.3002	10.4414	20.3607	1.97	1.95
4.	3.75×10^{-2}	5.7313	11.2333	22.2420	1.96	1.98
5.	5.00×10^{-2}	6.5768	12.8247	25.3930	1.95	1.98
6.	6.25×10^{-2}	7.1492	13.9410	27.4637	1.95	1.97



Fig. No.01

VARIATION OF RATE CONSTANT WITH THE CONCENTRATION OF MONOCHLOROACETIC ACID of TABLE -01

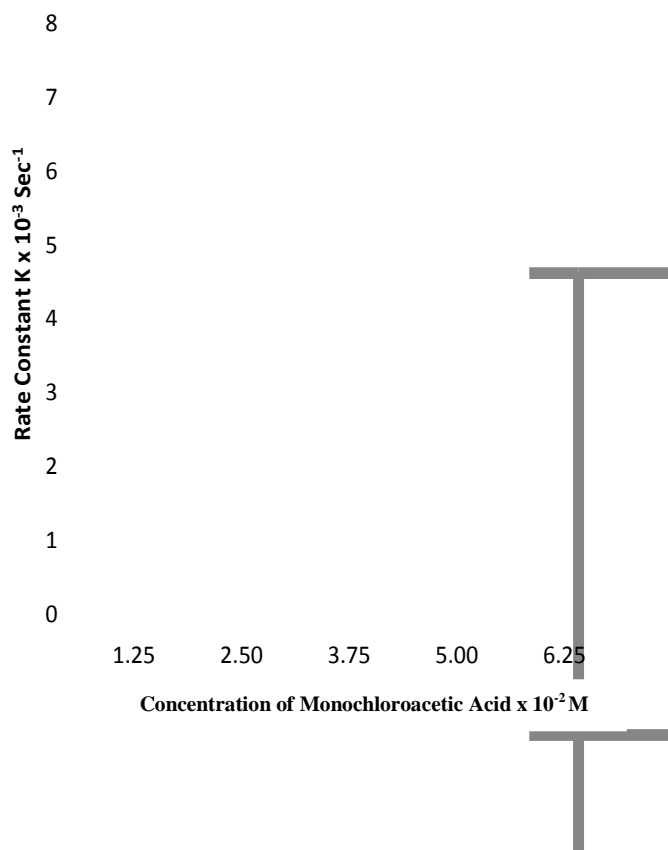
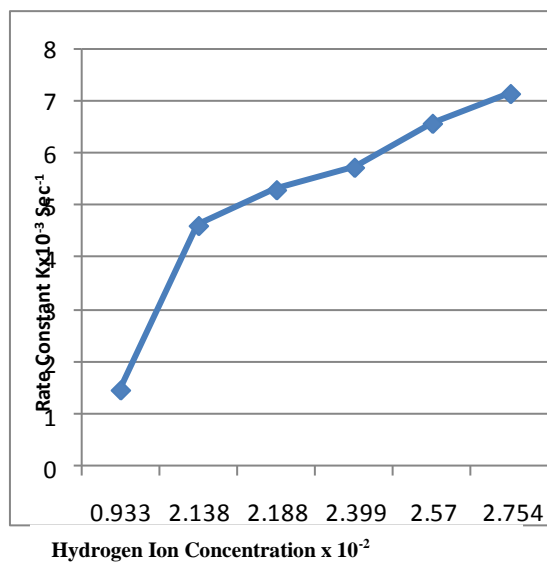


Fig. No.02

Variation of Rate Constant With The Hydrogen Ion Concentration Cf Table -01





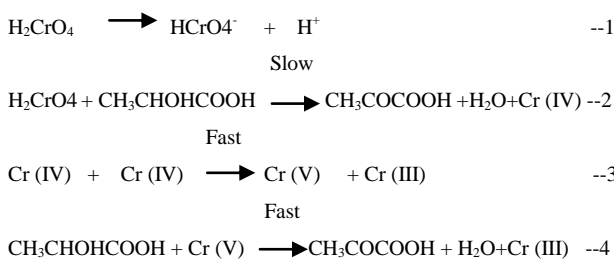
III. RESULTS AND DISCUSSION

The kinetics of oxidation of Lactic Acid by Chromic Acid in presence of moderately strong acid (Monochloroacetic Acid) has been studied. In the presence and absence of Monochloroacetic Acid under the experimental conditions the rate of disappearance of Chromium Cr (VI) shows a first order dependence. The products of the oxidation of Lactic Acid by Chromic Acid in presence of Monochloroacetic Acid is Pyruvic Acid, which is confirmed by usual tests⁷. Rate of reaction is increases in the presence of Monochloroacetic Acid (a moderately strong acid) shows positive catalysis which has been explained in several ways, the most important of these are,

- (a) Fast formation of the activated complex and less stability of an intermediate catalyst compounds.
- (b) Breaking of chain reaction.
- (c) Regenerancy of both the positive catalyst and the reactant from the intermediate compound.
- (d) Catalytic side reaction of decomposition.

In view of the authors observations it can be conclude that acceleration of the rate of oxidation of Lactic Acid by Chromic Acid in presence of Monochloroacetic Acid is case of positive catalysis. Hexavalent Chromium exists primarily as Chromic Acid (H_2CrO_4), Hydrogen Chromate Ion ($HCrO_4^-$) and Chromate Ion (CrO_4^{2-}), depending on the values of pH. In acidic medium dichromate exists predominantly as monomer ($HCrO_4^-$) and Chromic Acid (H_2CrO_4) and (H_2CrO_4), plays a role of active species. Formation of Pyruvic Acid suggested that the cleavage of C-H of Lactic Acid. Mechanism proposed for the reaction is in conformity with the product, mechanistic and kinetic studies.

IV. PROPOSED MECHANISM OF REACTION



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