

CO OXIDATION OF OXALIC ACID AND GLUTARIC ACID BY CHROMIC ACID IN PRESENCE OF SULPHURIC ACID

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ABSTRACT

The kinetics of co oxidation of Oxalic Acid and Glutaric Acid by Chromic Acid in presence of Sulphuric Acid has been studied. The Chromic Acid oxidation of a mixture of Oxalic Acid and Glutaric Acid proceeds much faster than that of either of the two substrates alone. The products are Mesooxalic Acid (Glutaric Acid) and Carbon dioxide (Oxalic Acid). Reaction is catalysis by H^+ has been noticed. The results show that the logarithm of the rate constants of oxidation increases with the increase in the concentration of Sulphuric Acid. Kinetics of oxidation of mixture of Oxalic Acid and Glutaric Acid by Chromic Acid shows first order reaction, order of the reaction is also one in presence of Sulphuric Acid. Kinetic data and spectrophotometric results show the formation of intermediate (VI) – Glutaric Acid and (VI) – Oxalic Acid. The complex finally decomposes to give reaction product. A mechanism consistent with the observed kinetic data has been proposed. The kinetic parameters such as catalytic constant, dielectric constant and temperature coefficient are calculated.

I INTRODUCTION

The term Chromic Acid is usually used a mixture made by adding concentrated Sulphuric Acid to a dichromate, which may contain a variety of compounds, including solid Chromium trioxide. Chromic Acid may also refer to the molecular species, H_2CrO_4 of which the trioxide is the anhydride. Chromic Acid features Chromium in an oxidation state of + 6 or (VI). Molecular Chromic Acid principally made by adding Chromium trioxide to water. Chromic Acid has long been used as an oxidizing agent in preparative organic chemistry; it is only in comparatively past years that kinetic or mechanistic investigations have been conducted. Since the first kinetic studies performed by Westheimer and Novick⁹ on the Chromic Acid oxidation of isopropyl alcohol, investigations have been carried out on the mechanism of oxidation of hydrocarbons, aldehydes, ketones, carboxylic acids, ethers, olefins and glycols as well as alcohols. Oxidation of a variety of organic compounds by Chromic Acid has been extensively studied. Bakore¹ have studied the oxidation of a number of α hydroxyl acids (Lactic Acid, Malic Acid and Mandelic Acid) and explained the mechanism on the basis of the Kwart-Francis³

scheme, which is a minor variation of the well known Westheimer⁵ mechanism. However, no kinetic data for the co oxidation of Oxalic Acid and Glutaric Acid by Chromic Acid in presence of Sulphuric Acid are known.

Materials and methods; All the chemicals were of AR grade, Oxalic Acid (G. R. Merck) Glutaric Acid (Pure, E. Merck) Chromium trioxide (Qualigens) and Sulphuric Acid (B.D.H.) and all other chemicals were used without further purification. Solutions were prepared in doubly distilled water. Solutions of the oxidant and reaction mixtures containing known quantities of the substrates (Oxalic Acid – 25 ml, Glutaric Acid – 25 ml) Chromic Acid-25ml, Sulphuric Acid – 25ml and other necessary chemicals were separately thermo stated ($\pm 0.1^{\circ}\text{C}$). The reaction was initiated by mixing the requisite amounts of the oxidant with the reaction mixture, monitored by following the rate of disappearance of Cr (VI) by spectrophotometrically. In order to investigate the effect of Sulphuric Acid on the co- oxidation of Oxalic Acid & Glutaric Acid by Chromic Acid, a series of kinetic runs were performed by keeping the concentrations of Chromic Acid, Oxalic Acid and Glutaric Acid constant at 0.0040 M, 0.0350 M and 0.0350 M respectively, while the concentration of Sulphuric Acid had varied from 0.0225 M to 0.1800 M. The rate constant and others kinetic data of various reaction mixtures at 29°C are recorded below in the table No 01 & 02.

Table No.01
RATE CONSTANT, pH VALUE & H⁺ ION CONCENTRATION

| S. No. | Concentration of H ₂ SO ₄ | Rate Constants K x10 ⁻³ min ⁻¹ | pH value at 29 ^o C | H ⁺ ion Concentration x 10 ⁻² |
|--------|---|--|-------------------------------|---|
| 1 | 0.0000M | 4.3350 | 1.98 | 1.047 |
| 2 | 0.0225M | 6.5462 | 1.51 | 3.090 |
| 3 | 0.0450M | 8.5120 | 1.43 | 3.715 |
| 4 | 0.0675M | 9.8025 | 1.37 | 4.266 |
| 5 | 0.0900M | 11.9044 | 1.31 | 4.898 |
| 6 | 0.1125M | 13.9865 | 1.27 | 5.370 |
| 7 | 0.1350M | 15.3502 | 1.22 | 6.025 |
| 8 | 0.1575M | 18.4203 | 1.17 | 6.761 |
| 9 | 0.1800SM | 19.9021 | 1.13 | 7.413 |

FIG. No. 01: VARIATION OF RATE CONSTANT WITH THE CONCENTRATION OF H₂SO₄ OF TABLE – 01
FIG. No. 02: VARIATION OF RATE CONSTANT WITH THE HYDROGEN ION CONCENTRATION OF H₂SO₄ OF TABLE - 01

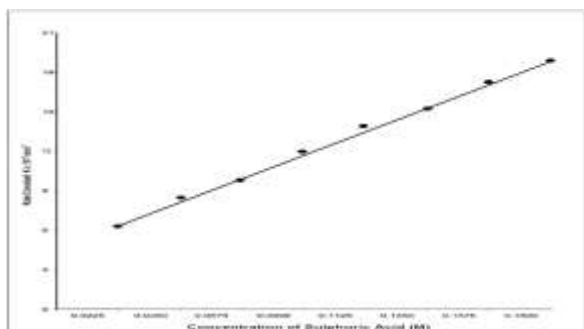


Fig. No. 01

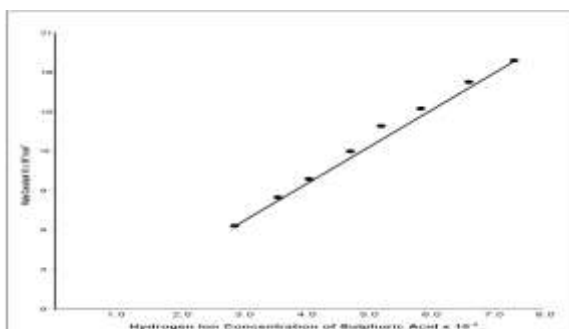


Fig. No. 02

Table No.02
CATALYTIC CONSTANT & DIELECTRIC CONSTANT AT 29°C

| S. No. | Concentration of H ₂ SO ₄ | Catalytic Constant K _H ⁺ × 10 ⁻¹ | Dielectric Constant |
|---|---|---|---------------------|
| 1 | 0.0000M | 4.3350 | 1.98* |
| 2 | 0.0225M | 6.5462 | 1.51 |
| 3 | 0.0450M | 8.5120 | 1.43 |
| 4 | 0.0675M | 9.8025 | 1.37 |
| 5 | 0.0900M | 11.9044 | 1.31 |
| 6 | 0.1125M | 13.9865 | 1.27 |
| 7 | 0.1350M | 15.3502 | 1.22 |
| 8 | 0.1575M | 18.4203 | 1.17 |
| 9 | 0.1800M | 19.9021 | 1.13 |
| Average Value = 1.6803 × 10⁻¹ | | | 1.895 |

Not included in the average

Table No.03
RATE CONSTANT AT DIFFERENT TEMPERATURES

| S. No. | Concentration of H ₂ SO ₄ | Rate constant K × 10 ⁻³ min ⁻¹ | | |
|--------|---|--|---------|---------|
| | | 29°C | 39°C | 49°C |
| 1 | 0.0000M | 4.3350 | 8.4966 | 16.7383 |
| 2 | 0.0225M | 6.5462 | 12.6996 | 25.1452 |
| 3 | 0.0450M | 8.5120 | 16.8537 | 32.8648 |
| 4 | 0.0675M | 9.8025 | 19.2129 | 37.6572 |
| 5 | 0.0900M | 11.9044 | 23.3326 | 45.9652 |
| 6 | 0.1125M | 13.9865 | 27.6937 | 54.0018 |

| | | | | |
|---|----------|---------|---------|---------|
| 7 | 0.1350M | 15.3502 | 30.5468 | 60.4828 |
| 8 | 0.1575M | 18.4203 | 36.2879 | 70.3987 |
| 9 | 0.1800SM | 19.9021 | 39.4457 | 77.7081 |

Table No.04
TEMPERATURE COEFFICIENT

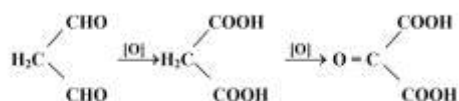
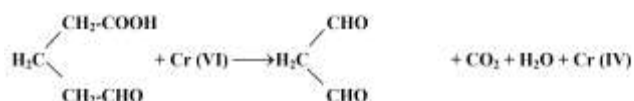
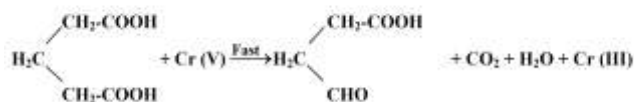
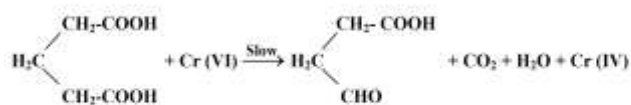
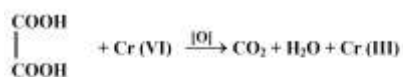
| S. No. | Concentration of H ₂ SO ₄ | Temperature Coefficient | |
|--------|---|-----------------------------------|-----------------------------------|
| | | K ₃₉ / K ₂₉ | K ₄₉ / K ₃₉ |
| 1 | 0.0000M | 1.96 | 1.97 |
| 2 | 0.0225M | 1.94 | 1.98 |
| 3 | 0.0450M | 1.98 | 1.95 |
| 4 | 0.0675M | 1.96 | 1.96 |
| 5 | 0.0900M | 1.96 | 1.97 |
| 6 | 0.1125M | 1.98 | 1.95 |
| 7 | 0.1350M | 1.99 | 1.98 |
| 8 | 0.1575M | 1.97 | 1.94 |
| 9 | 0.1800SM | 1.98 | 1.97 |

II RESULTS AND DISCUSSION

In the co-oxidation of Oxalic Acid and Glutaric Acid by Chromic Acid the kinetic behavior of the reaction is the same in the presence of Sulphuric Acid as in its absence as shown in the observation (Table No. 01). The reaction rate however increases with the increase in the concentration of Sulphuric Acid in the system. A graph obtained between rate constant and concentration of Sulphuric Acid (Fig. No. 01) suggest that the rate is more or less linear function of the concentration of Sulphuric Acid. A graph obtained (Fig. No. 02) between rate constant and Hydrogen ion concentration also suggest that Co-oxidation reaction is first order with respect to Hydrogen ion concentration. Reaction mixture containing Oxalic Acid, Glutaric Acid and Chromic Acid were stirred in water at 29°C for 48 hours. The solvent removed using a rotator evaporator under reduced pressure. The residue was extracted using diethyl ether in separator funnel. The organic layer was concentrated with a rotator evaporator. The product, Mesooxalic Acid was identified by its spot test. It is also confirmed by its melting point. The evolution of Carbon dioxide was tested by a conventional lime water test. The pH value decreases quite naturally with the increase in the Sulphuric Acid concentration. No significant change in the values of dielectric constant and catalytic constant of the system is observed by the concentration of the added

Sulphuric Acid. Finally, the oxidation reaction was studied at three different temperatures, i.e., 29^oC, 39^oC and 49^oC keeping all other experimental conditions constant. Values of rate constants and temperature coefficient are given in Table No-03 and - 04. As the value of temperature coefficient is equal to two, hence no unusual effect of temperature has been observed. As the rate of the reaction is altered in presence of Sulphuric Acid, hence reaction is catalyzed. The rate of reaction does not depend on the concentration of Hydrogen ion only. Thus the acid effect is not due to specific acid catalysis, it seems to be due to general acid catalysis. The catalyzed co oxidation of Oxalic Acid and Glutaric Acid can be explained by considering the Rocek⁸ mechanism which considers the formation of a ternary complex of Cr (VI) involving both Oxalic Acid and Glutaric Acid and the decomposition of the mixed ligand complex through a 3e-transfer step at the rate determining step.

III MECHANISM OF THE REACTION



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