

KINETICS AND MECHANISM OF OXIDATION OF MIXTURE OF OXALIC ACID AND DL-MALIC ACID BY CHROMIC ACID IN PRESENCE OF SULPHURIC ACID

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ABSTRACT

In the present work, kinetics and mechanism of oxidation of Oxalic Acid and DL-Malic Acid by Chromic Acid in presence of Sulphuric Acid, have been studied with a view to elucidate the mechanism of the reaction in aqueous medium, isolate and identify the products and produce a reaction of mechanism. Effect of Sulphuric Acid on the oxidation of mixture of Oxalic Acid and DL-Malic Acid by Chromic Acid has been studied at three different temperatures. The rate of the oxidation increases with the increase in the concentration of Sulphuric Acid. The order of reaction is one with respect to Chromic Acid and also one with respect to mixture of Oxalic Acid + DL-Malic Acid. The kinetic parameters such as rate constant, temperature coefficient and catalytic constant are determined.

I INTRODUCTION

Amongst various oxidants, Chromic Acid is one of the most versatile oxidant. All Chromium compounds are coloured. Chromium is a transitional element, some of its compounds are used to oxidize inorganic and organic compounds. Kinetics and mechanistic studies of Chromic Acid oxidation of α hydroxyl acid abound in the literature. The reaction follows either two electrons or three electrons one step oxidation of substrates by Chromic Acid. Organic substrates generally undergo at most a two electrons oxidation in a single step. One step three electron reduction of an oxidant involves more than one molecule of an organic substrate in the activated complex. Rocek et al⁵, have reported that such three electrons oxidation can take place in Chromium (VI)-substrates complex. One substrate is an organic acid carrying a second functional group and second substrate molecule is either identified with the first or it may be a compound with a single functional group such as an alcohol. The latter case represents a co oxidation in which two different substrates are oxidized simultaneously. In the co oxidation of Malic Acid and Arsenic (III) by Chlorochromate in aqueous Acetic Acid, Sambrani and Raju⁶ found that both Arsenic (III) and Oxalic Acid were oxidized concertedly in a three equivalent step. Ansari¹⁰ and his associates also reported three equivalent step of the oxidation Malonic Acid by Chromic Acid.

According to Bronsted theory of acid and base catalysis¹¹, un dissociated molecule catalyze the reaction rate. Weak acid can also catalyze the reaction rate.

II EXPERIMENTAL

All the chemicals were of AR grade, Oxalic Acid (Merck), DL-Malic Acid, Chromium trioxide (Qualigens), Sulphuric Acid (B.D.H.) and all other chemicals were used of highest purity available as commercially. Standard solution of known Oxalic Acid, DL-Malic Acid was prepared by accurate weighing of the amount required and dissolving it quickly in double distilled water. Stock solution of Chromium (VI) was prepared by dissolving of Chromium trioxide in double distilled water and was standardized iodometrically. The reacting solutions were kept in a thermostat for about half an hour. The temperature regulation was within 29°C (±0.1°C). After the solution had attended the experimental temperature of the thermostat, then 25 ml of each reactant was pipette out and immediately transferred into the flask. An aliquot of 5ml of the reaction mixture was then immediately withdrawn and its optical density (O.D.) measured at once. Progress of the reaction was measured by using spectrophotometer. Data so obtained at 29°C on various reaction mixtures containing different concentration of Sulphuric Acid, while the concentration of Oxalic Acid, DL-Malic Acid and Chromic Acid were kept constant at $2.50 \times 10^{-1}M$, $2.50 \times 10^{-1}M$ and $8.20 \times 10^{-3} M$ respectively. Concentration of Sulphuric Acid was varied from $1.20 \times 10^{-2} M$ to $9.60 \times 10^{-3}M$ respectively. Kinetic data are recorded in table No.01 and 02.

TABLE No. 01
RATE CONSTANT $K \times 10^{-3} \text{ min}^{-1}$

S. No	Concentration of Sulphuric Acid (M)	Rate Constant in presence of H_2SO_4	Hydrogen ion Concentration $\times 10^{-2}$
1	0.00×10^{-2}	6.6085	0.726
2	1.20×10^{-2}	8.3194	1.023
3	2.40×10^{-2}	10.3825	1.738
4	3.60×10^{-2}	14.6632	2.291
5	4.80×10^{-2}	18.1665	3.090
6	6.00×10^{-2}	22.0835	3.981
7	7.20×10^{-2}	26.1375	4.365
8	8.40×10^{-2}	30.3023	4.786
9	9.66×10^{-2}	34.9275	5.370

Fig1: Variation of Rate Constant with the Concentration of Sulphuric Acid of TABLE -01

Fig 2: Variation of Rate Constant with the Hydrogen Ion Concentration of TABLE -01

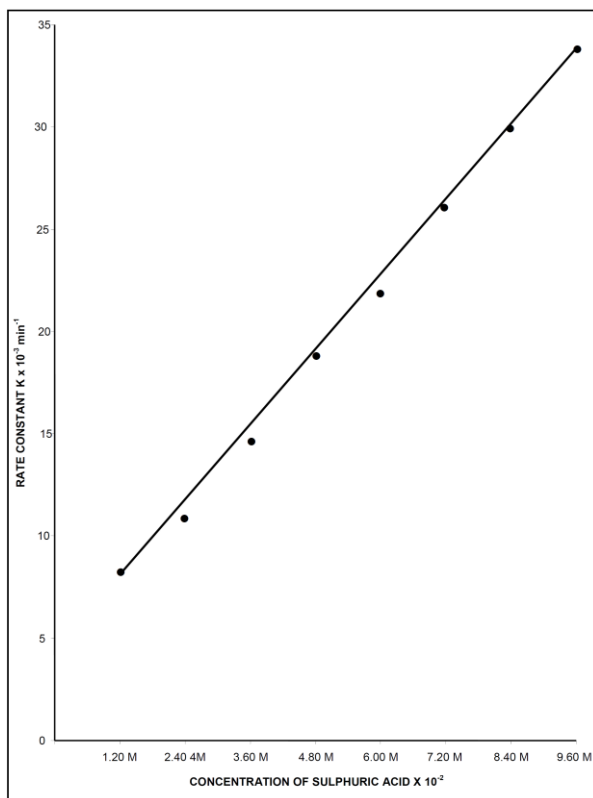


Fig1

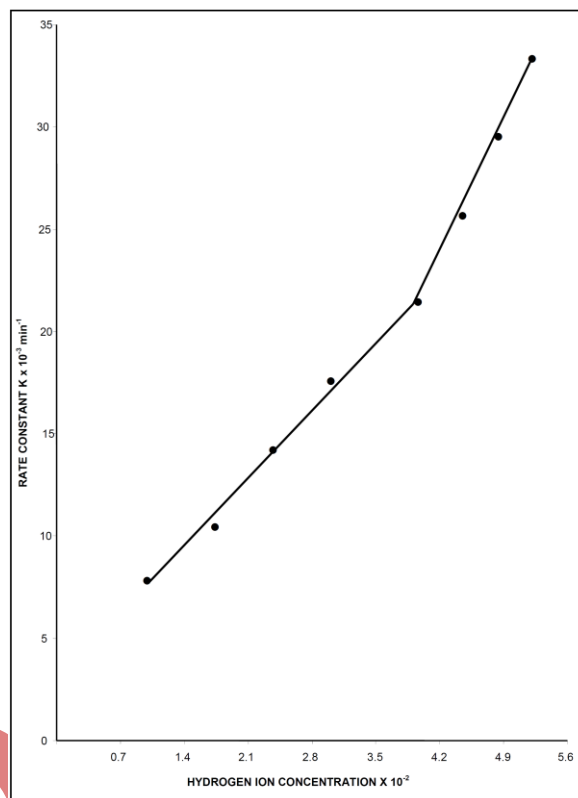


Fig 2

TABLE No.02
CATALYTIC CONSTANT AND DIELECTRIC CONSTANT

S. No.	Concentration of Sulphuric Acid	Catalytic Constant $K_{H^+} \times 10^{-1}$	Dielectric Constant
1	0.00×10^{-2}	----	1.801*
2	1.20×10^{-2}	1.6724	1.672
3	2.40×10^{-2}	2.1715	1.669
4	3.60×10^{-2}	3.5158	1.664
5	4.80×10^{-2}	3.7405	1.662
6	6.00×10^{-2}	3.8872	1.660
7	7.20×10^{-2}	4.4740	1.659
8	8.40×10^{-2}	4.9506	1.651
9	9.66×10^{-2}	5.2736	1.640
Average Value = 3.7107×10^{-1}			1.660

* Not included in the average

TABLE NO. 03
RATE CONSTANT AT DIFFERENT TEMPERATURES

S. No.	Concentration of Sulphuric Acid (M)	RATE CONSTANT K X 10 ⁻³ min ⁻¹		
		29 ^o C	39 ^o C	49 ^o C
1	0.00 X 10 ⁻²	6.6085	13.0848	25.6463
2	1.20 X 10 ⁻²	8.3194	16.2228	31.7967
3	2.40 X 10 ⁻²	10.3825	20.5574	40.2924
4	3.60 X 10 ⁻²	14.6632	28.8865	56.6175
5	4.80 X 10 ⁻²	18.1665	35.6063	69.0763
6	6.00 X 10 ⁻²	22.0835	43.7253	85.2644
7	7.20 X 10 ⁻²	26.1375	51.4909	99.3774
8	8.40 X 10 ⁻²	30.3023	59.0895	114.6336
9	9.66 X 10 ⁻²	34.9275	67.4101	131.4496

Table No. 04
TEMPERATURE COEFFICIENT

S. No.	Concentration of Sulphuric Acid(M)	Temperature Coefficient	
		K ₃₉ / K ₂₉	K ₄₉ / K ₃₉
1	0.00 X 10 ⁻²	1.98	1.96
2	1.20 X 10 ⁻²	1.95	1.96
3	2.40 X 10 ⁻²	1.98	1.96
4	3.60 X 10 ⁻²	1.97	1.96
5	4.80 X 10 ⁻²	1.96	1.94
6	6.00 X 10 ⁻²	1.98	1.95
7	7.20 X 10 ⁻²	1.97	1.93
8	8.40 X 10 ⁻²	1.95	1.94
9	9.60 X 10 ⁻²	1.93	1.95

III RESULTS AND DISCUSSION

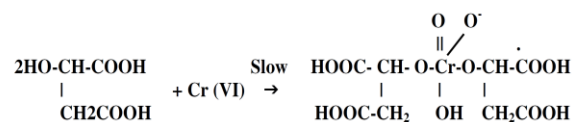
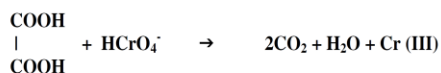
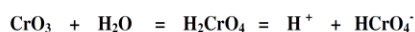
The rate of the reaction is affected by the Sulphuric Acid concentration, the extent of which depends on the following two factors; (1) The concentration of added Acid in the reaction mixture.(2) The nature of the added

Acid. As the rate of the reaction is altered in presence of Sulphuric Acid, hence the reaction is catalyzed. The order of the reaction with respect to Chromic Acid remains unaltered (one) in the presence of Sulphuric Acid in the system. A graph obtained between the rates constant and added concentration of Sulphuric Acid / Hydrogen ion concentration (Fig No. 01 and 02) suggests that the rate is linear function of the concentration of Sulphuric Acid. The pH value decrease quite naturally with the increase in the Sulphuric Acid concentration. It will be explained in several ways. Most important of these appears to be, (a) fast formation of the activated complex, (b) intermediate compound regenerates both the positive catalyst and the reactants, catalytic side reaction or decomposition and breaking of chain reaction

The rate however 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. It will be worthwhile to state that the values of temperature coefficient of reaction depend upon the reaction themselves. It is observed from the table no-04 that temperature coefficient is fairly constant. The values of temperature coefficient are approximately equal to two. The energy of activation is acquired by collision only. The temperature effect is thus purely thermal. It seems that the source of acquiring energy of activation is practically the same at all temperatures. There is no other way of acquiring energy at the temperature of experiment. Hence the discussion of the results obtained at 29°C will suffice, for it will hold, good the data observed at other temperature also, the difference being in the values of the rate constants only. 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.

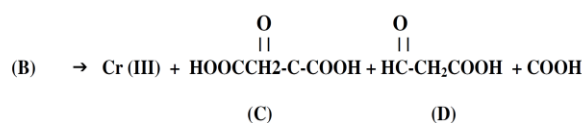
In order to study the overall oxidation products of mixture of Oxalic Acid +DL-Malic Acid by Chromic Acid were mixed in equimolar amounts. The reaction mixture containing Oxalic Acid +DL-Malic Acid and Chromic Acid was kept at room temperature for a long time. After mixing the reactants, it was observed that initial light yellow colour changed to light blue in the course of the reaction. This clearly indicates that the oxidation of the reactants proceeds through different stages and the reduction of Cr (VI) to Cr (III) in the oxidation of mixture of Oxalic Acid + DL- Malic Acid by Chromic Acid. Products were extracted with ether by solvent extraction method and identified as Malonic Acid and Carbon dioxide. Malonic Acid was identified by its melting point and spot tests⁸. Carbon dioxide was confirmed by passing the gas in lime water, which turned milky.

IV MECHANISM OF REACTION



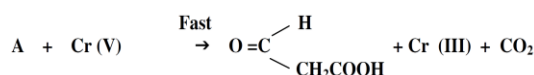
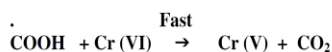
(A)

(B)



(C)

(D)



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