

KINETICS AND MECHANISM OF OXIDATION OF MIXTURE OF DL-MALIC ACID AND L (+) TARTARIC ACID BY CHROMIC ACID IN PRESENCE OF HYDROCHLORIC ACID AND SODIUM CHLORIDE

Rupali Verma¹, Shaikh Ishrat Bano Ibrahim², Smita Shukla³, B.K.Mishra⁴

¹ Department of Chemistry, Bansal Institute of Science & Technology, Bhopal (India)

² Department of Chemistry, S.V.S's Arts & Science College, Dondaicha, Duhule (India)

³ Department of Chemistry, R. K. D. F. Institute of Science & Technology, Bhopal (India)

⁴ Department of Chemistry, Laxmipati Institute of Science & Technology, Bhopal (India)

ABSTRACT

Kinetics and mechanism of oxidation of DL-Malic Acid and L(+)Tartaric Acid by Chromic Acid in presence of Hydrochloric Acid and Sodium Chloride 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 mechanism. Effect of Hydrochloric Acid and Sodium Chloride on the oxidation of mixture of DL-Malic Acid and L (+) Tartaric Acid by Chromic Acid has been studied at three different temperatures. The rate of the oxidation increases with the increase in the concentration of Hydrochloric Acid, while the reaction rate is decreases with the increase in the concentration of Sodium Chloride. The order of reaction is one with respect to Chromic Acid and also one with respect to mixture of DL-Malic Acid and L (+) Tartaric Acid .The kinetic parameters such as rate constant, temperature coefficient and catalytic constant are determined.

I. INTRODUCTION

Chromium occurs in the environment mainly in the elemental state Cr^0 or in compounds of Cr (III), the trivalent species or hexavalent Cr (VI)¹⁰. In soils and sediments, Chromium may be present in one of the two thermodynamically stable oxidation states, Cr (III) or Cr (VI)⁹. Cr (VI) constitutes a significant health hazard and the World Health Organization (WHO) has, therefore, established a limit of 0.05 mg/lit for Cr (VI) in drinking water⁶. Compounds of Cr (VI) are generally more soluble in water than are those of Cr (III). Chromium (III) presents only a low health risk. Chromium (III) as a metal ion has a tendency to be absorbed specifically on clay and oxide surfaces and hydrolyze within the ordinary environmental pH range (pH=3-9). 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. Z. Khan¹², Mishra¹³ and his associates also reported three equivalent step of the oxidation of Malonic Acid by Chromic Acid. According to Bronsted theory of an acid and base catalysis¹¹, un dissociated molecule catalyze the reaction rate. Acetic Acid¹³ can also catalyze the reaction rate at low concentration.

Experimental: All the chemicals were of AR grade, DL - Malic Acid (BDH), L (+) Tartaric Acid (BDH), Sodium Chloride (BDH), Chromium trioxide (Qualigens), Hydrochloric Acid (B.D.H.) and all other chemicals were used of highest purity available as commercially. Standard solution of known DL-Malic Acid- (+) Tartaric 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 25°C ($\pm 0.1^\circ\text{C}$). After the solution had attended the experimental temperature of the thermostat, then 20 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 25°C on various reaction mixtures containing different concentration of Hydrochloric Acid and Sodium Chloride, while the concentration of DL-Malic Acid, L (+) Tartaric Acid and Chromic Acid were kept constant at $1.25 \times 10^{-1}\text{M}$, $1.25 \times 10^{-1}\text{M}$ and $4.80 \times 10^{-3}\text{M}$ respectively. Concentration of Hydrochloric Acid and Sodium Chloride was varied from $1.00 \times 10^{-2}\text{M}$ to $8.00 \times 10^{-2}\text{M}$ respectively. Kinetic data are recorded in table No. 1, 2, 3 & 4.

TABLE No. 1

Rate Constant $K \times 10^{-3} \text{ min}^{-1}$

S. No	Concentration of HCl (M)	Rate Constant in presence of HCl	Hydrogen ion Concentration $\times 10^{-2}$
1	0.00×10^{-2}	6.4765	0.933
2	1.00×10^{-2}	8.5238	2.399
3	2.00×10^{-2}	9.6388	2.951
4	3.00×10^{-2}	10.9443	3.311
5	4.00×10^{-2}	12.4488	3.802
6	5.00×10^{-2}	13.0805	4.467
7	6.00×10^{-2}	16.2235	5.129
8	7.00×10^{-2}	17.9985	5.888
9	8.00×10^{-2}	19.9830	6.457

TABLE No. 2

Rate Constant $K \times 10^{-3} \text{ min}^{-1}$

S. No.	Concentration of NaCl (M)	Rate Constant in presence of NaCl	Hydrogen ion Concentration $\times 10^{-2}$
1	0.00×10^{-2}	6.4756	0.933

2	1.00×10^{-2}	5.2952	1.118
3	2.00×10^{-2}	4.6775	1.660
4	3.00×10^{-2}	4.1150	2.138
5	4.00×10^{-2}	3.7520	2.455
6	5.00×10^{-2}	3.1164	2.951
7	6.00×10^{-2}	2.7745	3.226
8	7.00×10^{-2}	2.4565	3.467
9	8.00×10^{-2}	2.1886	3.631
Average Value = 3.7107×10^{-1}			1.660

TABLE No. 3

CATALYTIC CONSTANT AND DIELECTRIC CONSTANT

S. No	Concentration of HCl (M)	Catalytic Constant $K_H^+ \times 10^{-1}$	Dielectric Constant
1	0.00×10^{-2}	-	1.898*
2	1.00×10^{-2}	0.8534	1.844
3	2.00×10^{-2}	1.0716	1.839
4	3.00×10^{-2}	1.3494	1.833
5	4.00×10^{-2}	1.5708	1.830
6	5.00×10^{-2}	1.6799	1.826
7	6.00×10^{-2}	1.7054	1.823
8	7.00×10^{-2}	1.9569	1.820
9	8.00×10^{-2}	2.0917	1.818
Average Value = 1.5349×10^{-1}			1.829

*Not included in the average

TABLE No. 4

Catalytic Constant and Dielectric Constant

S. No.	Concentration of NaCl (M)	Catalytic Constant $K_H^+ \times 10^{-1}$	Dielectric Constant
1	0.00×10^{-2}	-	1.898*
2	1.00×10^{-2}	-1.0571	1.878
3	2.00×10^{-2}	-1.0842	1.873
4	3.00×10^{-2}	-1.1045	1.864
5	4.00×10^{-2}	-1.1106	1.859

6	5.00×10^{-2}	-1.1386	1.853
7	6.00×10^{-2}	-1.1476	1.849
8	7.00×10^{-2}	-1.1595	1.844
9	8.00×10^{-2}	-1.1809	1.841
Average Value $= -1.1229 \times 10^{-1}$			1.857

*Not included in the average

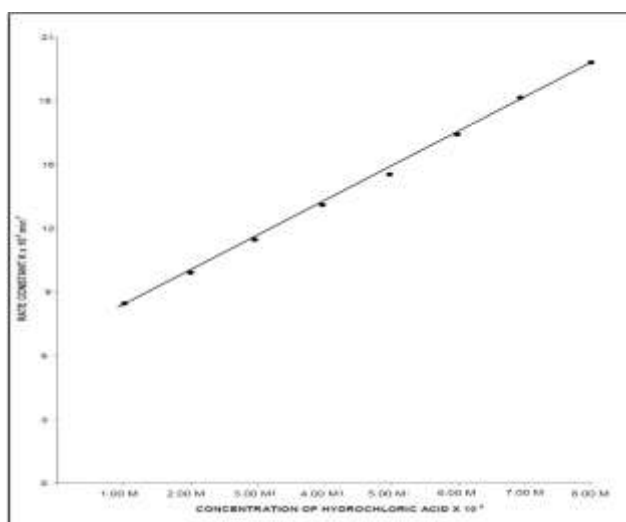


Fig. No-01 Variation Of Rate Constant With The Concentration Of Hydrochloric Acid Cf Table -01

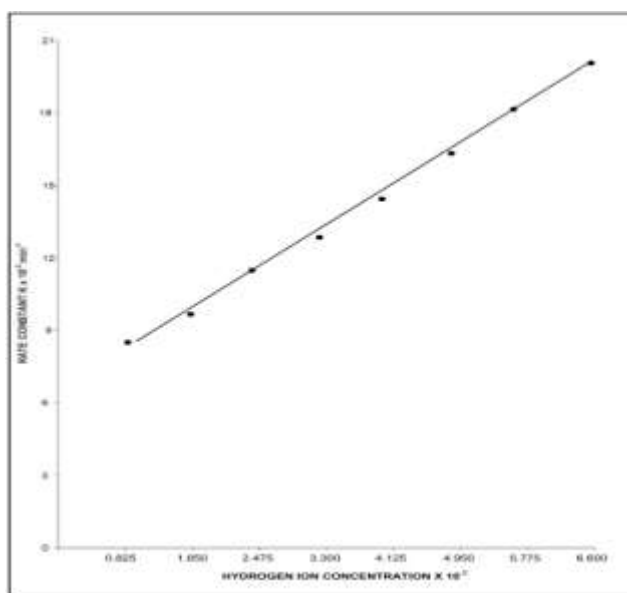


Fig. No.-02 Variation Of Rate Constant With The Hydrogen Ion Concentration Cf Table -01

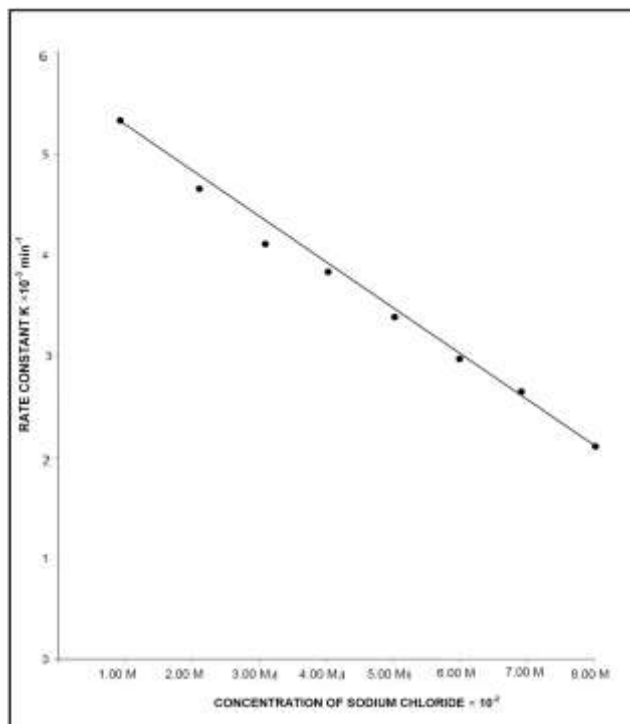


Fig. No.-03 Variation of Rate Constant With The Sodium Chloride Concentration of Table -04

II. RESULTS AND DISCUSSION

The rate of the reaction is affected by the Hydrochloric Acid concentration, the extent of which depends on the following two factors;

- (1) The concentration of added Hydrochloric Acid in the reaction mixture
- (2) The nature of the added Hydrochloric Acid.

As the rate of the reaction is altered in presence of Hydrochloric Acid, hence the reaction is catalyzed. The order of the reaction with respect to Chromic Acid and Hydrogen ion (Fig.No.02) remains unaltered i.e., one in the presence of Hydrochloric Acid in the system. A graph obtained between the rates constant and added concentration of Hydrochloric Acid (Fig No. 01) suggests that the rate is linear function of the concentration of Hydrochloric Acid. The increase in the rate of reaction in presence of Hydrochloric Acid is due to positive catalysis which has been explained in several ways, the most important of these appears to be;

- (a) Fast formation of the activated complex or to less stability of an intermediate catalyst compound
- (b) Intermediate compound regenerates both the positive catalyst and the reactant
- (c) Catalytic side reaction or decomposition
- (d) 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 and 05 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 25°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.

Table No. 5 Temperature Coefficient

S. No.	Concentration of Hydrochloric Acid(M)	Temperature Coefficient	
		K_{36} / K_{25}	K_{45} / K_{36}
1	0.00×10^{-2}	1.98	1.96
2	1.00×10^{-2}	1.97	1.92
3	2.00×10^{-2}	1.96	1.97
4	3.00×10^{-2}	1.95	1.97
5	4.00×10^{-2}	1.97	1.99
6	5.00×10^{-2}	1.95	1.96
7	6.00×10^{-2}	1.98	1.92
8	7.00×10^{-2}	1.95	1.96
9	8.00×10^{-2}	1.97	1.95

Table No. 6 Temperature Coefficient

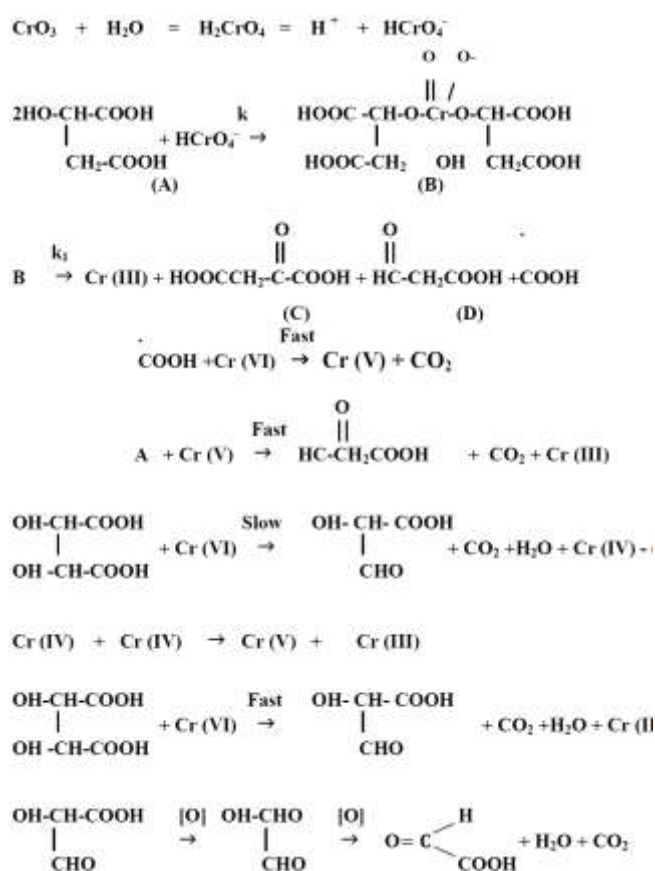
S. No.	Concentration of Sodium Chloride (M)	Temperature Coefficient	
		K_{35} / K_{25}	K_{45} / K_{35}
1	0.00×10^{-2}	1.98	1.96
2	1.00×10^{-2}	1.95	1.97
3	2.00×10^{-2}	1.98	1.96
4	3.00×10^{-2}	1.95	1.96
5	4.00×10^{-2}	1.98	1.97
6	5.00×10^{-2}	1.95	1.93
7	6.00×10^{-2}	1.98	1.97
8	7.00×10^{-2}	1.97	1.97
9	8.00×10^{-2}	1.97	1.95

It appears from the values of temperature coefficient (Table No.05 and 06) of the reaction in the presence of Sodium Chloride that this salt produced mostly primary salt effect which is attributed to the dependence of activity coefficient of ions and hence the activities of the reactants on the ionic strength of the system. The activity coefficient of ions always decreases by the addition of small quantity of salt. All reactions involving the ions should be expected to show a negative salt effect. The negative salt effect (Fig.No.03) is due to negative catalysis which has been explained in several ways, the most of these appears to be; (a) slow formation of the activated complex and more stability of an intermediate catalyze compound (b) regeneracy of both the negative catalyst and the reactant from the intermediate compound (c) breaking of chain reaction (d) catalytic side reaction or decomposition. No significant change in the average values of dielectric constant and average values of catalytic constant of the system is observed by the concentration of the added Hydrochloric 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 mixture of DL-Malic Acid, L (+) Tartaric

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 DL-Malic Acid, L (+) Tartaric Acid by Chromic Acid. Products were extracted with ether by solvent extraction method and identified as Malonic Acid (DL-Malic Acid), Glyoxalic Acid [L (+) Tartaric Acid] and Carbon dioxide. Liberation of Carbon dioxide shows that Chromic Acid is attacking of the –COOH group of DL-Malic Acid, L (+) Tartaric Acid. Malonic Acid and Glyoxalic Acid was identified by its melting point and spot tests⁸. Carbon dioxide was identified qualitatively by Ba(OH)₂¹² and also confirmed by passing the gas in lime water, which turned milky

III. MECHANISM OF REACTION



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