

KINETICS OF CO-OXIDATION OF DL-MALIC ACID AND L (+) TARTARIC ACID BY CHROMIC ACID IN PRESENCE OF SODIUM SULPHATE AND POTASSIUM SULPHATE

Rupali Verma¹, Shaikh Ishrat Bano Ibrahim², Bhavna Chauhan³,
B.K.Mishra⁴

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

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

³Department of Chemistry, Ramkrishan Memorial P.G.College Vidisha,, Bhopal (India)

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

ABSTRACT

Kinetics of Co-oxidation of DL-Malic Acid and L(+)/Tartaric Acid by Chromic Acid in presence of Sodium Sulphate and Potassium Sulphate have been studied with a view to elucidate the behavior of the reaction in aqueous medium, isolate and identify the products. Effect of Sodium Sulphate and Potassium Sulphate (separately) 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 co- oxidation of DL-Malic Acid and L (+) Tartaric Acid by Chromic Acid, decreases with the increase in the concentration of Sodium Sulphate or Potassium Sulphate in the system. The order of reaction is one with respect to oxidant and also one with respect to substrates .The kinetic parameters such as rate constant, temperature coefficient and catalytic constant is determined.

I. INTRODUCTION

There are several reports^{2,5} on the kinetics of the oxidation of Tartaric Acid by Chromium in different media. As the reaction has an induction period, except for Bakore and Narain⁹ others have not specified as to which part their rate constants belong. Tartaric Acid is differing from other dicarboxylic acids in that it has two –OH groups at different Carbon atoms. In particular, its reaction with Chromium (VI) is interesting because of mutagenic and carcinogenic activities of the latter. The redox chemistry of Tartaric Acid plays an important role because it may behave as a diol and /or as a carboxylic or α -hydroxyl acid. Malic Acid was first isolated from apple juice by Carl Wilhelm Scheele⁴ in 1785. Antoine Lavoisier⁶ in 1787 proposed the name acide malique, which is derived from the Latin word for apple, mālum.. Malic Acid has two stereo isomeric forms (L- and D-enantiomers), though only the L-isomer exists naturally. 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 al⁸, 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.

II. EXPERIMENTAL

All the chemicals were of AR grade, DL - Malic Acid (BDH), L (+) Tartaric Acid (BDH), Chromium trioxide (Qualigens), Sodium Sulphate (B.D.H.), Potassium Sulphate (BDH) and all other chemicals were used of highest purity available as commercially. Standard solution of known Sodium Sulphate and Potassium Sulphate was prepared by accurate weighing of the amount as required and dissolving it quickly in double distilled water. Stock solution of DL-Malic Acid, L (+) Tartaric Acid was prepared by dissolving in double distilled water and Chromic Acid by dissolving 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 in 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, 35°C and 45°C on various reaction mixtures containing different concentration of Sodium Sulphate and Potassium Sulphate, while the concentration of DL-Malic Acid, L (+) Tartaric Acid and Chromic Acid were kept constant at 1.25×10^{-1} M, 1.25×10^{-1} M and 4.80×10^{-3} M respectively. Concentration of Sodium Sulphate and Potassium Sulphate was varied from 1.00×10^{-2} M to 8.00×10^{-2} M respectively. Kinetic data are recorded in table No. 01 to 08.

TABLE No. 01 Rate Constant K X10⁻³ min⁻¹

S. No	Concentration of Na ₂ SO ₄ (M)	Rate Constant in presence of Na ₂ SO ₄ (M)	Hydrogen ion Concentration X 10 ⁻²
1	0.00 X 10 ⁻²	6.4765	0.933
2	1.00 X 10 ⁻²	5.4610	1.349
3	2.00 X 10 ⁻²	4.9865	1.622
4	3.00 X 10 ⁻²	4.2323	2.239
5	4.00 X 10 ⁻²	3.9226	2.512
6	5.00 X 10 ⁻²	3.6545	2.754
7	6.00 X 10 ⁻²	3.3988	2.951
8	7.00 X 10 ⁻²	3.0980	3.226
9	8.00 X 10 ⁻²	2.7987	3.467

Table No. 02 Rate Constant $K \times 10^{-3} \text{ min}^{-1}$

S. No	Concentration of K_2SO_4 (M)	Rate Constant in presence of K_2SO_4	Hydrogen ion Concentration $\times 10^{-2}$
1	0.00×10^{-2}	6.4756	0.933
2	1.00×10^{-2}	5.1164	1.259
3	2.00×10^{-2}	4.7320	1.585
4	3.00×10^{-2}	3.9875	2.239
5	4.00×10^{-2}	3.6239	2.512
6	5.00×10^{-2}	3.3486	2.692
7	6.00×10^{-2}	3.1320	2.818
8	7.00×10^{-2}	2.7381	3.090
9	8.00×10^{-2}	2.4438	3.311

Table no. 03 Catalytic Constant and Dielectric Constant

S. No	Concentration of Na_2SO_4 (M)	Catalytic Constant $K_H^+ \times 10^{-1}$	Dielectric Constant
1	0.00×10^{-2}	-	1.898*
2	1.00×10^{-2}	-0.7528*	1.873
3	2.00×10^{-2}	-0.9186	1.866
4	3.00×10^{-2}	-1.0023	1.859
5	4.00×10^{-2}	-1.0166	1.853
6	5.00×10^{-2}	-1.0247	1.849
7	6.00×10^{-2}	-1.0429	1.844
8	7.00×10^{-2}	-1.0473	1.841
9	8.00×10^{-2}	-1.0608	1.837
Average Value $= -1.0162 \times 10^{-1}$			1.852

*Not included in the average

TABLE No. 04 CATALYTIC CONSTANT AND DIELECTRIC CONSTANT

S. No.	Concentration of K_2SO_4 (M)	Catalytic Constant $K_H^+ \times 10^{-1}$	Dielectric Constant
1	0.00×10^{-2}	-	1.898*
2	1.00×10^{-2}	-1.0803	1.868
3	2.00×10^{-2}	-1.1006	1.860
4	3.00×10^{-2}	-1.1117	1.855
5	4.00×10^{-2}	-1.1356	1.849
6	5.00×10^{-2}	-1.1620	1.846
7	6.00×10^{-2}	-1.1868	1.841
8	7.00×10^{-2}	-1.2098	1.837
9	8.00×10^{-2}	-1.2180	1.834
Average Value = -1.1506×10^{-1}			1.848

*Not included in the average

Table No. 05 Rate Constant at Different Temperatures

S. No.	Concentration of Sodium Sulphate (M)	RATE CONSTANT $K \times 10^{-3} \text{ min}^{-1}$		
		25 ⁰ C	35 ⁰ C	45 ⁰ C
1	0.00×10^{-2}	6.4765	12.8235	25.1340
2	1.00×10^{-2}	5.4610	10.6490	21.0849
3	2.00×10^{-2}	4.9865	9.8234	19.4503
4	3.00×10^{-2}	4.2323	8.2530	16.2584
5	4.00×10^{-2}	3.9226	7.6491	14.9922
6	5.00×10^{-2}	3.6545	7.1263	14.0388
7	6.00×10^{-2}	3.3988	6.6616	12.9902
8	7.00×10^{-2}	3.0980	6.1340	11.7774
9	8.00×10^{-2}	2.7987	5.514	10.8063

TABLE No. 06 RATE CONSTANT AT DIFFERENT TEMPERATURES

S. No.	Concentration of Potassium Sulphate (M)	RATE CONSTANT $K \times 10^{-3} \text{ min}^{-1}$		
		25°C	35°C	45°C
1	0.00×10^{-2}	6.4756	12.8235	25.1340
2	1.00×10^{-2}	5.1164	10.0793	19.6547
3	2.00×10^{-2}	4.7320	9.3220	17.7119
4	3.00×10^{-2}	3.9875	7.7756	15.3957
5	4.00×10^{-2}	3.6239	7.1391	13.9212
6	5.00×10^{-2}	3.3486	6.5298	12.7983
7	6.00×10^{-2}	3.1320	6.2014	12.0306
8	7.00×10^{-2}	2.7381	5.3667	10.5187
9	8.00×10^{-2}	2.4438	4.8387	9.4839

Table No. 07 Temperature Coefficient

S. No.	Concentration of Sodium Sulphate (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}	1.95	1.98
3	2.00×10^{-2}	1.97	1.98
4	3.00×10^{-2}	1.95	1.97
5	4.00×10^{-2}	1.95	1.96
6	5.00×10^{-2}	1.95	1.97
7	6.00×10^{-2}	1.96	1.95
8	7.00×10^{-2}	1.98	1.92
9	8.00×10^{-2}	1.97	1.96

Table No. 08 Temperature Coefficient

S. No.	Concentration of Potassium Sulphate (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}	1.97	1.95
3	2.00×10^{-2}	1.97	1.99
4	3.00×10^{-2}	1.95	1.98
5	4.00×10^{-2}	1.97	1.95
6	5.00×10^{-2}	1.95	1.96
7	6.00×10^{-2}	1.98	1.94
8	7.00×10^{-2}	1.96	1.96
9	8.00×10^{-2}	1.98	1.96

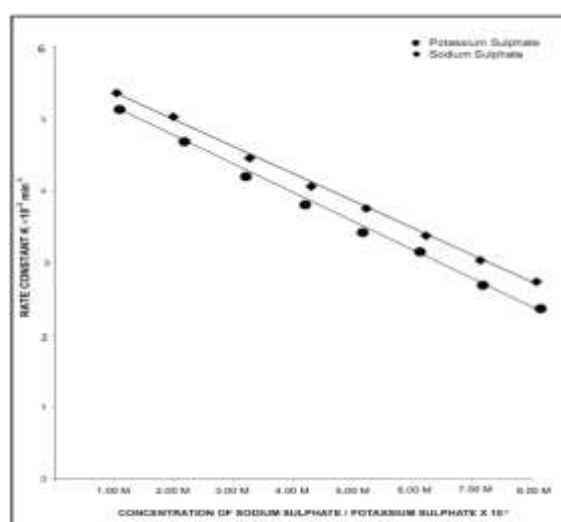


Fig. No.-01 Variation of Rate Constant With The Concentration of Na_2SO_4 & K_2SO_4 Cf TABLE No. 01&02

III. RESULTS AND DISCUSSION

Addition of salt to a reaction mixture may alter the rate of reaction. A peculiarity of salt effect is that a peculiar salt increases the rate of reaction while another retards it. It means that the salts of the same type may show different effect on the same reaction. In the co-oxidation of DL- Malic Acid and L (+) Tartaric Acid by Chromic Acid two salts (Sodium Sulphate and Potassium Sulphate) used by the author, retarded the rate of the reaction. It means that the effect of any one of two salts on the rate of reaction is of the same type, i.e., retarding effect. It is observed by the author that Potassium Sulphate is most effective in retarding the reaction rate. The difference in the degree of dissociation of two sulphates under the author's experimental conditions would amount to unequal contribution of each Sulphate towards the ionic strength and hence this could be one reason for the observed effect of sulphates of sodium and potassium in retarding the reaction rate. There might well be other properties specific of each ion and salt, for example, transmission coefficient, which could affect the reaction rate. 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-07 and 08 that temperature coefficient is fairly constant. The values of temperature 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 25⁰C 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.

It appears from the values of temperature coefficient of the reaction in the presence of Sodium Sulphate and Potassium Sulphate, that these salts 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 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 is determined and found to be order of 1.852 (Sodium Sulphate), 1.848 (Potassium Sulphate) and average values of catalytic constant is also determined and found to be order of -1.0162×10^{-1} (Sodium Sulphate), -1.1506×10^{-1} (Potassium Sulphate), is observed by the concentration of the added Sodium Sulphate and Potassium Sulphate.

IV. PRODUCT ANALYSIS

In order to study the overall Co-oxidation products of f 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. Malonic Acid and Glyoxalic Acid was identified by its melting point and spot tests³. Carbon dioxide was identified by passing the gas in lime water, which turned milky

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