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Kinetic and mechanistic study of oxidation of mixture of dicarboxylic acids by Chromic acid in presence of Sulphuric acid

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ABSTRACT

The kinetics of oxidation of mixture of Malonic acid + Tartaric acid by Chromic acid has been studied in presence of Sulphuric acid at 28ºC.The reaction follows first order kinetics with respect to each substrate, oxidant and hydrogen ion concentration. The method used here is Ostwald isolation method for study of rate of reaction. With increase in the concentration of Sulphuric acid the rate constant of the system increased. The oxidation of mixture of acids was studied at different concentration of Sulphuric acid. The rate constant, catalytic constant, dielectric constant and temperature coefficient have been determined for all the runs. Various thermodynamic parameters like energy of activation and frequency factor were also determined. The probable mechanism with result obtained has been proposed with the following rate equation.

$$-\frac{d[Cr(VI)(Sulphuric\ \ acid)]}{dt} = k\,[Cr\ (VI)][Malonic\ acid][Tartaric\ acid]\,[H^+]$$

Keywords:- Ostwald isolation, dielectric constant, catalytic constant, frequency factor.

INTRODUCTION

Dichromate, Chromyl chloride, Chromyl acetate and ditertiary butyl chromate are important chromium (VI) compounds used in Hexavalent Chromium[1-8] has been extensively used in analytical and preparative chemistry. Thus Chromic acid, aqueous the oxidation of variety of organic and inorganic substrate in solutions. The chemistry and reactivity pattern of these chromium compounds has been reviewed critically and extensively3-9.

The oxidation of Malonic acid by various metal ion oxidants has been reported with different results. The oxidation of Malonic acid and tartaric acid by Chromic acid exhibit a first order reaction kinetics. Sengupta and other coworkers[15-26] did not undertaken Hydrogen ion concentration dependence.

Experimental

Preparation of reagents :

All chemicals and reagents used in the work were analar grade and were manufactured by Merck, Reidel. Corning glassware's were employed and doubly distilled water is used through out the study, for preparation of solution. The rate of reaction of the oxidant and reductant were studied by monitoring the decrease in optical density using digital colorimeter at 420nm and pH value by digital pH meter Systronic model 335(electronic) also refractive index is measured by Abbe's refractrometer. All kinetic measurements were carried out and CO_2 and Carbonyl dicarboxylic acid has been found as end products. These products were identified by Physico chemical methods[18]. And they are confirmed by their usual tests.[10-14]

Product Analysis:

Product analysis was carried out under kinetic conditions. The studies were carried out in aqueous medium and at three different temperatures range of 28ºC, 38ºC and 48ºC. All the solutions were kept in a Toshniwal thermostat at constant temperature with accuracy ±0.10ºC. The required volume of these solutions for each run were mixed and analysed by colorimeter.

The first order reaction was obtained. and the different measured values are shown on the following tables:

Rate constants, pH values, H^+ ion concentration and K/H^+ values Table 1

S.No.	Concentration of Sulphuric Acid (M)	Rate Constants $Kx10^{-2}$ (min^{-1})	pH at 28°C	$[H^+]$ ion Concentration x 10^{-2}	K/H^+
1	0.0000	2.89	2.32	0.48	-
2	0.1000	3.54	2.09	0.81	6.115*
3	0.2000	4.20	1.93	1.17	5.800
4	0.3000	4.75	1.82	1.51	5.141
5	0.4000	5.60	1.73	1.86	5.257
6	0.5000	5.88	1.71	1.94	5.062
7	0.6000	4.25	2.07	0.85	5.000

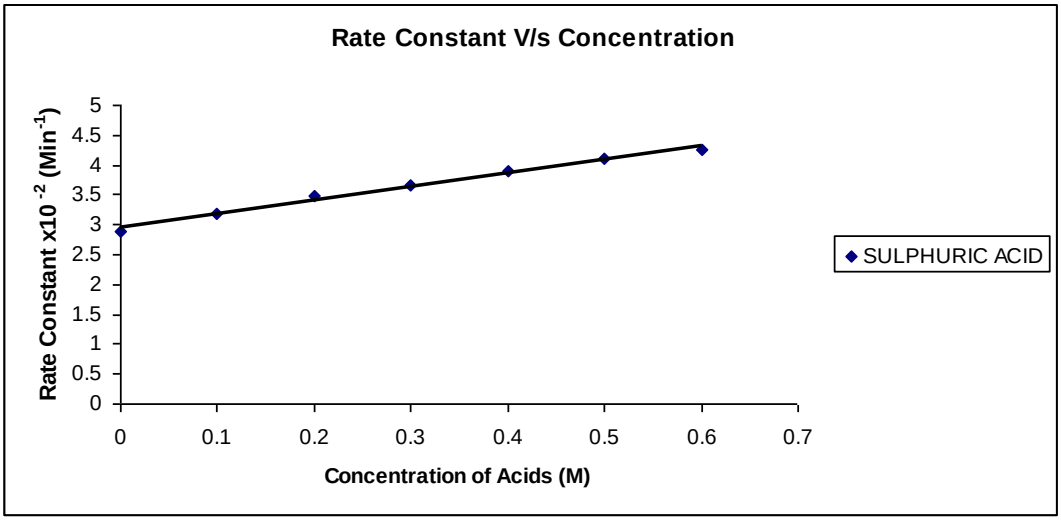
Salt Effect

In present investigation the author has observed the effect by increasing concentration of salts on the reaction mixture and retarding effect is observed on the rate constant.

Table 2

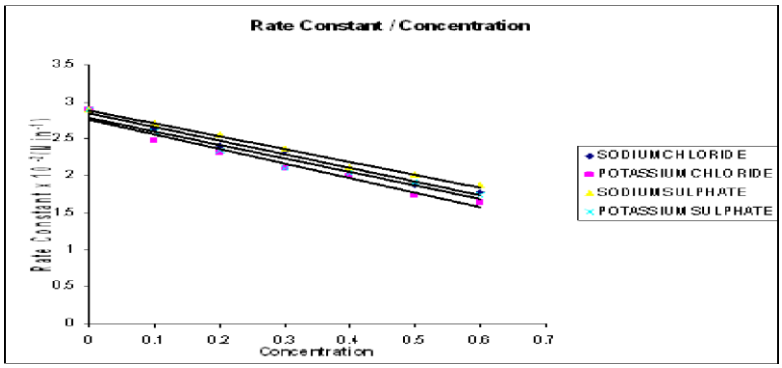
S. No.	Concentration of salts(M)	$Kx\ 10^{-2}$ (Min^{-1})			
		NaCl	KCl	Na_2SO_4	K_2SO_4
1	0.0000	2.89	2.89	2.89	2.89
2	0.1000	2.64	2.48	2.71	2.59
3	0.2000	2.41	2.32	2.56	2.34
4	0.3000	2.34	2.10	2.37	2.10
5	0.4000	2.10	2.00	2.12	2.04
6	0.5000	1.87	1.74	2.01	1.91
7	0.6000	1.78	1.64	1.88	1.74

Variation of rate constant with concentration of Sulphuric acid



Cf. Table no. 1

Variation of rate constant with concentration of salts



Cf. Table no. 2

Effect of Temperature:

The experiment was done at three different temperatures *ie*. 28ºC, 38ºC and 48ºC. and observation was that the rate of the reaction become almost doubled at every 10ºC rise in temperature. Hence reaction is normal and homogeneous and adhere to Arrhenius equation.

Rate constant at three different temperatures and pH values Table 3

S.No.	Concentration of Sulphuric Acid (M)	Rate Constants $Kx10^{-2}$ min^{-1}			pH at
		28°C	38°C	48°C	28°C
1	0.1000	3.18	6.23	12.65	3.18
2	0.2000	3.48	6.99	13.92	3.48
3	0.3000	3.65	7.26	14.60	3.65
4	0.4000	3.89	7.66	15.63	3.89
5	0.5000	4.02	8.12	16.08	4.10
6	0.6000	4.25	8.33	16.74	4.25

Temperature coefficients for all the reaction mixtures Table 4

S.No.	Concentration of Sulphuric Acid (M)	Temperature coefficient	
		K38/K28	K48/K38
1	0.1000	1.96	2.03
2	0.2000	2.01	1.99
3	0.3000	1.99	2.01
4	0.4000	1.97	2.04
5	0.5000	2.02	1.98
6	0.6000	1.96	2.01

Catalytic constant and dielectric constant Table 5

S.No.	Concentration of Sulphuric Acid (M)	Catalytic Constant x 10^{-1}	Dielectric Constant
1	0.1000	08.64*	1.685
2	0.2000	11.20	1.653
3	0.3000	12.32	1.639
4	0.4000	14.57	1.644
5	0.5000	15.41	1.619
6	0.6000	16.23	1.593
	Average	13.94	1.639

*Not included in average.

RESULT AND DISCUSSION

The oxidation of mixture of Malonic acid + Tartaric acid by Chromic acid were kinetically studied. In our investigation three main factors which affect the order of a chemical reaction, these are

1) Substrates
2) Oxidant
3) Hydrogen ion (H^+)

Here in this investigation order of reaction is one with respect to substrate, oxidant and $[H^+]$, hence rate of reaction is affected by the extent of acidwhich depends on certain factors like;

- Nature of added acid
- Concentration of added acid

In this reaction it is observed that the pH value of the reaction mixture do not change much by increasing concentration of Sulphuric acid.

The average values of Catalytic constant is found to be 13.94×10^{-1}

Energy of activation $\Delta E^{\#} = 12.754$ KCals and Frequency factor $A = 7.339 \times 10^7$

Hence the rate law is given as

$$-\frac{d[Cr(VI)(\text{Sulphuric acid})]}{dt} = k[Cr(VI)]$$

[Malonic acid] [Tartaric acid] $[H^+]$

CONCLUSION

The results obtained from above investigation shows that the end product of oxidation of Malonic acid + Tartaric acid is Carbondioxide and Carbonyl di carboxylic acid Which may confirmed by their ususal test. Several workers reported that the reaction between Malonic acid and Tartaric acid does not involve chain reaction, same observations are seen by author too. In view of author's observations it can be concluded that the retardation of the rate of oxidation of mixture of Malonic acid +Tartaric acid by Chromic acid in presence of Salt, is due to negative catalytic effect. Release of Carbon dioxide, in the oxidation of Tartaric acid by Chromic acid, shows that Chromic acid is attacking the – COOH group of Tartaric acid, not –COOH group of Malonic acid. Oxidation should therefore; take place on the methylene group of Malonic acid and it should involve two electron step. Hence proton of Malonic acid will be eliminated when Chromic acid attacked on > CH_2 and hence Carbonyl di carboxylic acid *i.e.* Meso Oxalic acid is obtained which is not oxidized by Chromic acid, while Tartaric acid is fully oxidized in to Carbon dioxide.[27-36]

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