MECHANISTIC STUDY OF OXIDATION OF MIXTURE OF OXALIC ACID AND MALONIC ACID BY CHROMIC ACID IN PRESENCE OF SULPHURIC ACID AND SALTS

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ABSTRACT:

The oxidation of mixture of Oxalic acid + Malonic acid in presence of Sulphuric acid in aqueous medium is reported here. The reaction is of first order with respect to each substrate; oxidant and $[H^+]$ .The oxidation of mixture of acids was studied at different concentration of H_2SO_4. The products are CO_2 and carbonyl di carboxylic acid. The rate constant increases with increase in concentration of added acid .The rate constant, catalytic constant, dielectric constant and effect of temperature were also determined. Various thermodynamic parameters like energy of activation, frequency factor were also determined. A mechanism consistent with result obtained has been proposed with the following rate equation:

$$-\frac{d[Cr(vi)]}{dt} = K[Cr(vi)](Malonic acid)(Oxalic acid)\ [H+]$$

KEYWORDS: *Mechanistic study, rate constant, catalytic constant, dielectric constant*

1. INTRODUCTION

Chromium (vi) has frequently used as an oxidant both in preparative and analytical chemistry .thus Chromyl chloride, chromic acid aqueous dichromate are the important Cr(vi) compounds used in oxidation of a wide variety of organic and in organic compounds in solution [1-7]. The kinetics of oxidation of mixture of dicarboxylic acid [4-5] and oxalic acid in particular has been the subject of detailed kinetic studies. The reactivity pattern of dicarboxylic acids in mixture of acids is little known [7-8].

2. EXPERIMENTAL

All the chemicals used were of analar grade manufactured by B.D.H., Merck, and Reidel .corning glassware's were employed and doubly distilled water is used through the study for preparations of solutions. The course of reaction was followed by Bausch & Lomb spcetronic 20 spectrophotometer and digital pH meter Systronic model 335(electronic) and refractive index is measured by Abbe's refractometer. The qualitative study was made under kinetic conditions and CO_2 and carbonyl dicarboxylic acid has been detected as the end products. The products were identified by physico-chemical methods [9]. The CO_2 and carbonyl dicarboxylic acid are confirmed by their usual tests.

2.1 Kinetic Analysis

The reaction was carried out in aqueous medium. The studies were carried out in the temperature range of 25°C to 45°C. All the solution were kept in a Toshniwal thermostat at constant temperature with accuracy ±0.10°C.the required volumes of these solution for each run were mixed and analyzed

spectrophotometrically. The first order reaction was obtained. Dielectric constant and catalytic constant were also determined for each run, shown in tables 2.

Table 1. Concentration and pH values

S.No.	Concentration (M)	$K*10^{-3}(Min^{-1})$	pH	$[H^+]*10^{-1}$
1	0.000	1.92	2.15	0.0707
2	0.100	3.04	2.09	0.0821
3	0.200	3.30	1.91	0.1230
4	0.300	3.69	1.76	0.1737
5	0.400	4.51	1.60	0.2511
6	0.500	5.45	1.51	0.3090
7	0.600	5.95	1.42	0.3801
8	0.700	6.70	1.33	0.4677
9	0.800	7.59	1.26	0.5495

2.2 Salt Effect

In our present investigation the authors have determined the effect of added salts. The salt effect depends on the nature of the reaction itself. In present investigation salt shows accelerating effect on rate constant [10].

2.3 Effect Of Temprature

The reaction was studied at three different temperature e.g. 25°C,35°C,45°C for the reaction ,the rate constants are also given , temperature coefficient is approximately two .hence reaction is of normal and homogenous. It was found that the data recorded adhere to Arrhenius equation. With increase in the temperature (every 10°C), the rate constant was almost double.

3. RESULT AND DISCUSSION

The oxidation of mixture of Oxalic acid +Malonic acid were kinetically studied, in our investigation there are three factors which affect the order of a chemical reaction. These are

➢ Concentration of oxidant
➢ Concentration of mixture acids
➢ H^+ concentration

The authors have studied the effect of Sulphuric acid on mixture of oxalic acid +Malonic acid by chromic acid in aqueous medium The order of the reaction is one with respect to substrate, oxidant and $[H^+]$,hence the rate of reaction is affected by the extent of acid with dependence on certain factors like;

1. Nature of added acid
2. Concentration of added acid

The pH values of such reaction mixture do not change much by the concentration of added H_2SO_4. The average value of catalytic constant is calculated and found to be in the order of 10.99 **x10^{-2}**.

$E_a = 13.47$ Kcals.

$\Delta H^{\ddagger} = 31.056$ K Cals.

$A = 3.36 \times 10^7$

Hence the rate law for this reaction is given as:

$$-\frac{d[Cr(vi)]}{dt} = K[Cr(vi)](Malonicacid)(Oxalicacid)[\text{H}+]$$

3.1 PRODUCT ANALYSIS

The main products of oxidation of mixture of oxalic acid+Malonic acid by chromic acid appear to be Carbon di oxide and carbonyl di carboxylic acid which may be confirmed by their usual test[9].Several workers [8,11-12] reported that the reaction between Malonic acid and Chromic acid does not involve chain or free radical mechanism, authors too found the same observation. In the mixture of Oxalic acid + Malonic acid liberation of Carbon di oxide shows that Chromic acid is attacking the –COOH group of Oxalic acid (as Oxalic acid does not have active Methylene group) not –COOH group of Malonic acid. Oxidation should 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 is obtained [5]. Thus the proposed mechanism for oxidation of mixture of Oxalic acid +Malonic acid by Chromic acid is as under:
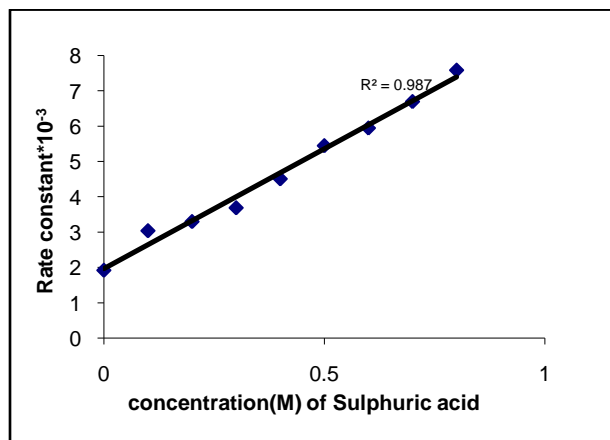

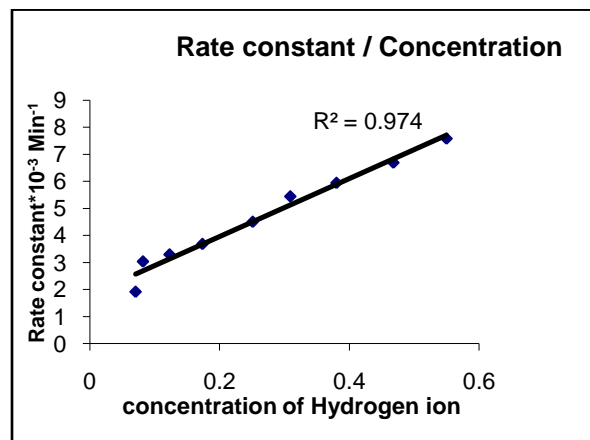**Fig.1** Variation of rate constant with the Concentration of Sulphuric acid

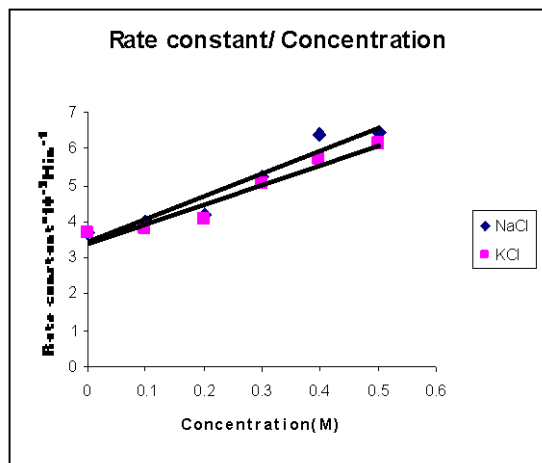**Fig. 2** Variation of rate constant with Hydrogen ion concentration

Fig. 3 Effect of NaCl and KCl on the oxidation of reaction mixture in presence of Sulphuric acid
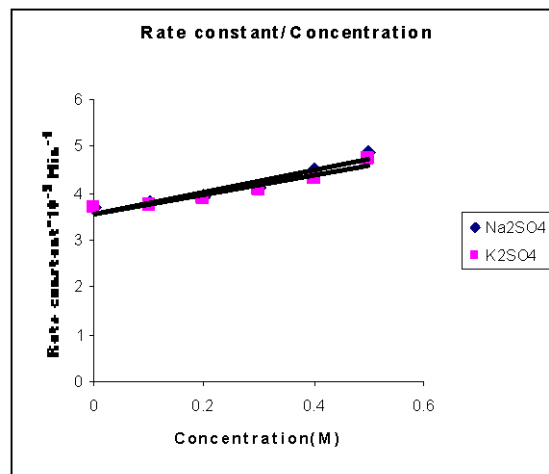

Fig. 4 Effect of Na_2SO_4 and K_2SO_4 on the oxidation of reaction mixture in presence of Sulphuric acid

Table 2. Rate constant at different temperature and pH value

S.No.	Concentration (M)	$K*10^{-3}$(Min^{-1})			pH
		25°C	35°C	45°C	
1	0.000	1.92	3.82	7.56	2.15
2	0.100	3.04	5.98	11.97	2.09
3	0.200	3.30	6.66	13.26	1.91
4	0.300	3.69	7.26	14.32	1.76
5	0.400	4.51	8.74	17.06	1.60
6	0.500	5.45	10.9	20.60	1.51
7	0.600	5.95	12.01	22.83	1.42
8	0.700	6.70	13.06	26.13	1.33
9	0.800	7.59	15.18	29.44	1.26

Table 3. Temperature coefficients for all the reaction mixtures

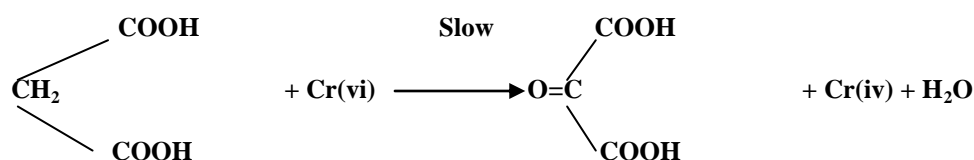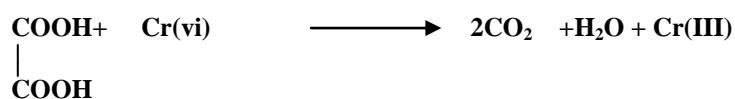| S. No.	Concentration of **Sulphuric** acid	TEMPERATURE COEFFICIENT	
		K_{35}/K_{25}	K_{45}/K_{35}
1	0.000	1.89	1.92
2	0.100	1.95	1.95
3	0.200	2.01	1.98
4	0.300	1.89	1.95
5	0.400	1.90	1.95
6	0.500	2.01	2.00
7	0.600	1.96	1.96
8	0.700	2.01	2.03
9	0.800	1.98	1.99

Table 4. Effect of salts on the oxidation of reaction mixture in presence of Hydrochloric acid
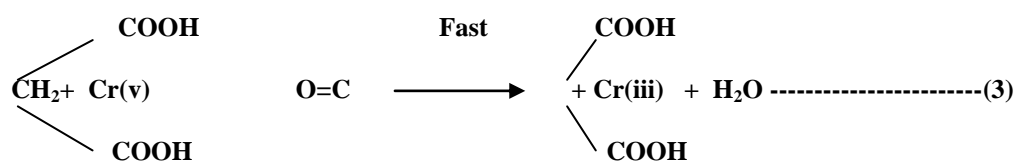
S.No.	Concentration (M)	$K*10^{-3}(Min^{-1})$			
		NaCl	KCl	Na_2SO_4	K_2SO_4
1	0.000	3.69	3.69	3.69	3.69
2	0.100	3.98	3.78	3.82	3.75
3	0.200	4.20	4.08	3.96	3.88
4	0.300	5.25	5.01	4.14	4.09
5	0.400	6.40	5.71	4.48	4.29
6	0.500	6.47	6.12	4.88	4.74

Table 5. Catalytic constant and Dielectric constant

S.No.	Concentration (M)	Catalytic constant$*10^{-2}$	Dielectric constant
1	0.000	-	1.305
2	0.100	13.64	1.303
3	0.200	11.21	1.301
4	0.300	10.19	1.299
5	0.400	10.31	1.297
6	0.500	11.42	1.296
7	0.600	10.60	1.294
8	0.700	10.22	1.292
9	0.800	10.31	1.290
	Average	**10.99**	**1.297**

4. MECHANISM OF REACTION

$CrO_3 + H_2O \rightleftharpoons H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+$ --------------------(1)

COOH + Cr(vi) $\longrightarrow$ $2CO_2$ + H_2O + Cr(III)
|
COOH

CH_2 (COOH, COOH) + Cr(vi) $\xrightarrow{\text{Slow}}$ O=C (COOH, COOH) + Cr(iv) + H_2O

Cr(vi) + Cr (iv) $\longrightarrow$ Cr(v)--(2)

$$\begin{array}{ccc} \text{CH}_2 + \text{Cr(v)} & O=C \xrightarrow{\text{Fast}} & + \text{Cr(iii)} + \text{H}_2\text{O} \end{array} \text{-----------------------(3)}$$

(Reaction showing oxalic/malonic acid structures with COOH groups)

5. CONCLUSION

The oxidation of mixture of Oxalic acid +Malonic acid were kinetically studied, in our investigation there are three factors which affect the order of a chemical reaction. These are

- Concentration of oxidant
- Concentration of mixture acids
- H^+ concentration

The authors have studied the effect of Sulphuric acid on mixture of oxalic acid +Malonic acid by chromic acid in aqueous medium The order of the reaction is one with respect to substrate, oxidant and $[H^+]$,hence the rate of reaction is affected by the extent of acid with dependence on certain factors like;

1. Nature of added acid
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The pH values of such reaction mixture do not change much by the concentration of added H_2SO_4. The average value of catalytic constant is calculated and found to be in the order of 10.99 **x10^{-2}**.

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