

KINETICS AND MECHANISM OF OXIDATION OF MIXTURE OF OXALIC ACID AND ADIPIC ACID BY CHROMIC ACID IN PRESENCE OF ACETIC ACID

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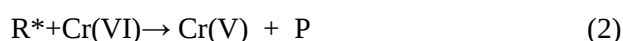
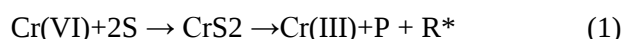
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ABSTRACT

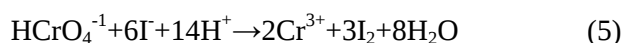
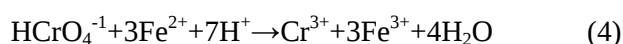
The kinetics of oxidation of mixture of Oxalic Acid and Adipic Acid by Chromic Acid in presence of Acetic Acid has been studied. The products are Succinic Acid and Carbon dioxide. The rate of oxidation increases with the increase in the concentration of Acetic Acid. Kinetics of oxidation of mixture of Oxalic Acid and Adipic Acid by Chromic Acid shows first order reaction at 27°C, order of the reaction is also one in presence of Acetic Acid. A mechanism consistent with the observed kinetic data has been proposed. The kinetic parameters such as catalytic constant, dielectric constant and temperature coefficient are calculated.

I INTRODUCTION

Several kinetic studies of Chromic Acid oxidation of different type of organic substrate have been carried out by different workers^{2,5,6,7} to understand the mechanistic aspects of reduction of Cr(VI) to Cr(III), to explore the effect of the substituent on the redox activity of Cr(VI). The oxidation of oxalic acid, co oxidation of carboxylic acid with oxalic acid and the oxidation of several carboxylic acids by acid chromate ion (HCrO_4^-) by substrate (S) producing radicals (R^*). The radical reduce additional Cr(VI) to Cr(V) giving products.



Chromic Acid has been long and successfully used as an oxidizing agent for both preparative and analytical purposes. The procedure underlying the stoichiometric equation (4) and (5)



Equation (4) and (5) are among the classic method of quantitative analysis.

Materials and methods; All the chemicals were of AR grade, Oxalic Acid (Merck) Adipic Acid (Merck) Chromium trioxide (Qualigens) and Acetic Acid (B.D.H.) and all other chemicals were used of highest purity

available commercially. Solutions were prepared in doubly distilled water. Solutions of the oxidant and reaction mixtures containing known quantities of the substrates (Oxalic Acid - 20ml, Adipic Acid - 20ml) Chromic Acid- 20ml, Acetic Acid - 20ml and other necessary chemicals were separately thermo stated ($\pm 0.1^{\circ}\text{C}$). The reaction was initiated by mixing the requisite amounts of the oxidant with the reaction mixture, monitored by following the rate of disappearance of Cr (VI) by spectrophotometrically. Data so obtained at 27°C on various reaction mixtures containing different concentration of Acetic Acid, while the concentration of Oxalic Acid, Adipic Acid and Chromic Acid were kept constant at 0.1750M, 0.1250M and 0.0038M respectively, concentration of Acetic Acid was varied from 0.0125 M to 0.1000M respectively.

Table No.01

RATE CONSTANT, pH VALUES AND HYDROGEN ION CONCENTRATION

S. No.	Concentration of Acetic Acid	Rate Constants $K \times 10^{-3} \text{ min}^{-1}$	pH value at 27°C	Hydrogen ion Concentration $\times 10^{-2}$
1	0.0000 M	5.3920	2.07	0.851
2	0.0125 M	6.1140	1.97	1.072
3	0.0250 M	6.7123	1.93	1.175
4	0.0375 M	6.9000	1.88	1.318
5	0.0500 M	7.1825	1.82	1.514
6	0.0625 M	7.6024	1.78	1.660
7	0.0750 M	7.8825	1.75	1.779
8	0.0875 M	8.1286	1.71	1.950
9	0.1000 M	8.5901	1.66	2.188

VARIATION OF RATE CONSTANT WITH THE CONCENTRATION OF ACETIC ACID of TABLE – 01

VARIATION OF RATE CONSTANT WITH THE HYDROGEN ION CONCENTRATION OF ACETIC ACID of TABLE - 01

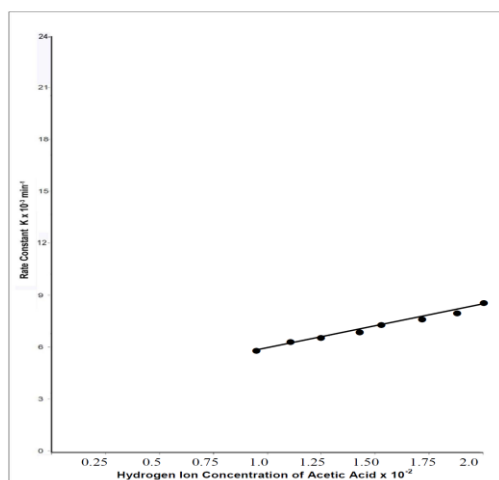


Fig. No: 1

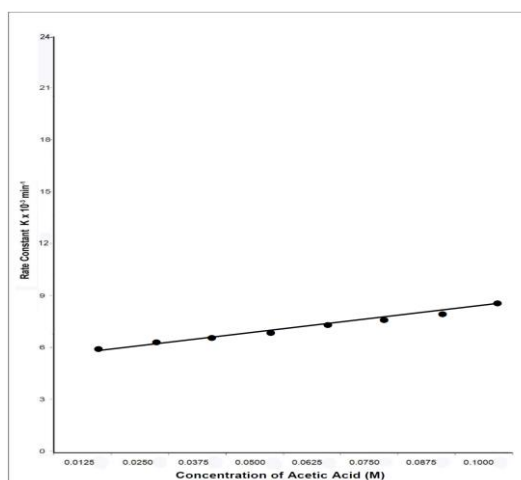


Fig. No: 2

TABLE NO: 2
CATALYTIC CONSTANT AND DIELECTRIC CONSTANT

S. No.	Concentration of Acetic Acid	Catalytic Constant $K_H^+ \times 10^{-1}$	Dielectric Constant
1	0.0000 M	-	1.959*
2	0.0125 M	0.0674	1.903
3	0.0250 M	1.1235	1.900
4	0.0375 M	1.1439	1.887
5	0.0500 M	1.1829	1.882
6	0.0625 M	1.1331	1.877
7	0.0750 M	1.4005	1.871
8	0.0875 M	1.4031	1.869
9	0.1000 M	1.4617	1.864
Average Value = 1.1394×10^{-1}			1.882

* Not included in the average

Table No: 3
RATE CONSTANT AT DIFFERENT TEMPERATURES

S. No.	Concentration of Acetic Acid	Rate constant $K \times 10^{-3} \text{ min}^{-1}$		
		27°C	37°C	47°C
1	0.0000 M	5.3920	10.5680	20.8202
2	0.0125 M	6.1140	12.0441	23.9681
3	0.0250 M	6.7123	13.2902	25.9155
4	0.0375 M	6.9000	13.3863	26.3723
5	0.0500 M	7.1825	13.8625	27.4472
6	0.0625 M	7.6024	14.9770	29.3550
7	0.0750 M	7.8825	15.4515	30.4362
8	0.0875 M	8.1286	16.0122	31.7045
9	0.1000 M	8.5901	16.7516	32.9981

TABLE NO: 4
TEMPERATURE COEFFICIENT

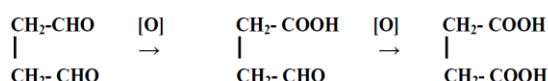
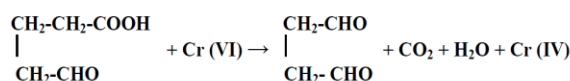
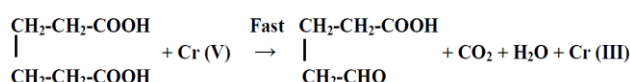
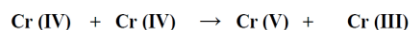
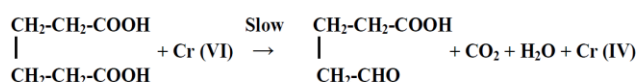
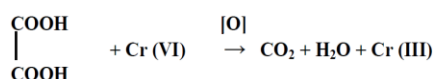
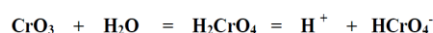
S. No.	Concentration of Acetic Acid	Temperature Coefficient	
		K_{37} / K_{27}	K_{47} / K_{37}
1	0.0000 M	1.96	1.97
2	0.0125 M	1.97	1.99
3	0.0250 M	1.98	1.95
4	0.0375 M	1.94	1.97
5	0.0500 M	1.93	1.98
6	0.0625 M	1.97	1.96\
7	0.0750 M	1.96	1.97
8	0.0875 M	1.97	1.98
9	0.1000 M	1.95	1.97

II RESULTS AND DISCUSSION

Reaction mixture containing Oxalic Acid, Adipic Acid and Chromic Acid were stirred in water at 27°C for 48 hours. The solvent removed using a rotator evaporator under reduced pressure. The residue was extracted using diethyl ether in separator funnel. The organic layer was concentrated with a rotator evaporator. The product,

Succinic Acid was identified by its spot test³. Product Succinic Acid was also confirmed by its melting point. The evolution of Carbon dioxide was tested by a conventional lime – water^{9,10} test. The order of the reaction with respect to Chromic Acid remains unaltered in the presence of Acetic Acid concentration in the system. A graph obtained between the rate constant and added concentration of Acetic Acid (Fig No. 01) suggests that the rate is a linear function of the concentration of Acetic Acid. Reaction is also first order with respect to H^+ as shown in Fig No.-02. The pH value decreases quite naturally with the increase in the Acetic Acid concentration. No significant change in the values of dielectric constant and catalytic constant of the system is observed by the concentration of the added Acetic Acid. Finally, the oxidation reaction was studied at three different temperatures, i.e., 27°C, 37°C and 47°C keeping all other experimental conditions constant. Values of rate constants and temperature coefficient are given in Table No-03 and - 04. As the value of temperature coefficient is equal to two, hence no unusual effect of temperature has been observed. As the rate of the reaction is altered in presence of Acetic Acid, hence reaction is catalyzed. The rate of reaction does not depend on the concentration of H^+ ion only. Thus the acid effect is not due to specific acid catalysis, it seems to be due to general acid catalysis.

Mechanism of the reaction:



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