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KINETICS OF OXIDATION OF MIXTURE OF OXALIC ACID AND ADIPIC ACID BY CHROMIC ACID IN PRESENCE OF SODIUM CHLORIDE AND POTASSIUM CHLORIDE.

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ABSTRACT

Effect of Sodium Chloride and Potassium Chloride on the co oxidation of Oxalic Acid and Adipic Acid by Chromic Acid has been studied. The products are Succinic Acid and Carbon dioxide. The rate of oxidation decreases with the increase in the concentration of Sodium Chloride and Potassium Chloride. It is found that Potassium Chloride is the most effective in retarding the reaction rate comparison to Sodium Chloride. The order of reaction is one in presence of Sodium Chloride and Potassium Chloride. The temperature coefficient at three deferent temperatures, catalytic constant and dielectric constant are determined.

I INTRODUCTION

The aqueous chemistry of Cr (VI) is significant, in basic solution, the yellow tetrahedral chromate ions CrO_4^{--} exist, with increasing acidity the yellow colour of the solution turns orange due to the formation of the dichromate ion $Cr_2O_7^{--/}$as a result of protonation and dimerisation,Cr(VI) is normally reduced to Cr(III) in a redox reaction, since the intermediate Cr(IV) and Cr(V) species are unstable under ordinary conditions. Cr(VI) is an excellent reducing agent. All available information indicates that Chromium (VI) is a very strong oxidant which will react very rapidly with any available reducing reagent.

II EXPERIMENTAL

All the chemicals were of. AR grade, Oxalic Acid (Merck) Adipic Acid (Merck) Chromium trioxide (Qualigens), Sodium Chloride (B.D.H.), Potassium Chloride (B.D.H.) and all other chemicals were used of highest purity available commercially. The solutions were prepared in double distilled water. The reacting solutions were kept in a thermostat for about half an hour. The temperature regulation was within ±0.1°C, after the solution had attended the 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 An aliquot of 5ml of the reaction mixture was then immediately withdrawn and its optical density (O.D.) measured at once.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 27°C on various reaction mixtures containing different concentration of Sodium Chloride and Potassium Chloride, 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 Sodium Chloride and Potassium Chloride was varied from 0.0125 M to 0.1000M respectively.

TABLE No: 1
RATE CONSTANT K X10^{-3} MIN $^{-1}$

S. No	Concentration of Salts	Rate Constant in presence of NaCl	Rate constant in presence of KCl
1	0.0000 M	5.3920	5.3920
2	0.0125 M	4.6715	4.3703
3	0.0250 M	4.5830	4.1035
4	0.0375 M	4.4141	3.8001
5	0.0500 M	4.1233	3.7150
6	0.0625 M	3.3944	3.2907
7	0.0750 M	3.0148	3.1978
8	0.0875 M	2.8300	2.5757
9	0.1000 M	2.8002	2.5323

TABLE NO: 2
CATALYTIC CONSTANT AND DIELECTRIC CONSTANT

S. No.	Concentration of Sodium Chloride	Catalytic Constant K_H^+ x 10^{-1}	Dielectric Constant
1	0.0000 M	----	1.959*
2	0.0125 M	-0.6275	1.917
3	0.0250 M	-0.6579	1.913
4	0.0375 M	-0.7252	1.907
5	0.0500 M	-0.8582	1.900
6	0.0625 M	-1.2320	1.885
7	0.0750 M	- 1.3995	1.880
8	0.0875 M	-1.4395	1.877
9	0.1000 M	-1.1846	1.873
Average Value = - 1.0155 x 10^{-1}			**1.894**

* Not included in the average

TABLE NO: 3
RATE CONSTANT AT DIFFERENT TEMPERATURES

S. No.	Concentration of Sodium Chloride	Rate constant K x 10^{-3} min^{-1}		
		27^0C	37^0C	47^0C
1	0.0000 M	5.3920	10.5683	20.8196
2	0.0125 M	4.6715	9.2235	17.9859
3	0.0250 M	4.5830	8.8910	17.0708
4	0.0375 M	4.4141	8.5634	17.1267
5	0.0500 M	4.1233	8.0404	15.7593
6	0.0625 M	3.3944	6.6862	13.1049
7	0.0750 M	3.0148	5.9396	11.4633
8	0.0875 M	2.8300	5.4941	10.5486
9	0.1000 M	2.8002	5.5160	10.7562

TABLE NO: 4
TEMPERATURE COEFFICIENTS

S. No.	Concentration of Sodium Chloride	Temperature Coefficient	
		K_{37} / K_{27}	K_{47} / K_{37}
1	0.0000 M	1.96	1.97
2	0.0125 M	1.97	1.95
3	0.0250 M	1.94	1.92
4	0.0375 M	1.94	2.00
5	0.0500 M	1.95	1.96
6	0.0625 M	1.97	1.96
7	0.0750 M	1.97	1.93
8	0.0875 M	1.94	1.92
9	0.1000 M	1.97	1.95

TABLE NO: 5
CATALYTIC CONSTANT AND DIELECTRIC CONSTANT

S. No.	Concentration of Potassium Chloride	Catalytic Constant K_{H^+} x 10^{-1}	Dielectric Constant
1	0.0000 M	----	1.959*
2	0.0125 M	-1.0369	1.922
3	0.0250 M	-1.176	1.915
4	0.0375 M	-1.2939	1.911
5	0.0500 M	-1.3018	1.907
6	0.0625 M	-1.3887	1.889
7	0.0750 M	-1.3846	1.883
8	0.0875 M	-1.6584	1.880
9	0.1000 M	-1.5359	1.875

Average Value = - 1.3470 x 10^{-1}	**1.897**

* Not included in the average

VARIATION OF RATE CONSTANT WITH THE CONCENTRATION OF SODIUM CHLORIDE cf TABLE -01

VARIATION OF RATE CONSTANT WITH THE CONCENTRATION OF POTASSIUM CHLORIDE cf TABLE -01

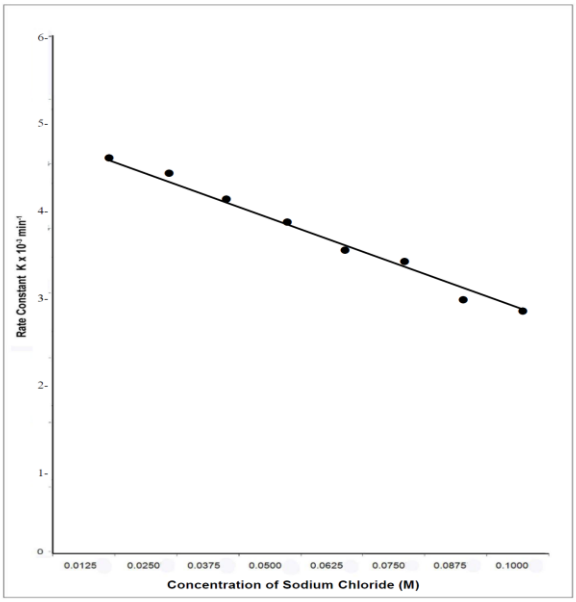

Fig. No: 1

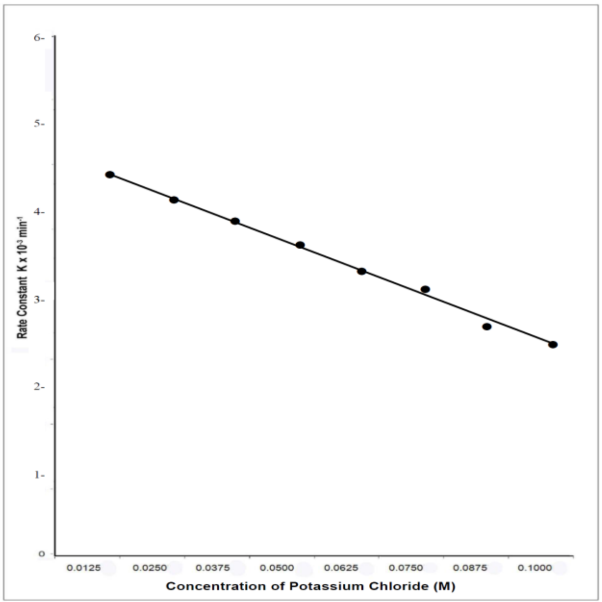

Fig.No: 2

TABLE NO: 6
RATE CONSTANT AT DIFFERENT TEMPERATURES

S. No.	**Concentration of Potassium Chloride** 2-	**Rate constant K x 10^{-3} min^{-1}**		
		27^0C	**37^0C**	**47^0C**
1	0.0000 M	5.3920	10.5683	20.8196
2	0.0125 M	4.3703	8.5794	16.7297
3	0.0250 M	4.1035	7.9598	15.2829
4	0.0375 M	3.8001	7.3720	14.7440
5	1- 0.0500 M	3.7150	7.2443	14.1987
6	0.0625 M	3.2907	6.4813	12.7033
7	0.0750 M	3.1978	6.3001	12.1591
8	0.0875 M	2.5757	4.9974	9.5951
9	0.1000 M	2.5323	4.9880	9.7267

Concetration of Potassium Chloride (M)

TABLE NO: 7
TEMPERATURE COEFFICIENT

S. No.	Concentration of Potassium Chloride	Temperature Coefficient	
		K_{37} / K_{27}	K_{47} / K_{37}
1	0.0000 M	1.96	1.97
2	0.0125 M	1.97	1.95
3	0.0250 M	1.94	1.92
4	0.0375 M	1.94	2.00
5	0.0500 M	1.95	1.96
6	0.0625 M	1.97	1.96
7	0.0750 M	1.97	1.93
8	0.0875 M	1.94	1.92
9	0.1000 M	1.97	1.95

III RESULTS AND DISCUSSION

The product, Succinic Acid was identified by its spot test[3]. Product Succinic Acid also confirmed by its melting point. The Carbon dioxide was tested by a lime water test. The order of the reaction with respect to Chromic Acid remains unaltered in the presence of Sodium Chloride and Potassium Chloride concentration in the system. A graph obtained between the rates constant and added concentration of Sodium Chloride and Potassium Chloride (Fig No. 01 and 02) suggests that the rate is linear function of the concentration of Sodium Chloride and Potassium Chloride. The pH value decrease quite naturally with the increase in the Sodium Chloride and Potassium Chloride concentration. The author's observations (Table No-1) show that the reaction rate is decreases as increase in the concentration of Sodium Chloride and Potassium Chloride in the system. It is observed that Potassium Chloride is the most effective than Sodium Chloride to retard the rate constant. The difference in the degree of dissociation of two chlorides under the author's experimental conditions would amount to unequal contribution of each chloride towards the ionic strength and hence this could be one reason for the observed effects of chlorides of Sodium and Potassium in retarding the reaction rate. Thus the observed effect could be due to such specific properties. The decrease in the reaction rate in presence of chlorides of Sodium and Potassium is due to negative catalysis which can be explained by several[2,6,9] ways.

Most important of them are;

(a) Slow formation of the activated complex and more stability of an intermediate catalyst 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 values of dielectric constant and catalytic constant of the system is observed by the concentration of the added Acetic Acid. Several[6,7,10] workers reported that the salt effect is only primary, if the temperature coefficient of the reaction is independent of addition of the salt concentration. It is clear from the Table No.-04 and 07 that each of these salt produced mostly primary salt effect which is attributed to the dependence of activity coefficient of ions and hence the activities of the reaction on the ionic strength of the system. The activity coefficient of ions always decreases by the addition of small quantities of the salt. All reactions involving the ions should be expected to show a negative salt effect.

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