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Kinetics and mechanism of oxidation of mixture of oxalic acid and phthalic acid by chromic acid in presence of chlorosubstituted acetic acid (monochloroacetic acid) and salts

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ABSTRACT

Kinetics and mechanism of oxidation of mixture of oxalic acid and phthalic acid by Chromic Acid in presence of monochloroacetic acid (chlorosubstituted acetic acid) and salts have been studied with spectrophotometerically in the temperature range 25°C. The reaction rate follows first order kinetics with respect to mixture of oxalic acid + phthalic acid, chromic acid and hydrogen ion concentration. In order to rate determination, Ostwald's isolation method was used. Rate of the reaction is increases with the increase in the added concentration of monochloroacetic acid. Kinetics parameters were determined at different concentrations of monochloroacetic acid and salts. The probable products of oxidation mixture are carbon dioxide and phthalic anhydride. Kinetic parameters such as catalytic constant, temperature coefficient and pH values are calculated. Probable mechanism for the reaction is proposed based on the experimental observations.

I INTRODUCTION

Phthalic acid is an aromatic dicarboxylic acid, with formula $C_6H_4(CO_2H)_2$. It is an isomer of isophthalic acid and terephthalic acid. Although phthalic acid is of modest commercial importance, the closely related derivative phthalic anhydride is a commodity chemical produced on a large scale. Phthalic acid is produced by the catalytic oxidation of naphthalene directly to phthalic anhydride and a subsequent hydrolysis of the anhydride. Phthalic acid was first obtained by French chemist Auguste Laurent[4] in 1836 by oxidizing naphthalene tetrachloride. Believing the resulting substance to be a naphthalene derivative, he named it "naphthalic acid". After the Swiss chemist Jean Charles Galissard de Marignac [11] determined its correct formula, Laurent[4] gave it its present name. Manufacturing methods in the nineteenth century included oxidation of naphthalene tetrachloride with nitric acid, or, better, oxidation of the hydrocarbon with fuming sulphuric acid, using mercury or mercury (II) sulphate as a catalyst. Oxalic acid in concentrated form can have harmful effects through contact and if ingested, manufacturers provide details in Material Safety Data Sheets (MSDS). It is not identified as mutagenic or carcinogenic, there is a possible risk of congenital malformation in the fetus, may be harmful if inhaled, and is extremely destructive to tissue of mucous membranes and upper respiratory tract, harmful if swallowed; harmful to and destructive of tissue and causes burns if absorbed through the skin or is in contact with the eyes. Symptoms and effects include a burning sensation, cough, wheezing, laryngitis, shortness of breath, spasm, inflammation and edema of the larynx, inflammation and edema of the bronchi, pneumonitis, pulmonary edema.

Chromium in aqueous solutions exists in both trivalent, Cr (III) and hexavalent Cr (VI) species. However, these two oxidation states are characterized by different physical and chemical behavior and toxicity. The compounds of Chromium (VI) pose serious dangers to biological systems, whereas those of Chromium (III) are relatively non-toxic. On the other hand, Chromium (VI) is one of the most versatile available oxidizing agents for the oxidation of organic compounds. It can be reduced to lower oxidation states by various biological and chemical reductants. The chemistry of the intermediate oxidation states of Chromium Cr (V) and Cr (IV), which observed during the oxidation of organic substrates by Chromium (VI) was attracted many researchers because of their implication in the mechanism of Chromium–induced cancers. Oxidation of organic compounds by Chromic Acid has been extensively studies.Westheimer[36] considered that the oxidation of alcohols by Chromic Acid involves reversible formation of a chromate ester which slowly decomposes by a process catalyzed by base. Mishra et al[7,22], have studied the oxidation of a number of acids and explained the mechanism on the basis of the Westheimer's[36] mechanism

II. MATERIALS AND METHOD

All the chemicals and reagents were of AnalaR grade Monochloroacetic Acid (Merck), Chromium Trioxide (Qualigens), Phthalic Acid (Merck) and others all chemicals were used as available commercially. Corning glassware's was employed and doubly distilled water is used throughout the experiment. Progress of the reaction was monitored by following the rate disappearance of Cr (VI) (decrease in optical density O.D) by using digital spectrophotometer and pH value by digital pH meter and refractive index by refractrometer.

2.1 Product Analysis

Equimolar amount of substrates and oxidant mixed together was kept for 24 hours. It was observed that initial light yellow colour changed to light blue colour, this clearly indicated that the reduction of Cr (VI) to Cr (II).The main oxidative product were identified as carbon dioxide and phthalic anhydride. Phthalic anhydride was confirmed by its melting point and other usual test while carbon dioxide by lime water tests.

The concentration of Chromic acid, Oxalic acid and Phthalic acid were kept constant at 8.25×10^{-3} M, 2.25×10^{-1} M and 3.25×10^{-1} respectively while the concentration of Monochloroacetic acid and salts have varied from1.00×10^{-1} M to $6.00.x\ 10^{-1}$ M respectively. Kinetic parameters such as rate constants, pH values, temperature coefficient catalytic constant and dielectric constant at 25°C of various reaction mixtures are given below in table no.01 to 09.

Table No-01

S. No	Concentrati- on of MCA (M)	Rate Constant K x 10^{-3} min-^{1}	pH values x10^{-2} at 25°C	Catalytic Constant	Dielectric Constant
1.	1.00 x10^{-2}	2.0571	1.75	0.3589	1.892
2.	2.00 x10^{-2}	2.1455	1.71	0.3589	1.889
3.	3.00 x10^{-2}	2.2775	1.69	0.4093	1.884
4.	4.00 x10^{-2}	2.3558	1.66	0.4178	1.881
5.	5.00 x10^{-2}	2.5525	1.60	0.4422	1.879
6.	6.00.x10^{-2}	2.7412	1.57	0.4827	1.875
Average Value				**0.4095**	**1.883**

Table No-02

Rate constants in presence of monochloroacetic acid (MCA) + salts at 25°C

S. No	Concentration of salt + MCA	Rate Constant K x 10^{-3} min-^{1} at 300K			
		NaCl + MCA	KCl + MCA	Na_2SO_4 + MCA	K_2SO_4 + MCA
1.	1.00 x10^{-2}	2.3578	2.0868	4.0553	2.9728
2.	2.00 x10^{-2}	2.4564	2.2125	4.2358	3.3365
3.	3.00 x10^{-2}	2.6570	2.3365	4.4005	3.4524
4.	4.00 x10^{-2}	2.8885	2.4482	4.5651	3.6520
5.	5.00 x10^{-2}	3.0995	2.6105	4.7235	30995
6.	6.00.x10^{-2}	3.3716	2.8275	5.0473	4.0023

Table No-03

Catalytic constants in presence of monochloroacetic acid (MCA) + salts at 25°C

S. No	Concentration of salt + MCA	NaCl + MCA	KCl + MCA	Na_2SO_4 + MCA	K_2SO_4 + MCA
1.	1.00 x10^{-2}	0.4486	0.3308	1.0895	0.6838
2.	2.00 x10^{-2}	0.4532	0.3690	1.0872	0.7718
3.	3.00 x10^{-2}	0.4950	0.3906	1.0999	0.7824
4.	4.00 x10^{-2}	0.5630	0.4099	1.0830	0.8026
5.	5.00 x10^{-2}	0.5748	0.4444	1.0621	0.8138
6.	6.00.x10^{-2}	0.6540	0.5978	1.0890	0.8098
Average Value = 0.5314			**0.4238**	**1.0852**	**0.7774**

Table No-04

Dielectric constant in presence of monochloroacetic acid (MCA) + salts at 25°C

S. No	Concentration of salt + acid	Rate Constant K x 10^{-3} min-^{1} at 25^{O}C			
		NaCl + MCA	KCl + MCA	Na_2SO_4 + MCA	K_2SO_4 + MCA
1.	1.00 x10^{-2}	1.886	1.889	1.880	1.883
2.	2.00 x10^{-2}	1.884	1.886	1.878	1.880
3.	3.00 x10^{-2}	1.880	1.882	1.875	1.877

4.	4.00 x10^{-2}	1.876	1.879	1.873	1.875
5.	5.00 x10^{-2}	1.873	1.876	1.869	1.871
6.	6.00.x10^{-2}	1.870	1.873	1.866	1.869
Average Value = 1.878			**1.880**	**1.873**	**1.875**

Table No-05

Temperature coefficient at different temperatures in presence of Monochloroacetic Acid (MCA)

S. No	Concentration of Acetic Acid (M)	Rate constants Kx10^{-3}at 25^{O}C	Rate constants Kx10^{-3} at35^{O}C	Rate constants Kx10^{-3} at 45^{O}C	Temperature Coefficient	
					K_{35} / K_{25}	K_{45} / K_{35}
1.	1.00 x10^{-2}	2.0571	4.0731	8.0239	1.98	1.97
2.	2.00 x10^{-2}	2.1455	4.2052	8.3263	1.96	1.98
3.	3.00 x10^{-2}	2.2775	4.4867	8.7490	1.97	1.95
4.	4.00 x10^{-2}	2.3558	4.5703	9.0034	1.94	1.97
5.	5.00 x10^{-2}	2.5525	5.0284	9.8054	1.97	1.95
6.	6.00.x10^{-2}	2.7412	5.4276	10.6380	1.98	1.96

Table No-06

Temperature coefficient at different temperatures in presence of Monochloroacetic Acid + NaCl

S. No	Concentration of Acetic Acid (M)	Rate constants Kx10^{-3}at 25^{O}C	Rate constants Kx10^{-3} at 35^{O}C	Rate constants Kx10^{-3} at 45^{O}C	Temperature Coefficient	
					K_{35} / K_{25}	K_{45} / K_{35}
1.	1.00 x10^{-2}	2.3578	4.5977	9.1035	1.95	1.98
2.	2.00 x10^{-2}	2.4564	4.8145	9.4847	1.96	1.97
3.	3.00 x10^{-2}	2.6570	5.2609	10.2587	1.98	1.95
4.	4.00 x10^{-2}	2.8885	5.6326	11.0962	1.95	1.97
5.	5.00 x10^{-2}	3.0995	6.1060	11.7846	1.97	1.93
6.	6.00.x10^{-2}	3.3716	6.7095	13.0164	1.99	1.94

Table No-07

Temperature coefficient at different temperatures in presence of Monochloroacetic Acid + KCl

S. No	Concentration of Acetic Acid (M)	Rate constants Kx10^{-3}at 25^{O}C	Rate constants Kx10^{-3} at 35^{O}C	Rate constants Kx10^{-3} at 45^{O}C	Temperature Coefficient	
					K_{35} / K_{25}	K_{45} / K_{35}
1.	1.00 x10^{-2}	2.0868	4.0693	7.9758	1.95	1.96
2.	2.00 x10^{-2}	2.2125	4.3808	8.6301	1.98	1.97
3.	3.00 x10^{-2}	2.3365	4.6263	8.9287	1.98	1.93
4.	4.00 x10^{-2}	2.4482	4.7985	9.4530	1.96	1.97
5.	5.00 x10^{-2}	2.6105	5.1688	10.0275	1.98	1.94
6.	6.00.x10^{-2}	2.8275	5.5136	10.8618	1.95	1.97

Table No-08

Temperature coefficient at different temperatures in presence of Monochloroacetic Acid + Na_2SO_4

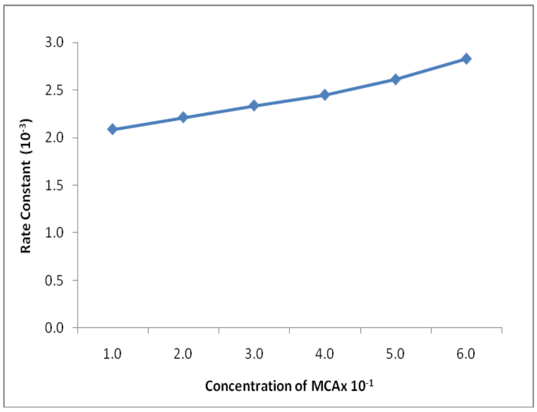
S. No	Concentration of MCA (M)	Rate constants $Kx10^{-3}$at 25^OC	Rate constants $Kx10^{-3}$ at 35^OC	Rate constants $Kx10^{-3}$ at 45^OC	Temperature Coefficient	
					K_{35} / K_{25}	K_{45} / K_{35}
1.	$1.00 x10^{-2}$	4.0553	7.9889	15.4187	1.97	1.93
2.	$2.00 x10^{-2}$	4.2358	8.3445	16.4387	1.97	1.97
3.	$3.00 x10^{-2}$	4.4005	8.7130	17.2517	1.98	1.98
4.	$4.00 x10^{-2}$	4.5651	9.0389	17.5355	1.98	1.94
5.	$5.00 x10^{-2}$	4.7235	9.3525	18.3310	1.98	1.96
6.	$6.00.x10^{-2}$	5.0473	9.7918	19.2898	1.94	1.97

Table No-09

Temperature coefficient at different temperatures in presence of Monochloroacetic Acid + K_2SO_4

S. No	Concentration of Acetic Acid (M)	Rate constants $Kx10^{-3}$at 25^OC	Rate constants $Kx10^{-3}$ at 35^OC	Rate constants $Kx10^{-3}$ at 45^OC	Temperature Coefficient	
					K_{35} / K_{25}	K_{45} / K_{35}
1.	$1.00 x10^{-2}$	2.9728	5.7078	11.2443	1.92	1.97
2.	$2.00 x10^{-2}$	3.3365	6.6063	12.8822	1.98	1.95
3.	$3.00 x10^{-2}$	3.4524	6.7667	13.5266	1.96	1.99
4.	$4.00 x10^{-2}$	3.6520	7.0849	13.9572	1.94	1.97
5.	$5.00 x10^{-2}$	30995	7.6820	15.1336	1.97	1.97
6.	$6.00.x10^{-2}$	4.0023	7.7244	15.2171	1.93	1.97

Value of temperature coefficients is determine at three different temperatures i.e., 25^OC, 35^OC and45^OC and found fairly constant as it is equal to 2at every 10^OC rise in temperature, so the temperature effect is purely thermal and reaction is normal and homogeneous and adhere to Arrhenius equation..



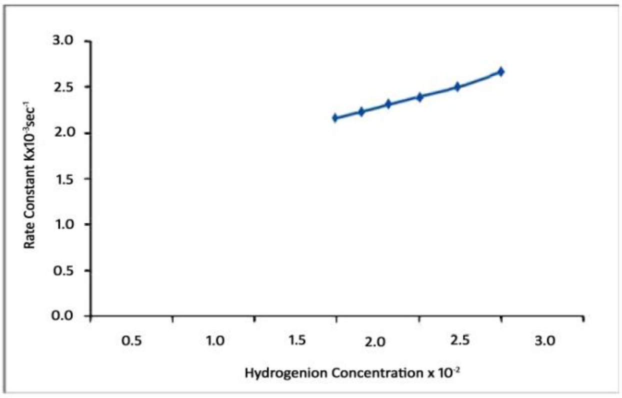


Fig.No.01 : VARIATION OF RATE CONSTANT WITH THE CONCENTRATION OF MCA cf TABLE -01

Fig. No.-02 :VARIATION OF RATE CONSTANT WITH THE HYDROGEN ION CONCENTRATIONOF MCA cf

III RESULTS AND DISCUSSION

In the oxidation of mixture of oxalic acid and phthalic acid by chromic acid in presence of monochloroacetic acid there are three main factors which affect the order of a chemical reaction, these are;

(a) Concentration of oxalic acid and phthalic acid
(b) Concentration of Cr(VI)
(c) Concentration of hydrogen ion

Here in the oxidation of acid mixture the order of reaction is one with respect to each. Hence rate of reaction is affected by the extent of acid which depends on certain factors such as;

(a) Nature of monochloroacetic acid
(b) Concentration of monochloroacetic acid

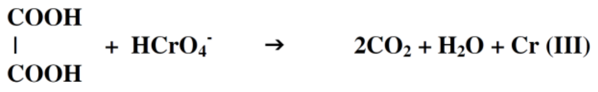
In the oxidation reaction it is observed that pH value of the reaction mixture do not much change by increasing the concentration of monochloro-acetic acid. The average value of Catalytic constant is found to be order of 0.4095 and average value of dielectric constant is order of1.883.

IV CONCLUSION

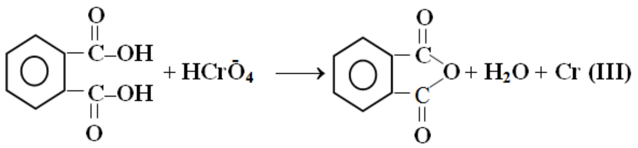
Over all oxidation end product of mixture of oxalic acid and phthalic acid are carbon dioxide and phthalic anhydride, which may confirmed by their usual test. In view of the author's observations it can be concluded that the accelerating of the rate of oxidation of acid mixtire by chromic acid in presence of monochloroacetic acid and salts is positive catalysis effect. Liberation of carbon dioxide shows that chromic acid is attacking the –COOH group of oxalic acid not of phthalic acid.

MECHANISM

$$\mathbf{CrO_3 + H_2O = H_2CrO_4 = H^+ + HCrO_4^-}$$



$$\begin{array}{l}\mathrm{COOH}\\ \mid\\ \mathrm{COOH}\end{array} + \mathrm{HCrO_4^-} \rightarrow 2\mathrm{CO_2} + \mathrm{H_2O} + \mathrm{Cr\ (III)}$$



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