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KINETICS AND MECHANISM OF OXIDATION OF L-ASCORBIC ACID BY CHROMIC ACID IN PRESENCE OF HYDROCHLORIC ACID

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ABSTRACT

The kinetics of oxidation of L-Ascorbic Acid by Cr (VI) in presence of Hydrochloric Acid has been studied spectrophotometerically at 301K. The oxidation product was Dehydroascorbic Acid. Reaction rate is increases in the presence of Acetic Acid have been noticed. The rate of the oxidation reaction is depends on the nature of oxidant and pH of the medium. The results show that the logarithm of the rate constants of oxidation increases with the increase in the concentration of Hydrochloric Acid. Kinetics of oxidation of L-Ascorbic Acid by Chromic Acid shows first order reaction, order of the reaction is also one in presence of Hydrochloric Acid. The kinetic parameters such as catalytic constant, dielectric constant and temperature coefficient are calculated.

I. INTRODUCTION

L-Ascorbic Acid is a good biological reducing agent. The redox reaction of L-Ascorbic Acid is a fundamental interest in chemistry, biochemistry, pharmacology and several areas of medicines. It is used one or two electron reductant in chemical and biological systems. Ascorbic Acid is classed as a reduction. The ascorbate anion is stabilized by electron delocalization. For this reason, Ascorbic Acid is much more acidic than would be expected if the compound contained only isolated hydroxyl groups. The ascorbate ion is the predominant species at typical biological pH values. It is a mild reducing agent and antioxidant. It is oxidized with loss of one electron to form a radical cation and then with loss of a second electron to form Dehydroascorbic Acid. It typically reacts with oxidants of the reactive oxygen species, such as the hydroxyl radical. Such radicals are damaging to animals and plants at the molecular level due to their possible interaction with nucleic acids, proteins and lipids. Sometimes these radicals initiate chain reactions. Ascorbate can terminate these chain radical reactions by electron transfer. Ascorbic Acid is special because it can transfer a single electron, owing to the resonance-stabilized nature of its own radical ion, called semi dehydro ascorbate. The net reaction is:

$$RO\bullet + C_6H_7O_6^{-} \rightarrow ROH + C_6H_6O_6^{\bullet -}$$

The oxidized forms of ascorbate are relatively un reactive and do not cause cellular damage. However, being a good electron donor, excess ascorbate in the presence of free metal ions can not only promote but also initiate free radical reactions, thus making it a potentially dangerous pro-oxidative compound in certain metabolic contexts. A large number of investigations have been directed towards understanding the mechanism of Chromic Acid oxidation of organic substrates. Bogdan Banas[4] has reported a stopped-flow study of the oxidation reaction of Ascorbic Acid with Chromic Acid. Babatunde O.A.[5] has reported kinetics approach to the mechanism of oxidation of L-Ascorbic Acid by periodate ion in acidic medium. Eleftheria K. Koliou and Panayiotis V. Ioannou[6] have reported prepration of dehydro-l-Ascorbic Acid dimer by air oxidation of l-Ascorbic Acid in the presence of catalytic amounts of Copper (II) acetate & Pyridine Carbohydrate. Jiang D.,Liu L.,Yagnik G.B., and Zhou F.[10] have reported, rate and mechanism of Ascorbic Acid oxidation by molecular oxygen by Cu (II). However, no kinetic data for the oxidation of L-Ascorbic Acid by Chromic Acid in presence of Hydrochloric Acid are known.

II. MATERIALS AND METHODS

L-Ascorbic Acid was purchased from the S.D.F.Chem, Chromium Trioxide was purchased from the Qualigens and Hydrochloric Acid was purchased from the Merck. All the chemicals were used as received. All the solutions were prepared in doubly distilled water. Chromic Acid was prepared by dissolving known amount of Chromium Trioxide in double distilled water and its concentration was checked iodometrically. Solutions of different concentrations were prepared by proper dilution of stock solution. Solutions of the oxidant and reaction mixture containing known quantities of the substrate - L-Ascorbic Acid, oxidant - Chromic Acid, Hydrochloric Acid and other necessary solutions were separately thermo stated (± 0.1^0C).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 spectro photometrically. To know the effect of concentrations and temperature on the oxidation of L-Ascorbic Acid by Chromic Acid in presence of Hydrochloric Acid under first order conditions by keeping the concentration of L-Ascorbic Acid at least twenty four times in excess over Chromic Acid. In order to investigate the effect of Hydrochloric Acid on the oxidation of L-Ascorbic Acid by Chromic Acid, a series of kinetic runs were performed by keeping the concentrations of Chromic Acid and L-Ascorbic Acid constant at 4.25×10^{-3} M and 1.00×10^{-1} M respectively, while the concentration of Hydrochloric Acid had varied from 1.25×10^{-2} M to 8.75 M. The rate constant and temperature coefficient of various reaction mixtures at 301K, 311K and 321K are recorded below in the table No 01.

Table No. 01

S. No.	Concentration of HCl (M)	Rate constant K x 10^{-3} min^{-1}			Temperature Coefficient	
		301K	311K	321K	K_{311} / K_{301}	K_{321} / K_{311}
1	0.00×10^{-2}	3.9615	7.7249	15.2955	1.95	1.98
2	1.25×10^{-2}	8.2558	16.1814	31.8772	1.96	1.97

3	2.50×10^{-2}	8.7458	17.3167	33.7675	1.98	1.95
4	3.75×10^{-2}	9.3428	18.3189	36.0744	1.96	1.97
5	5.00×10^{-2}	10.0656	19.9299	39.0626	1.98	1.96
6	6.25×10^{-2}	10.5195	20.7274	40.4183	1.97	1.95
7	7.50×10^{-2}	11.1264	21.7685	43.1017	1.96	1.98
8	8.75×10^{-2}	11.6454	22.9414	44.7358	1.97	1.95

To know the pH value, Hydrogen ion concentration, catalytic constants and dielectric constant at different concentrations of Hydrochloric Acid at 301K temperature a series of kinetic runs were performed by keeping the concentrations of Chromic Acid and L-Ascorbic Acid constant at 4.25×10^{-3} M and 1.00×10^{-1} M respectively, while the concentration of Hydrochloric Acid had varied from 1.25×10^{-2} M to 8.75 M respectively, values are recorded in the table No.02.

Table No. 02

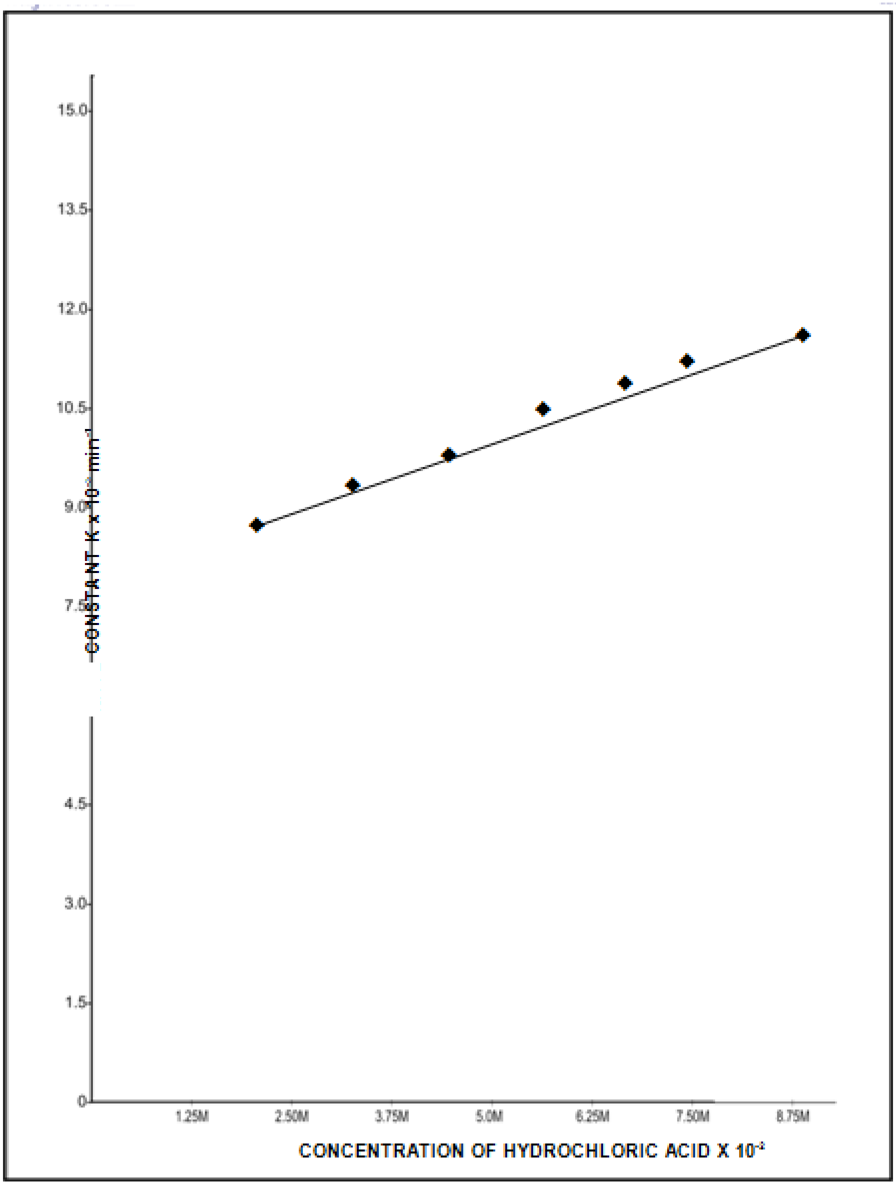
S. No	Concentration of HCl (M)	pH Value	H^+ Ion Concentration	Catalytic Constant	Average Value of Catalytic Constant	Dielectric Constant	Average Value of Dielectric Constant
1	0.00×10^{-2}	1.99	1.023	-	2.1931	1.918*	1.860
2	1.25×10^{-2}	1.68	2.089	2.0557		1.869	
3	2.50×10^{-2}	1.65	2.239	2.1368		1.865	
4	3.75×10^{-2}	1.61	2.455	2.1920		1.863	
5	5.00×10^{-2}	1.53	2.754	2.2164		1.861	
6	6.25×10^{-2}	1.53	2.951	2.2230		1.858	

7	7.50 x 10^{-2}	1.50	3.162	2.2596		1.855	
8	8.75 x 10^{-2}	1.47	3.388	2.2680		1.852	

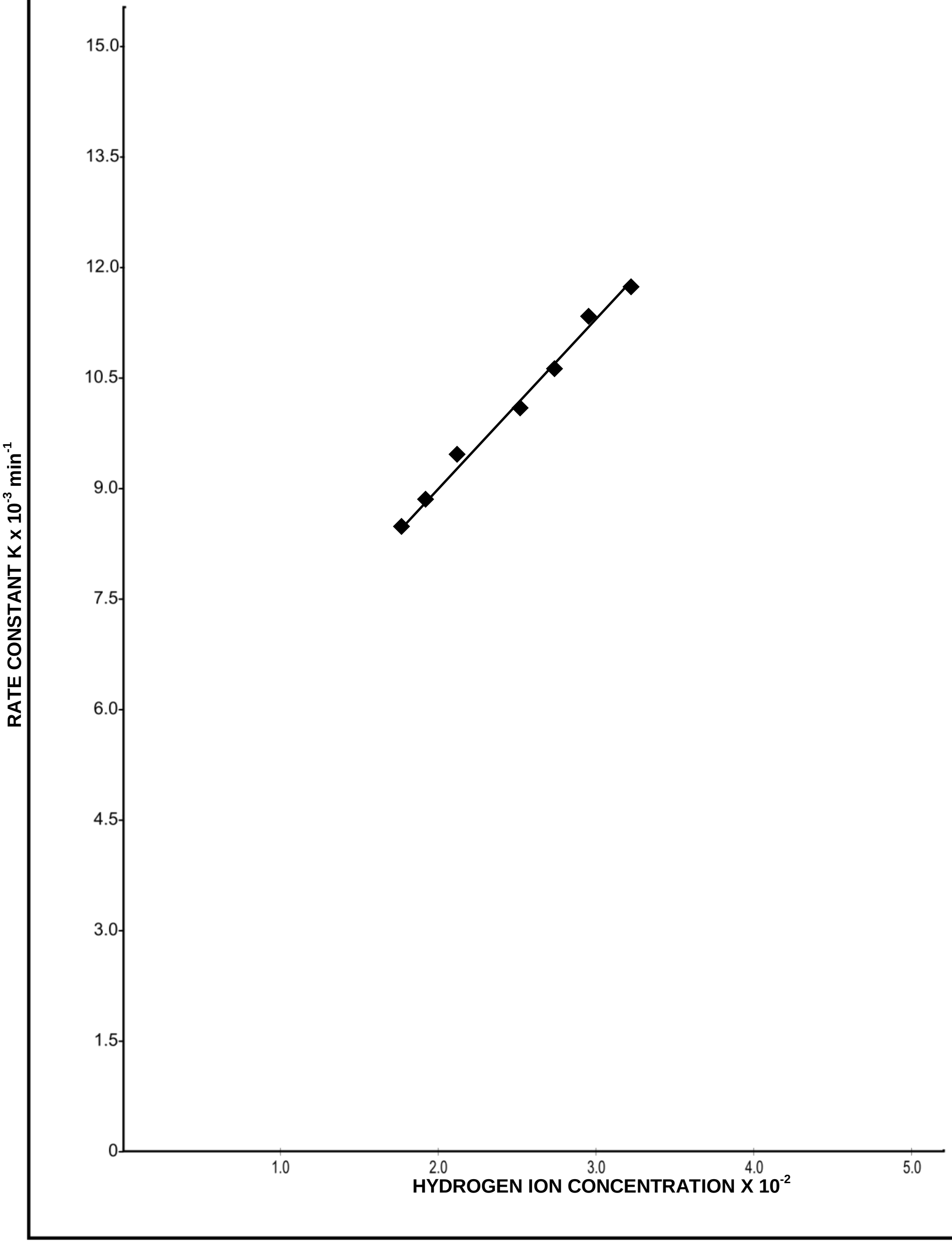
* Not included in the average

Fig No. 1

VARIATION OF RATE CONSTANT AT 301K TEMPERATURE WITH THE CONCENTRATION OF HYDROCHLORIC ACID cf TABLE – No.1



VARIATION OF RATE CONSTANT AT 301K TEMPERATURE WITH THE HYDROGEN ION CONCENTRATION cf TABLE – 01 and 02

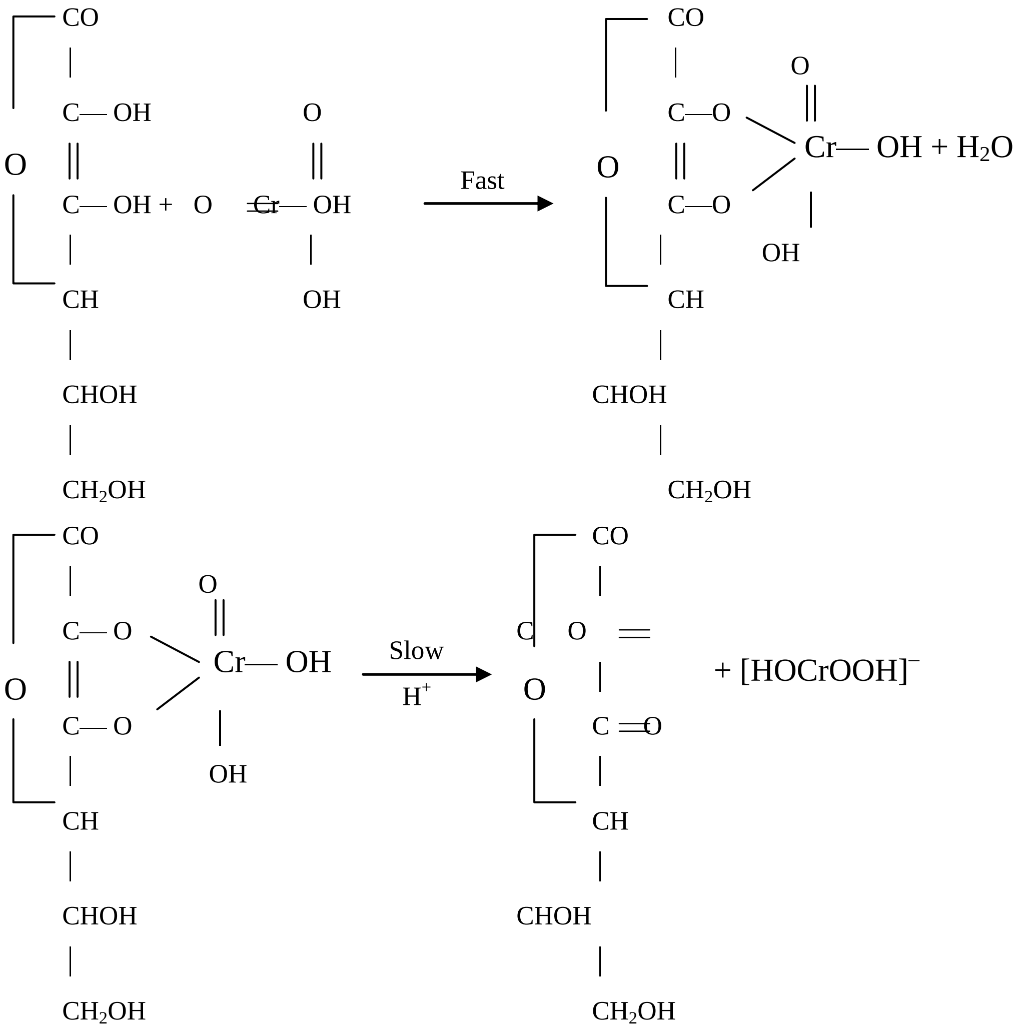


RESULT AND DISCUSSION;We have made a detailed study of the L-Ascorbic Acid - Chromic Acid reaction in presence of Hydrochloric Acid at different concentrations and temperatures. Our main goals have been to detect end product and give a proposed mechanism of the reaction. In the oxidation of L-Ascorbic Acid by Chromic Acid the kinetic behavior of the reaction is the same in the presence of Hydrochloric Acid as in its absence as shown in the observation (Table No. 01).The reaction rate however increases with the increase in the concentration of Hydrochloric Acid in the system. A graph obtained between rate constant and concentration of Hydrochloric Acid (Fig. No. 01) suggest that the rate is linear function of the concentration of Hydrochloric Acid. A plot obtained (Fig. No. 02) between rate constant and Hydrogen ion concentration also suggest that oxidation reaction is first order with respect to Hydrogen ion concentration. The reaction follows first order kinetics with respect to oxidant and substrate. The total order is two. The kinetic equation proposed for the oxidation of L-Ascorbic Acid by Chromic Acid is given below;

$$-\frac{d\,[\,Cr\,(VI)\,]}{dt} = K\,[Cr\,(VI)][\,L\text{-Ascorbic Acid}][\,HCl]$$

In order to study the overall oxidation product of L-Ascorbic Acid by Chromic Acid reaction, all reactants were mixed in equimolar amounts. After twenty four hours it was observed that initial light yellow colour changed to light blue colour which indicates the reduction of hexavalent Chromium to trivalent Chromium . The main oxidative product of L-Ascorbic Acid was identified as Dehydroascorbic Acid[12,14,26]. It was also confirmed by its M.P. On the basis of the above results the author proposed the following mechanism;

$$CrO_3 \;+\; H_2O \;=\; H_2CrO_4 \;=\; H^+ \;+\; HCrO_4^-$$



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