



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

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### ABSTRACT

The kinetics of oxidation of L-Ascorbic Acid ( $H_2A$ ) by Chromic Acid in presence of Sulphuric Acid has been studied at 301K temperature. The oxidation product was Dehydroascorbic Acid (DA). Reaction is catalysis by  $H^+$  has been noticed. The results show that the logarithm of the rate constants of oxidation increases with the increase in the concentration of Sulphuric 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 Sulphuric Acid. The kinetic parameters such as catalytic constant, dielectric constant and temperature coefficient are calculated.

### INTRODUCTION

A large no of investigations have been directed towards understanding the mechanism of Chromic Acid oxidation of organic substrates. All available information<sup>1,2,3,6</sup> indicates that Chromium (VI) is a very strong oxidant which will react very rapidly with any other reducing reagent..Chromic Acid principally made by adding Chromium Trioxide to water. Chromic Acid has long been used as an oxidizing agent in preparative organic chemistry; it is only in comparatively past years that kinetic or mechanistic investigations have been conducted.

The first careful and detailed investigation into the mechanism of Chromium (VI) reduction was provided by Novick and Westheimer<sup>7</sup> using isopropyl alcohol as substrate. Studying the Chromium (VI) reduction in water-acidic medium they suggested that the first step of Chromium (VI) reduction is an ester formation between the chromate and substrate, which is a fact a complexation of Chromium (VI) by the substrate(s). Later, the Chromium (VI) complex formation was confirmed specrophotometrically for many organic and inorganic substrates. Klaning and Symons<sup>9</sup> have studied the complexation of chromates with different alcohols and have shown that complex formation is connected with the appearance of a few band ( $\lambda=450\text{nm}$ ) in the visible spectrum assigned to a charge transfer from oxygen to Chromium.

The Westheimer<sup>10</sup> mechanism is also accepted for the oxidation of some other substrates. It should be noted, however, that the Chromium (VI) reduction might also proceed in systems where no  $\text{Cr}^{\text{VI}}-\text{S}$  formation takes

place. Thus oxidation of many Hydrocarbons and Ethers by Chromium (VI) can proceed although no evidence for any complex formation has been found.

## **II MATERIALS AND METHODS**

All chemicals were commercially available and used as received from the manufacturer. They were of AR grade, H<sub>2</sub>A (Sun Chem) Chromium Trioxide (Qualigens). Sulphuric Acid (B.D.H.). All the solutions were prepared in doubly distilled water. [Cr (VI)] was prepared by dissolving known amount of Chromium Trioxide. Solutions of the oxidant and reaction mixture containing known quantities of the substrate H<sub>2</sub>A, Chromic Acid, Sulphuric Acid 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 spectro photo metrically. In order to investigate the effect of Sulphuric Acid and temperatures on the oxidation of H<sub>2</sub>A by Chromic Acid, a series of kinetic runs were performed by keeping the concentrations of Chromic Acid and H<sub>2</sub>A constant at  $4.25 \times 10^{-3}$  M and  $1.00 \times 10^{-1}$  M respectively, while the concentration of Sulphuric Acid had varied from  $1.25 \times 10^{-2}$  M to  $8.75 \times 10^{-2}$  M. The rate constant and temperature coefficients of various reaction mixtures at 301K, 311K and 321K temperature are recorded below in the table No 01.

**Table No. 1**

<b>S. No.</b>	<b>Concentration of H<sub>2</sub>SO<sub>4</sub> (M)</b>	<b>Rate constant K x 10<sup>-3</sup> min<sup>-1</sup></b>			<b>Temperature Coefficient</b>	
		<b>301K</b>	<b>311K</b>	<b>321K</b>	<b>K<sub>311</sub> / K<sub>301</sub></b>	<b>K<sub>321</sub> / K<sub>311</sub></b>
1	$0.00 \times 10^{-2}$	2.3523	4.6576	9.0822	1.98	1.95
2	$1.25 \times 10^{-2}$	9.0927	17.7308	34.9296	1.95	1.97
3	$2.50 \times 10^{-2}$	10.1431	19.8805	39.3633	1.96	1.98
4	$3.75 \times 10^{-2}$	10.4573	20.6009	40.1717	1.97	1.95
5	$5.00 \times 10^{-2}$	11.9235	23.1316	45.5692	1.94	1.97
6	$6.25 \times 10^{-2}$	12.0993	23.9566	46.7161	1.98	1.95
7	$7.50 \times 10^{-2}$	12.4930	24.4863	48.2380	1.96	1.97
8	$8.75 \times 10^{-2}$	14.1494	27.873	54.6337	1.97	1.96

The pH value, Hydrogen ion concentration, catalytic constant and dielectric constant at different concentrations of Sulphuric Acid at 301K temperature are recorded in the table No.2.

**Table No.2**

**pH VALUE, H<sup>+</sup> ION CONCENTRATION, CATALYTIC CONSTANT AND DIELECTRIC CONSTANT**

Initial concentration of Chromic Acid =  $4.25 \times 10^{-3}$  M

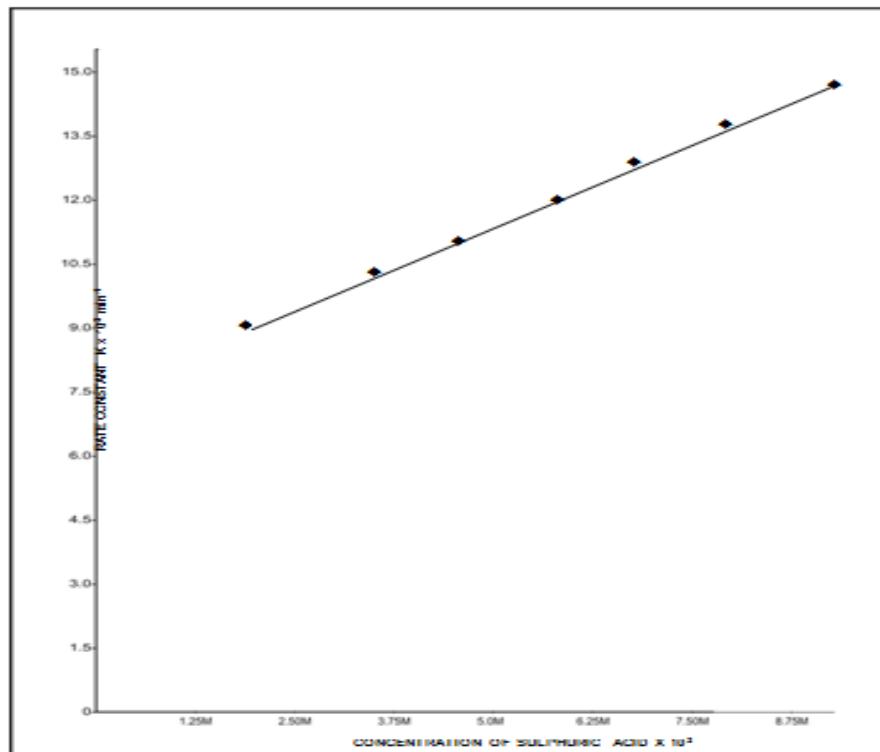
Initial concentration of H<sub>2</sub>A =  $1.00 \times 10^{-3}$  M

S. No	Concentration of H <sub>2</sub> SO <sub>4</sub> (M)	pH Value	H <sup>+</sup> Ion Concentration	Catalytic Constant	Average Value of Catalytic Constant	Dielectric Constant	Average Value of Dielectric Constant
1	$0.00 \times 10^{-2}$	1.95	1.122	-	2.3022	1.801*	1.750
2	$1.25 \times 10^{-2}$	1.51	3.090	2.1814		1.758	
3	$2.50 \times 10^{-2}$	1.46	3.469	2.2458		1.756	
4	$3.75 \times 10^{-2}$	1.45	3.584	2.2614		1.753	
5	$5.00 \times 10^{-2}$	1.43	3.715	2.3072		1.751	
6	$6.25 \times 10^{-2}$	1.38	4.169	2.33380		1.747	
7	$7.50 \times 10^{-2}$	1.37	4.266	2.3771		1.745	
8	$8.75 \times 10^{-2}$	1.31	4.898	2.4086		1.743	

\* Not included in the average

**Fig. No.1**

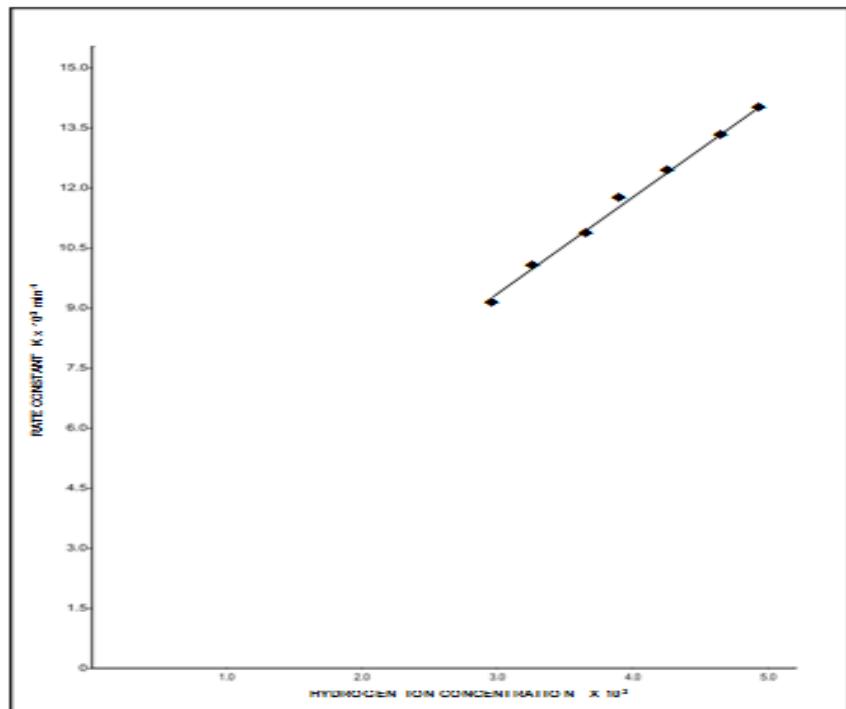
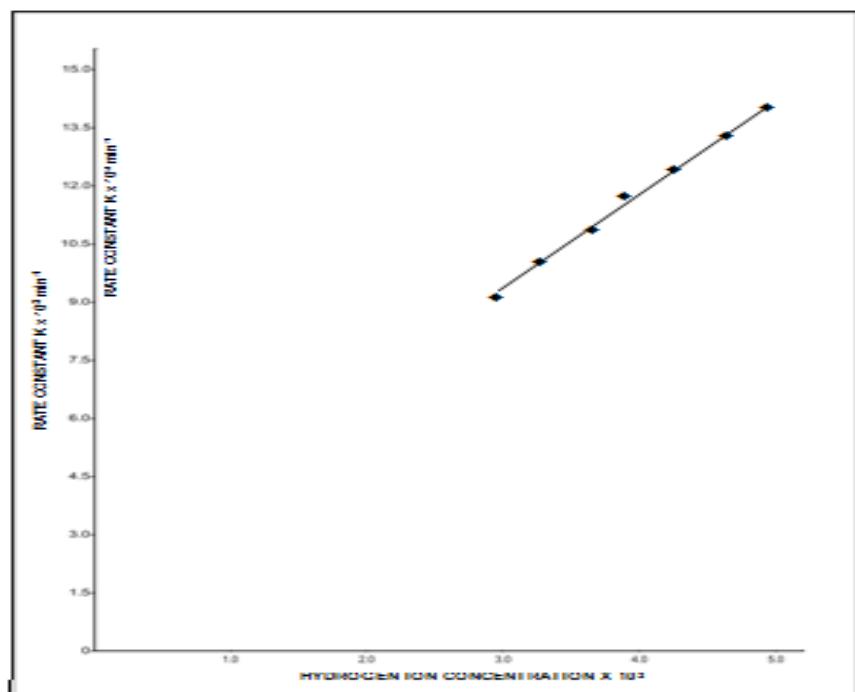
**VARIATION OF RATE CONSTANT AT 301K TEMPERATURE WITH THE CONCENTRATION OF SULPHURIC ACID cf TABLE – 1**





**Fig. No. 2**

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



### III RESULT AND DISUSSION

The kinetic behavior of the oxidation reaction of H<sub>2</sub>A by Chromic Acid in presence of Sulphuric Acid is the same as in its absence as shown in the observation (Table No.01).The reaction rate however increases with the increase in the concentration of added Sulphuric Acid in the system. A plot obtained between the rate constant and concentration of Sulphuric Acid (Fig. No.01) suggest that the rate is linear function of the added concentration of Sulphuric Acid. Oxidation reaction of H<sub>2</sub>A in presence of Sulphuric Acid is first order with respect to Hydrogen ion concentration as shown in Fig No 02. The order of reaction with respect to oxidant is one and also one with respect to substrate. Total order of the oxidation reaction is two. The pH value of the system decreases quite naturally with the increase in the added Sulphuric Acid concentration. The average value of dielectric constant is determined and found to be of the order of 1.750.The average value of catalytic constant is also determined and found to be of the order of 2.3022. In view of the data given in table No.01, no unusual effect of temperature has been observed.

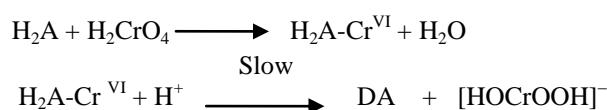
The kinetic equation proposed for this reaction is given below;

$$-\frac{d [ \text{Cr (VI)} ]}{dt} = K [ \text{Cr (VI)} ] [ \text{H}_2\text{A} ] [ \text{H}_2\text{SO}_4 ]$$

To determine the overall end products of the oxidation of H<sub>2</sub>A by [Cr (VI)] reaction, both reactants were mixed in equimolar amounts. After twenty four hours it was seen that initial light yellow colour changed to light blue colour which indicates the reduction of [Cr (VI)] to [Cr (III)]. The main oxidative product of H<sub>2</sub>A was identified as Dehydroascorbic Acid (DA)<sup>4,5,8</sup>. It was also confirmed by its Melting Point. On the basis of the above results the author proposed the following mechanism;



Fast



The overall reaction may be written as;



Where,

[H<sub>2</sub>A] = L-Ascorbic Acid

[Cr (VI)] = Chromic Acid

[C] = Concentration of Complex

[P] = Concentration of Product

[B] = Concentration of By Product

The rate law derived on the basis of above mechanism is as follows;

$$-\frac{d [\text{C}]}{dt} \propto [\text{C}] = K [\text{C}]$$

Concentration of complex, [C] can be calculated by applying steady state concept.

Rate of formation of complex = Rate of disappearance of complex

$$k^I_I [H_2A] [Cr(VI)]_{eqm} = k^I_{-I}[C] + k[C]$$

Where  $[H_2A]$  equilibrium concentration of L-Ascorbic Acid

Since  $[Cr(VI)]_{total} = [Cr(VI)]_{eqm} + [C]$

Therefore

$$[Cr(VI)]_{eqm} = [Cr(VI)]_{total} - [C]$$

Hence,

$$k^I_I [H_2A] \{ [Cr(VI)]_I - [C] \} = (k^I_{-I} + K) [C]$$

$$k^I_{-I} [H_2A] [Cr(VI)]_I - k_I [H_2A] [C] = (k^I_{-I} + K) [C]$$

Therefore

$$\{k^I_{-I} + K + k^I_I\} [H_2A] - [C] = k^I_I [H_2A] [Cr(VI)]_I$$

$$\begin{aligned} [C] &= \frac{k^I_I [H_2A] [Cr(VI)]_I}{k^I_{-I} + K + k^I_I [H_2A]} \\ &= \frac{[H_2A] [Cr(VI)]_I}{\frac{k^I_{-I} + K}{k^I_I} + [H_2A]} \\ &= \frac{[H_2A] [Cr(VI)]_I}{k_m + [H_2A]} \end{aligned}$$

Hence;

$$\text{Rate} = k [C]$$

$$= \frac{[H_2A] [Cr(VI)]_I}{k_m + [H_2A]}$$

$$= k_I [Cr(VI)]_I = k_{obs} [Cr(VI)]_I$$

Where,

$$k_I = k \frac{[H_2A]}{k_m + [H_2A]}$$

$$\frac{1}{k} = \frac{k_m}{k} - \frac{1}{[H_2A]} + \frac{1}{k}$$

Therefore,  $k_m$  can be calculated by slope /intercept of plot  $1/k_I$  Vs  $1/[H_2A]$

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