

## Kinetics and Mechanism of Oxidation of Ethyl Acetoacetate by Chromic Acid in the Presence and Absence of Oxalic Acid

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### Abstract

*The kinetics of oxidation of ethyl acetoacetate has been investigated in the presence and absence of oxalic acid, in a moderately conc. sulphuric acid medium. The oxidation follows the kinetics of the first order with respect to the oxidant (VI) and first order with respect to the [Ester]. The reaction is overall of the second order. The reactions are acid catalyzed and the rates are independent of added salts. In the absence of oxalic acid the reaction is overall second order, first order in each reactant. In presence of oxalic acid the rate of oxidation increases. The values of thermodynamic parameters have been evaluated. A probable mechanism consistent with the kinetic data has been proposed.*

**Keywords:** kinetics, oxidation, mechanism, ethyl acetoacetate.

### Introduction

In the oxidation of esters by a series of oxidants like Ce(IV)<sup>1</sup>, Co(III)<sup>2</sup>, Mn(VII)<sup>3</sup>, Mn(III)<sup>4</sup>, Tl(III)<sup>5</sup>, (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>)<sup>6</sup>, Cr(VI)<sup>7</sup>, etc. an attempt is made to find out whether the ester is (i) directly oxidized or (ii) it undergoes hydrolysis prior to oxidation. But earlier workers have provided no conclusive evidence. An attempt is being made to overcome this controversy by studying the kinetics and mechanism of oxidation of ethyl acetoacetate by chromic acid in acetic acid-water mixture (iii) to find out whether a one-electron transfer or three-electron transfer reaction takes place in the present case.

### Experimental

All the chemicals used were of AR grade. The course of the reaction is studied Spectrophotometrically at 350nm using Erma Japan photo electric photometer AE-11 at various concentrations of chromic acid, esters, acids and salts and also oxalic acid. 20% acetic acid was used for the course of reaction.

### Results And Discussion

#### A) Oxidation of Ester in Absence of Oxalic Acid

##### Effect of variation of [oxidant]

Keeping the concentrations of substrate and Sulphuric acid constant, the [chromic acid] is varied. It was observed that the plot of log O.D. Vs Time is linear indicating the pseudo-first order rate constant.

**Effect of variation of [Ester]**

Under constant  $[H_2SO_4]$  and [oxidant], and increasing [ester], the values of the rate constants increase. It is found that the reaction is of the first order with respect to the [substrate]. A plot of  $\log K$  Vs  $\log [Ester]$  gives a slope 1.2. (Table no.1)

**Effect of variation of  $[H_2SO_4]$** 

Under constant [substrate] and [oxidant], the rate of reaction increased with increasing  $[H_2SO_4]$ . Hence the reactions are acid catalyzed. The slope of the graph,  $\log K$  Vs  $\log [H_2SO_4]$  is not unity; hence Bunnett's Hypothesis<sup>8</sup> is applied. The plot of  $\log K$  Vs  $-H_0$  (the Hammett's acidity function) is linear, indicating that the reactions are acid catalyzed and the slope of the graph is 0.74 as per expectation of ideal behavior.

The plot of  $(\log k + H_0)$  Vs  $\log a_w$  ( $a_w$  - activity of water) drawn, is linear with positive slope,  $w = 12.5$ , which indicates the involvement of water molecules in the reaction steps<sup>9</sup>

**Effect of variation of Temperature**

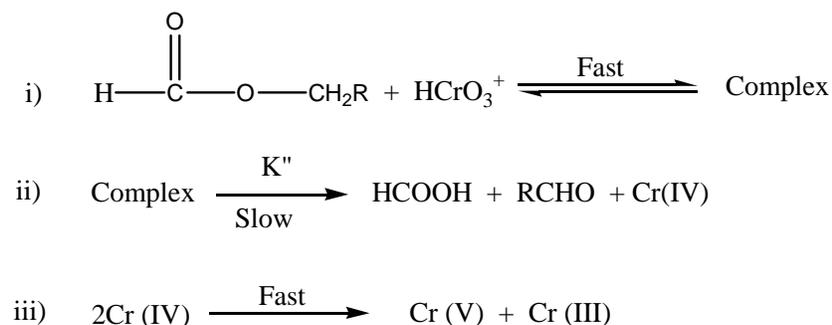
The course of the reaction was studied at various temperatures between the range  $20^\circ C$  to  $45^\circ C$ . The value of energy of activation is determined from the graph of  $\log K$  Vs  $1/T \times 10^3$ . The thermodynamic constants such as  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$  and  $A$ , the frequency factor have been calculated. The values of activation parameters for the studied reactions are in agreement with the related oxidations. The rate of oxidation of ester was found to be far greater than the corresponding hydrolysis rate, which is practically negligible.

In the present work, the reactions have negative values of entropy of activation (Table no. 2). The rate of disappearance of ester is slower and the activation complex is less probable<sup>10</sup>, if the entropy of activation of oxidation of ester has the large negative values. The plot of  $\Delta H^\ddagger$  Vs  $\Delta S^\ddagger$  is linear (Fig.2) giving a value of  $283^\circ K$  for the isokinetic temperature ( $\beta$ ) that is well below the experimental temperature range ( $298^\circ K$  to  $318^\circ K$ ).

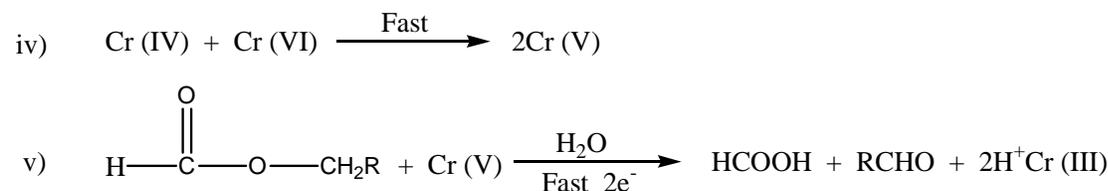
The reactions are characterized by the negative values of entropy of activation. These values have been found for outer sphere electron transfer reactions between ions of like charges<sup>11-13</sup>. The redistribution of energy along various degrees of freedom in the formation of activated complex suggests a complex molecule formation.

On the basis of the above discussion, the mechanism involving one-electron change is suggested.

### Mechanism



OR



On the basis of the experimental results and by applying the steady state condition to the above probable mechanism, the rate law is proposed.

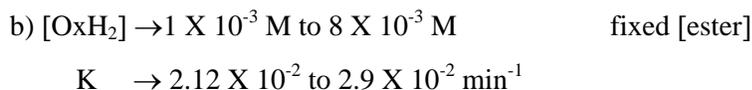
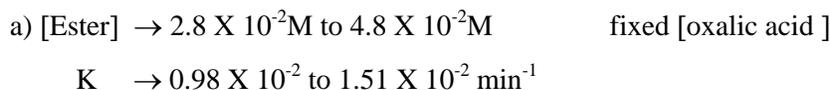
$$-d[\text{Cr(VI)}]/dt = \text{K}'' [\text{Cr(VI)}] [\text{Ester}]$$

Where K'' is the second order rate constant.

### B) Oxidation of Ester in Presence of Oxalic Acid

The rate of consumption of Cr(VI) when oxalic acid and ester present together is much greater than when either of the two substances is taken separately. The oxidation of ester alone by Cr(VI) is of first order. However, in the presence of oxalic acid, the order in ethyl acetoacetate is fractional (Table no. 3) (Fig.1). Similarly, at fixed concentration of ester, the order in oxalic acid is also fractional<sup>7</sup>.

On basis of this, we are trying to advocate a three-electron transfer mechanism, which is most likely.



Effect of Variation of [Ester]

[Oxidant] =  $4 \times 10^{-3}$  M,  $[\text{H}_2\text{SO}_4] = 2.56$  M,  $[\text{HOAc}] = 20\%$  v/v, Temp. = 308 K

Log [Ester]	K X 10 <sup>2</sup>	Log K
-1.3679	15.2	-0.8182
-1.4891	13.65	-0.8649
-1.5901	12.331	-0.909
-1.669	7.68	-1.1146
-1.7657	7.4106	-1.1301
-1.9003	4.997	-1.3013
-2.067	3.941	-1.4044
-2.3665	2.833	-1.5478

(Table no.1)

Effect of Variation of Temperature

[Oxidant] =  $4 \times 10^{-3}$  M, [Substrate] =  $5 \times 10^{-2}$  M,  $[\text{H}_2\text{SO}_4] = 2.56$  M,

Temp. K	KX10 <sup>-3</sup> sec	Activation parameter
293	1.054	$\Delta E^\ddagger = 9.5095$ kcal
298	1.4448	$\Delta H^\ddagger = 8.8962$ kcal/mole
303	1.7327	$\Delta S^\ddagger = 40.9983$ e.u.
308	2.1133	$\Delta G^\ddagger = 21.42633$ kcal/mole
313	2.8565	
318	3.6022	

(Table no. 2)

Effect of variation of Ester with constant OX-H<sub>2</sub>

Effect of variation of OX-H<sub>2</sub> with constant Ester

[Oxidant] =  $4 \times 10^{-3}$  M,  $[\text{H}_2\text{SO}_4] = 2.56$  M,  $[\text{OX-H}_2] = 5 \times 10^{-2}$  M

Temp. = 308 K,  $[\text{HOAc}] = 20\%$

1/ [Ester]	1/k	1/ [OX-H <sub>2</sub> ]	1/k
48.7805	10.7009	48.7805	6.725
56.6572	10.7689	56.6572	10.22
68.306	11.3507	68.306	15.16
88.4956	11.4679	87.7655	22.16
126.5823	12.1951	126.5823	25.47
243.9024	12.8024	243.9024	35.49

(Table no. 3)

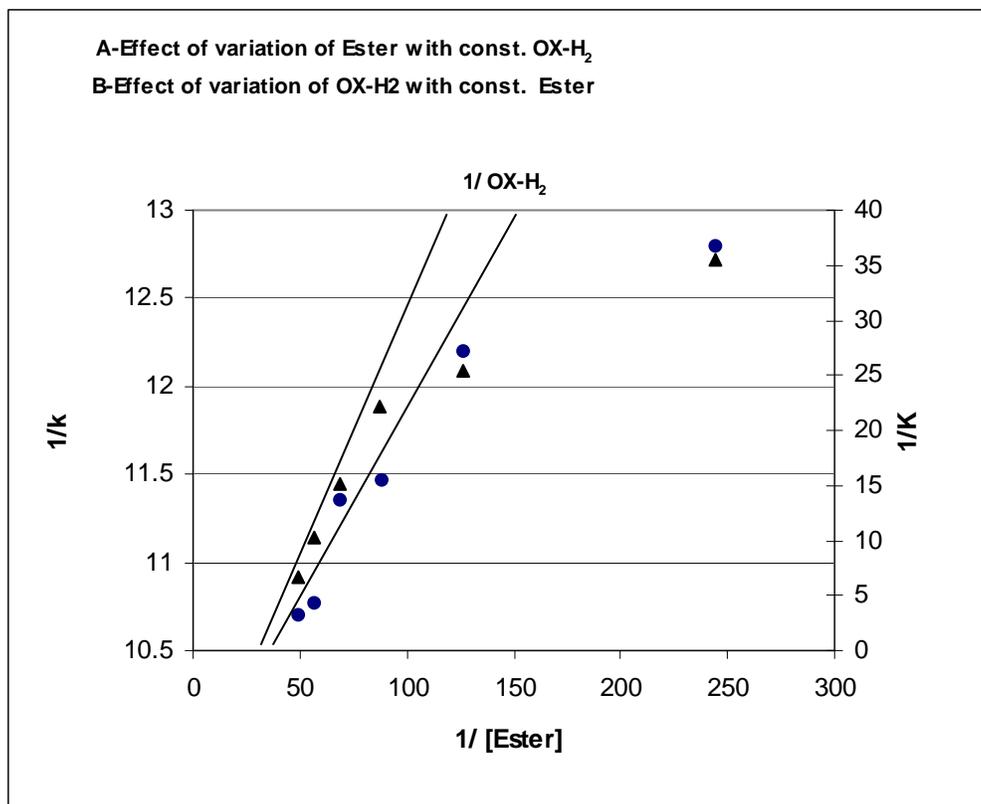


Fig. No. 1

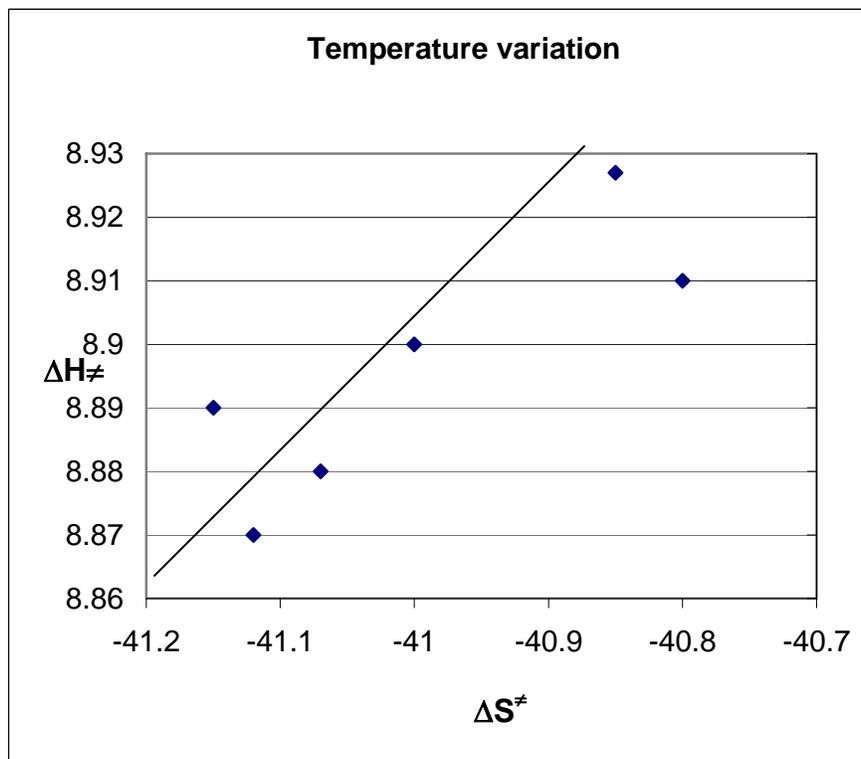
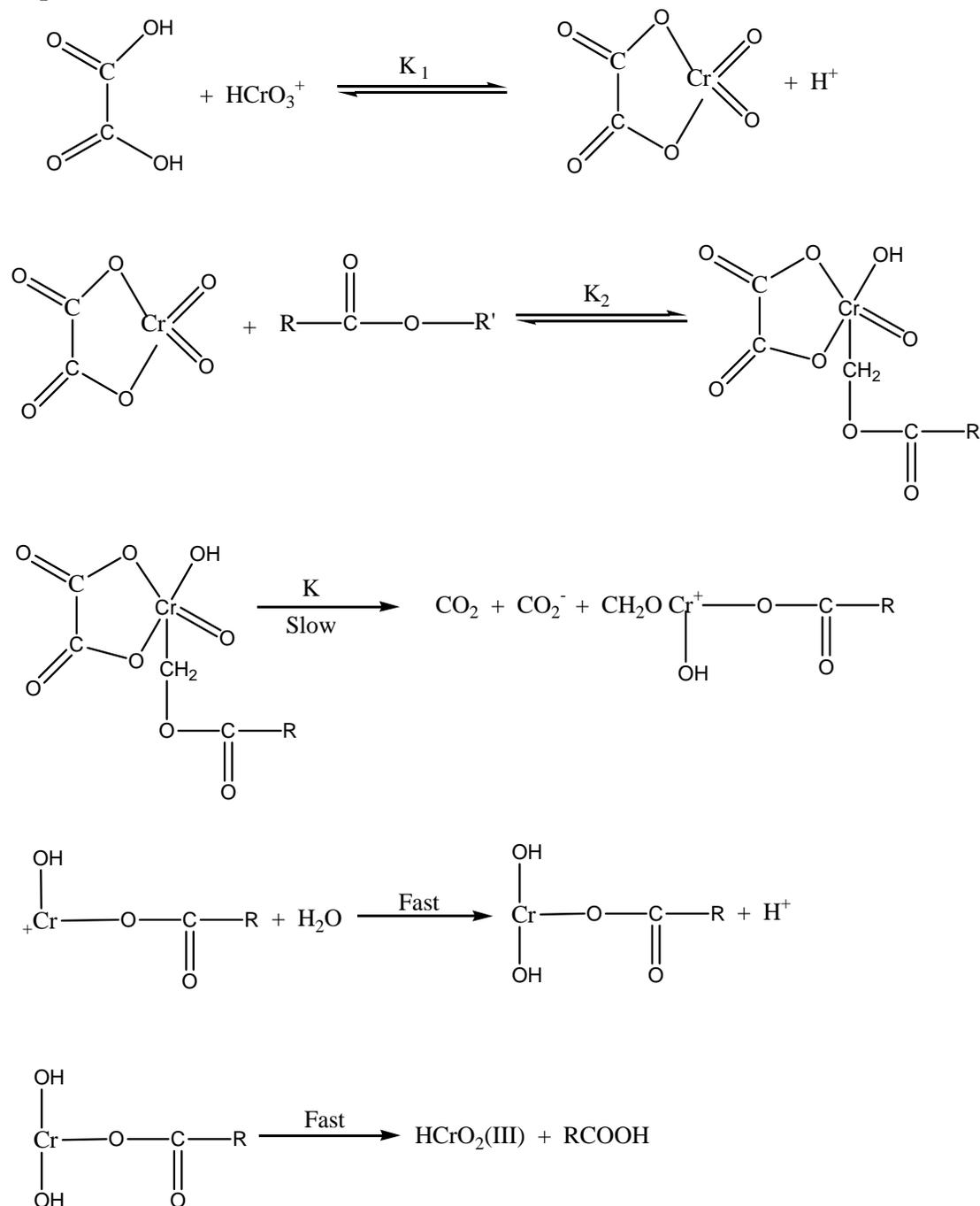


Fig. No. 2

## Mechanism

### In presence of oxalic acid



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