

## Kinetic and Mechanistic Study of Induced Oxidation of Mn(II) by Chromate in Presence of Iodide and Iron(II)

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The strong induced activity of Fe(II) in Mn(II)-Cr(VI) reaction was studied in acidic medium. Induction factor is found to be one. The rate law is derived as

$$\frac{1}{k'} = \frac{1}{k_3} + \frac{1}{k_1 k_3 [\text{H}^+]}$$

### INTRODUCTION

The induced<sup>1, 2</sup> oxidation is the phenomenon in which the acceleration of one reaction is due to the simultaneous occurrence of other reaction. In induced oxidation reaction,<sup>3</sup> inductor is continuously used up in order to induce the reaction, that distinguishes the induced oxidation from catalysed reaction.<sup>4</sup> Luther and Schilow<sup>5</sup> classified induced oxidation reactions into two classes; first is coupled reaction and second is induced chain reaction. Coupled reaction proceeds through coupled intermediate species, whereas the second type of reaction between acceptor and donor is catalysed by inductor. In Mn(II)-CrO<sub>4</sub><sup>2-</sup> reaction, Fe(II) induces the reaction. There has been much work carried out in the field of kinetics of oxidation of inorganic ions by chromate ion.<sup>6-9</sup> But less attention has been paid to induced oxidation reaction. Therefore, in the present work the induced oxidation reaction study has been undertaken.

### EXPERIMENTAL

Chemicals were of A.R., B.D.H., or G.R. grade and used without further purification. Solutions were prepared in double distilled water. The reaction mixtures were carried out in black painted or coloured bottle with stopper and were placed in thermostat.

The role of inductor was observed by keeping the concentrations of acceptor, oxidant, iodide and acid as constant and changing the concentration of inductor. Temperature was also kept constant in such a way that the roles of acceptor, oxidant, iodide, acid and temperature could be studied.

### RESULTS AND DISCUSSION

The data obtained in inductor variation clearly show that in presence of

inductor the reaction rate increased markedly (Table-1). The graph between rate constant versus concentration is a straight line

TABLE-1

$[\text{K}_2\text{CrO}_4] = 1 \times 10^{-3} \text{ mol dm}^{-3}$        $[\text{H}_2\text{SO}_4] = 8 \times 10^{-2} \text{ mol dm}^{-3}$   
 $[\text{MnSO}_4] = 5 \times 10^{-2} \text{ mol dm}^{-3}$   
 $[\text{KI}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$       Temp : 308 K.

S. No.	$[\text{FeSO}_4] \times 10^6 \text{ mol dm}^{-3}$	$\text{K} \times 10^4 \text{ mol dm}^{-3}$
1	0.00	0.345
2	1.00	0.809
3	1.50	1.430
4	2.00	1.620
5	2.50	2.550
6	3.00	3.410

TABLE-2

$[\text{MnSO}_4] = 5 \times 10^{-2} \text{ mol dm}^{-3}$        $[\text{H}_2\text{SO}_4] = 8 \times 10^{-2} \text{ mol dm}^{-3}$   
 $[\text{KI}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$   
 $[\text{FeSO}_4] = 2 \times 10^{-6} \text{ mol dm}^{-3}$       Temp : 308 K.

S. No.	$[\text{K}_2\text{CrO}_4] \times 10^3 \text{ mol dm}^{-3}$	$\text{K} \times 10^4 \text{ Sec}^{-1}$
1	0.50	1.62
2	1.00	1.65
3	1.50	1.65
4	2.00	1.62
5	2.50	1.63

TABLE-3

$[\text{K}_2\text{CrO}_4] = 1 \times 10^{-3} \text{ mol dm}^{-3}$        $[\text{FeSO}_4] = 2 \times 10^{-6} \text{ mol dm}^{-3}$   
 $[\text{KI}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$   
 $[\text{H}_2\text{SO}_4] = 8 \times 10^{-2} \text{ mol dm}^{-3}$       Temp : 308 K.

S. No.	$[\text{MnSO}_4] \text{ mol dm}^{-3}$	$\text{K} \times 10^4 \text{ Sec}^{-1}$
1	1.25	1.55
2	2.50	1.57
3	5.00	1.65
4	7.25	1.72
5	10.00	1.72

TABLE-4

$$\begin{aligned}
 [\text{K}_2\text{CrO}_4] &= 1 \times 10^{-3} \text{ mol dm}^{-3} \\
 [\text{H}_2\text{SO}_4] &= 8 \times 10^{-2} \text{ mol dm}^{-3} \\
 [\text{MnSO}_4] &= 5 \times 10^{-2} \text{ mol dm}^{-3}
 \end{aligned}$$

$$[\text{FeSO}_4] = 2 \times 10^{-6} \text{ mol dm}^3$$

$$\text{Temp} = 308 \text{ K.}$$

S. No.	[KI] $\times 10^4 \text{ mol dm}^{-3}$	K $\times 10^4 \text{ Sec}^{-1}$
1	2.0	3.41
2	4.0	6.42
3	6.0	9.43
4	8.0	12.20
5	10.0	16.40
6	12.0	20.30

TABLE-5

$$\begin{aligned}
 [\text{K}_2\text{CrO}_4] &= 1 \times 10^{-3} \text{ mol dm}^{-3} \\
 [\text{MnSO}_4] &= 5 \times 10^{-2} \text{ mol dm}^{-3} \\
 [\text{FeSO}_4] &= 2 \times 10^{-6} \text{ mol dm}^{-3}
 \end{aligned}$$

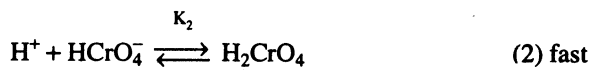
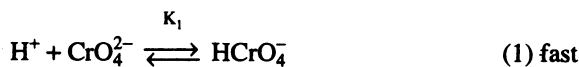
$$[\text{KI}] = 1 \times 10^{-3} \text{ mol dm}^3$$

$$\text{Temp} = 308 \text{ K}$$

S. No.	[H <sub>2</sub> SO <sub>4</sub> ] mol dm <sup>-3</sup>	K $\times 10^4 \text{ Sec}^{-1}$
1	2.0	0.425
2	4.0	0.771
3	6.0	1.22
4	8.0	1.65
5	10.0	2.05

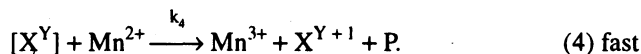
Rate dependence of the reaction with respect to oxidant was found to be one. Because the rate constant value is not varying with the concentrations of oxidant (Table-2), the graphs of  $\log(a-x)$  versus time are parallel lines. In acceptor variation rate constant value is constant in all concentrations of acceptor (Table-3). Therefore, order with respect to acceptor is zero. Iodide and acid influencing the reaction rate (Tables-4 and 5). The graph between  $\frac{1}{[\text{H}^+]}$  versus  $\frac{1}{K}$  is a straight line and corresponding constant can be obtained from intercepts and slope values.

From experimental findings, the possible mechanism is as follows:



where  $\text{X}^Y$  is ion  $\text{I}^-$  or  $\text{Fe}^{2+}$ .

As inductors,



$$\text{Rate:} \quad \frac{dx}{dt} = K_3 [H_2CrO_4] [X^Y] \quad (5)$$

$$= K_{obs} [HCrO_4^-] + [H_2CrO_4] \quad (6)$$

$$\text{Then,} \quad \frac{K_{obs}}{[X^Y]} \frac{K_3 [H_2CrO_4]}{[HCrO_4^-] + [H_2CrO_4]} \quad (7)$$

So we have

$$\frac{1}{k'} = \frac{1}{k_3} + \frac{[HCrO_4^-]}{k_3 [H_2CrO_4]}$$

$$\frac{1}{k'} = \frac{1}{k_3} + \frac{1}{k_3 k_1 [H^+]} \quad (8)$$

Eqs. (5), (7) and (8) show the following facts:

1. Order with respect to oxidant is one.
2. Order with respect to substrate is zero.
3. The reaction rate is dependent of inductor concentration.
4. The reaction rate must follow dependency with respect to hydrogen ion concentration.

## REFERENCES

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