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Kinetics and Mechanism of Induced Oxidation Reaction of Iodide by Chromate

J.S. AMPILY* and S.K. SOLANKI
School of Studies in Chemistry
Vikram University, Ujjain-456 010, India

The induced oxidation reaction of iodide by chromate has been studied. In this chromate-iodide reaction, chromate acts as an oxidant, iodide as acceptor and iron(II) as inductor. The reaction takes place in acid medium. From the observation and findings, the rate law obtained is as follows.

$$\frac{dx}{dt} = \frac{k_1K_1K_3[Fe^{2+}][I^-][H^+]^2[CrO_4^{2-}]}{1 + K_3[Fe^{2+}]}$$

INTRODUCTION

Induced oxidation[1] reaction is defined as the conversion of inductor by acceptor into product which attacks the acceptor. The term *induced oxidation* was first introduced by Kessler[2]. Induced oxidation involving by chromate ion is of two types[3]. In first case chromate ion acts as an oxidant, but in second case chromate ion acts as inductor. In this case chromate ion acts as an oxidant. An important characteristic of induced oxidation is induction[4] factor, *i.e.*, the ratio of mole equivalent of acceptor to that of inductor.

EXPERIMENTAL

All chemicals used were of purest grade available. Experiments were carried out in doubly distilled water.

Cr(IV) solution was prepared by dissolving requisite amount of potassium chromate (A.R or B.D.H) in doubly distilled water. Iodide solution is prepared by dissolving requisite amount of potassium iodide in double-distilled water. The solution was kept in a flask covered wth black paper. $FeSO_4$ solution was prepared by dissolving requisite amount of $FeSO_4$ in double distilled water (in presence of small amount of acetic acid). The reaction mixture were placed in thermostat at 303 K temperature for maintaining the temperature constant.

The typical reaction takes place in 5×10^{-3} mol dm^{-3} sulphuric acid. The mixture containing [oxidant] 5×10^{-3} mol dm^{-3}, $[K_1]$ 5×10^{-2} mol dm^{-3} and $[FeSO_4]$ 1×10^{-5} mol dm^{-3} respectively.

Stoichiometry of the reaction

Stoichiometry of the reaction is determined by mixing excess amount of potassium chromate with different quantities of acceptor and inductor in acid medium (5×10^{-3} mol dm^{-3}). The reaction mixtures were placed in a thermostat at 303 K temperature for 24 h. From the amount of unreacted potassium chromate, the stoichiometry is

$$CrO_4^{2-} + Fe^{2+} + 2I^- + 8H^+ \longrightarrow Cr(III) + Fe^{3+} + I_2 + 4H_2O$$

Order of reaction

The reaction followed a first order dependency in oxidant variation in the range 2.0×10^{-3} mol dm^{-3} to 6.0×10^{-3} mol dm^{-3} (Table 1). The graphs between log (a – x) versus time are parallel lines. In case of acceptor, the pseudo first order rate constant increases with increase in concentration of iodide in the range 1.0×10^{-2} mol dm^{-3} to 5×10^{-2} mol dm^{-3} (Table 2). The graph between log k versus log C is a straight line with unit slope.

TABLE 1

[KI] = 5×10^{-2} mol dm^{-3}, [$FeSO_4$] = 1×10^{-5} mol dm^{-3}, [H_2SO_4] = 5×10^{-3} mol dm^{-3}, Temp. = 303 K

S.No	[K_2CrO_4] $\times 10^3$ mol dm^{-3}	K $\times 10^4$ sec^{-1}
1	2.0	3.83
2	3.0	3.82
3	4.0	3.81
4	5.0	3.84
5	6.0	3.86

TABLE 2

[K_2CrO_4] = 5×10^{-3} mol dm^{-3}, [$FeSO_4$] = 1×10^{-5} mol dm^{-3}, [H_2SO_4] = 5×10^{-3} mol dm^{-3}, Temp. = 303 K

S.No.	[KI] $\times 10^2$ mol dm^{-3}	K $\times 10^4$ sec^{-1}
1	1.0	1.42
2	2.0	2.87
3	3.0	3.34
4	4.0	3.55
5	5.0	3.93

Role of inductor

Role of added $FeSO_4$ (0 to 3×10^{-5} mol dm^{-3}) was studied at 5×10^{-3} mol dm^{-3} [H_2SO_4], [oxidant] 5×10^{-3} mol dm^{-3} and at 303K temperature.

Under these conditions rate constant value increases due to the increase of Fe^{2+} ion (Table 3). The graph between ($FeSO_4$) versus rate constant is a straight line. This means that [$FeSO_4$] induces the chromate-iodide reaction.

TABLE 3

$[K_2CrO_4] = 5 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 5 \times 10^{-3}$ mol dm^{-3},
$[KI] = 5 \times 10^{-2}$ mol dm^{-3}, Temp. = 303 K

S. No.	$[FeSO_4] \times 10^5$ mol dm^{-3}	$K \times 10^4$ sec^{-1}
1	0.0	3.67
2	1.0	3.97
3	1.5	4.23
4	2.0	5.22
5	2.5	5.94
6	3.0	6.24

Role of H^+ ion

The results obtained in acid variation show that H^+ ion has an important role in chromate–iodide reaction. Cr(VI)[5, 6] in acid solution exists as $[HCrO_4^-]$. Acid concentration increases the rate constant value (Table 4).

TABLE 4

$[K_2CrO_4] = 5 \times 10^{-3}$ mol dm^{-3}, $[KI] = 5 \times 10^{-2}$ mol dm^{-3},
$[FeSO_4] = 1.0 \times 10^{-5}$ mol dm^{-3}, Temp. = 303 K

S. No.	$[H_2SO_4] \times 10^3$ mol dm^{-3}	$K \times 10^4$ sec^{-1}
1	2.50	2.21
2	3.75	3.15
3	5.00	3.73
4	6.25	4.90
5	7.50	5.04

Effect of Product and Scavenger

Effect of scavenger and product has been studied in presence of chromium sulphate, sodium perchlorate and mercuric acetate, but has no significance in chromate-iodide reaction. That means reaction is non-ion and non-chain.

RESULTS AND DISCUSSION

The experimental results lead to the mechanism as follows:

$$CrO_4^{2-} + H^+ \overset{K_1}{\rightleftarrows} HCrO_4^- \quad \text{fast} \qquad (1)$$

$$HCrO_4^- + H^+ \overset{K_2}{\rightleftarrows} H_2CrO_4 \quad \text{fast} \qquad (2)$$

$$H_2CrO_4 + Fe^{2+} \overset{K_3}{\rightleftarrows} [X] \quad \text{fast} \qquad (3)$$

$$[X] + I^- \xrightarrow[\text{slow}]{K_1} Cr(III) + HIO + Fe^{3+} \qquad (4)$$

(4) is the rate determining step.

$$H^+ + HIO + I^- \xrightarrow{K_2} I_2 + H_2O \tag{5}$$

At equilibrium,

$$K_3 = \frac{[X]}{\{[H_2CrO_4] - [X]\}[Fe^{2+}]} \tag{6}$$

$$[X] = \frac{K_3[H_2CrO_4][Fe^{2+}]}{1 + K_3[Fe^{2+}]} \tag{7}$$

Step (4) is considered as the rate determining step of the reaction.

$$\frac{dx}{dt} = k_1[X][I^-]$$

Substituting the value of [X],

$$[H_2CrO_4] = K_1[H^+]^2[CrO_4^{2-}]$$

$$\frac{dx}{dt} = \frac{k_1K_3[H_2CrO_4][Fe^{2+}][I^-]}{1 + K_3[Fe^{2+}]}$$

$$\frac{dx}{dt} = \frac{K_1k_1K_3[H^+]^2[Fe^{2+}][I^-][CrO_4^{2-}]}{1 + K_3[Fe^{2+}]}$$

i.e.,

$$\frac{dx}{dt} = \frac{K_1k_1K_3[H^+]^2[CrO_4^{2-}][Fe^{2+}][I^-]}{1 + K_3[Fe^{2+}]}$$

$$= K_{1\,Obs}[CrO_4^{2-}] = K_1(a - x) \tag{11}$$

$$K_{1\,Obs} = \frac{K_1k_1K_3[Fe^{2+}][I^-][H^+]^2}{1 + K_3[Fe^{2+}]} \tag{12}$$

and mathematically equation (12) reduces to

$$K_{1\,Obs} = \frac{2.303}{t}\log a/(a - x)$$

From the mechanism it was found that protons play an important role in electron transfer process. The added Fe^{2+} ions accelerate the chromate–iodide reaction, which means that Fe^{2+} induces the activity of oxidant and acceptor. The induction factor is found to be two. The reaction is found to be non-ionic and non-chain.

REFERENCES

1. Baford and C.T.H. Tipper, *Chemical Kinetics*, **7**, 518 (1972).
2. Kessler F. Pogg, *Ann. Chem.*, **199**, 218 (1868).
3. Westheimer, *Chem. Rev.*, **45**, 419 (1949).
4. D. Benon, Mechanism of Inorganic Reactions in Solutions, McGraw-Hill, p. 174, (1968).
5. G.S. Gokavi and J.R. Raju, *Indian J. Chem.*, **27A**, 494 (1988).
6. K.B. Wiberg, Oxidation in Organic Chemistry, Part A, Academic Press, New York (1965).

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