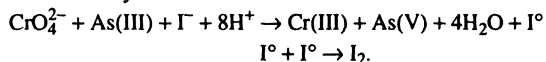


## Kinetics and Mechanism of Oxidation of Iodide by Chromate, Inhabitation of Arsenic (III)

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Kinetics and mechanism of iodide by chromate in presence of arsenic(III) was studied in acidic medium. Arsenic is negatively affecting the system. The total order of reaction is found to be two. The stoichiometry of the reaction is



### INTRODUCTION

Kinetics of oxidation of inorganic ions by chromate ion is a very interesting field in chemistry<sup>1-4</sup>. Chromate ion has been used as a very popular oxidant<sup>5-7</sup> yet even today the knowledge of the mechanism of the oxidation by chromate ion is fragmentary. Westheimer<sup>8</sup> reviewed the oxidation of organic and inorganic ions by chromate ion. In the chromate-iodide reaction, we used arsenic(III) as an inductor.<sup>9,10</sup> But from the observations, it was observed that arsenic(III) decreases the rate of the reaction. Therefore we introduce a new term *deductor* for arsenic(III), because it deduces the activity of oxidant and acceptor.

### EXPERIMENTAL

The chemicals used were of AR quality available. All solutions were prepared in double distilled water. Experiments were carried out in coloured or black painted bottle and the reaction bottles were prepared in thermostat for maintaining the constant temperature. The role of oxidant in the reaction was observed by changing the concentration of oxidant, while keeping other factors as a constant. The same method was used for studying the effect of acceptor, deductor, acid and temperature.

### RESULTS AND DISCUSSION

From data observed from oxidant variation, it was found that rate constants are constant throughout the concentrations of oxidant (Table 1). The graph between  $\log(a-x)$  versus time is a linear one. Therefore, the order with respect to oxidant is one. In case of acceptor the rate increases with the increase in concentration of iodide (Table 2). The graph between  $\log K$  versus  $\log C$  is a straight line graph with unit slope.

TABLE 1  
 $[KI] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{As}_2\text{O}_3] = 8 \times 10^{-4} \text{ mol dm}^{-3}$ ,  
 $[\text{H}_2\text{SO}_4] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ , Temp. = 303 K

S.No.	$[\text{K}_2\text{CrO}_4] \times 10^3$ $\text{mol dm}^{-3}$	$K \times 10^5$ $\text{Sec}^{-1}$
1.	2.0	6.15
2.	3.0	6.14
3.	4.0	6.14
4.	5.0	6.11
5.	6.0	6.14

TABLE 2  
 $[\text{K}_2\text{CrO}_4] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{As}_2\text{O}_3] = 8 \times 10^{-4} \text{ mol dm}^{-3}$ ,  
 $[\text{H}_2\text{SO}_4] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$  Temp. = 303 K

S.No.	$[KI] \times 10^2$ $\text{mol dm}^{-3}$	$K \times 10^5$ $\text{Sec}^{-1}$
1.	1.0	0.635
2.	2.0	1.72
3.	3.0	3.52
4.	4.0	5.20
5.	5.0	6.12

The role of arsenic(III) was observed; it was noted that arsenic decreases the rate markedly, that means it deduces the activity of oxidant (Table 3). The graph between rate constant versus concentration also agrees with the negative effect of arsenic. Acid plays an important role in this reaction (Table 4). It means protons support the electron transfer process. From the temperature variation data activation parameters were calculated.

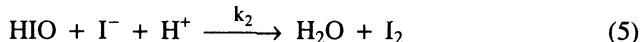
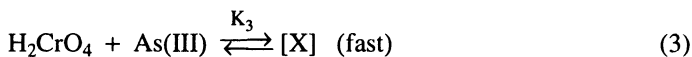
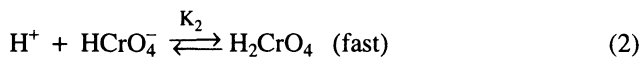
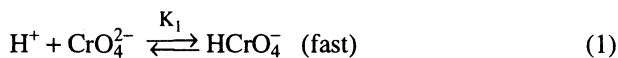
TABLE 3  
 $[\text{K}_2\text{CrO}_4] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[KI] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ ,  
 $[\text{H}_2\text{SO}_4] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ , Temp. = 303 K

S.No.	$[\text{As}_2\text{O}_3] \times 10^4$ $\text{mol dm}^{-3}$	$K \times 10^5$ $\text{Sec}^{-1}$
1.	0.00	8.52
2.	4.00	4.90
3.	8.00	6.10
4.	10.00	5.60
5.	12.00	4.23
6.	24.00	3.43

TABLE 4  
 $[K_2CrO_4] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[As_2O_3] = 8 \times 10^{-4} \text{ mol dm}^{-3}$ ,  
 $[KI] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ , Temp = 303 K

S.No.	$[H_2SO_4] \times 10^3 \text{ mol dm}^{-3}$	$K \times 10^5 \text{ Sec}^{-1}$
1.	2.50	6.13
2.	3.75	8.43
3.	5.00	10.43
4.	6.25	14.40
5.	7.50	17.30

In view of experimental observations and findings, the possible mechanism is as follows:



$$K_3 = \frac{[X]}{\{[H_2CrO_4] - [X]\}[As(III)]} \quad (6)$$

$$[X] = \frac{K_3[H_2CrO_4][As(III)]}{I + K_3[As(III)]} \quad (7)$$

Equation (4) is the rate determining step; so rate equation is

$$\frac{dx}{dt} = k_1[x][I^-] \quad (8)$$

From equation (7),

$$\frac{dx}{dt} = \frac{k_1 K_3 [H_2CrO_4][As(III)][I^-]}{I + K_3 [As(III)]} \quad (9)$$

Substituting the value of  $[H_2CrO_4]$ ,

$$\frac{dx}{dt} = \frac{k_1 k_1 k_3 [H^{2+}][CrO_4^{2-}][As(III)][I^-]}{I + K_3 [As(III)]} \quad (10)$$

$$= k_1 \text{ Obs} [CrO_4^{2-}] = K_1 \text{ Obs} (a - x) \quad (11)$$

$$k_1 \text{ Obs} = \frac{k_1 K_1 K_3 [H^{2+}][I^-][As(III)]}{I + K_3 [As(III)]} \quad (12)$$

Equation (12) reduces to

$$\frac{2.303}{t} \log \frac{a}{(a-x)}$$

The equations (11) and (12) confirm the following points:

1. Order with respect to oxidant is one.
2. Order with respect to substrate is one.
3. Deductor *i.e.* As(III) has influence on reaction rate.
4. Proton has very important role in chromate-iodide reaction.

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