

## Kinetics and Mechanism of Oxidation of Oxalic Acid with Bi(V) in HClO<sub>4</sub>-HF Mixture

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The kinetics of oxidation of oxalic acid with Bi(V) has been investigated in HClO<sub>4</sub> (1.0 M) and HF (1.5 M) mixture. The rate followed first order kinetics each in Bi(V) and oxalic acid. The reaction rate is independent of [H<sup>+</sup>]. Addition of HF and (F<sup>+</sup>) has not effect on the reaction rate. The reaction rates decreased with the increase in ionic strength. The mode of electron transfer from the substrate to Bi(V) has been indicated *via* bridged outer sphere mechanism.

**Key Words:** Kinetics, Oxidation, Oxalic acid, Bi(V), HClO<sub>4</sub>-HF Mixture.

### INTRODUCTION

Though Bi(V) has useful synthetic and analytical application<sup>1-3</sup> but its solution chemistry has not been well explored due to the inability to get Bi(V) in the solution in common solvent. However, Bi(V) is obtained in solution<sup>4</sup> in a mixture of HClO<sub>4</sub> (1.5 M) and HF (1.0 M) and is stable for long when refrigerated. The oxidation of oxalic acid with Bi(V) in HClO<sub>4</sub>-HF was undertaken for investigation to elucidate the mode of electron transfer from the substrate to the oxidant. Keeping in view of the fact that the redox reaction involving oxalic acid is of interests both from pure chemical and industrial points view.

### EXPERIMENTAL

**Preparation and standardization of Bi(V) solution:** A known quantity of sodium bismuthate (BDH AnalaR) was digested in known volume of the mixture of HF (1.5 M) and HClO<sub>4</sub> (1.0 M) and filtered for undissolved salt. The filtrate gave a clear and colourless solution of Bi(V). The solution of Bi(V) was standardized by modified iodometrically<sup>5</sup>. A known volume of Bi(V) solution was added to KI (0.1 M) solution and pH of the solution was adjusted to 2-3 with NaOH solution. Then the titration was carried out only in presence of EDTA with the standardized Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. Stock solution of an appropriate concentration of oxalic acid was

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prepared. All others chemicals were either of AnalR or GR grade. Doubly distilled and CO<sub>2</sub> free water used throughout the investigation.

Reactions were conducted in a Teflon bottle immersed in water bath thermostated at a desired temperature. The kinetic of the reaction was motivated by withdrawing aliquots of 5.0 mL at different intervals of time and estimating the remaining Bi(V) iodometrically.

## RESULTS AND DISCUSSION

The stoichiometry of the reaction was determined by taking an excess of Bi(V) concentration over that of oxalic acid at fixed concentration of [HClO<sub>4</sub>] = 1.0 mol dm<sup>-3</sup> and [HF] = 1.5 mol dm<sup>-3</sup>. These reactions were kept in a thermostated water bath at 20°C and the excess of Bi(V) was determined iodometrically<sup>1</sup> after ensuring the completion of the reaction after 12 h. The stoichiometry of the reaction was found to be 1:1 *i.e.* one mol of Bi(V) reacted with one mol of oxalic acid.

The stoichiometry ratio which is greater than this ratio account for the decomposition of Bi(V). Therefore more Bi(V) is consumed that required by oxalic acid. The stoichiometry indicates the formation of CO<sub>2</sub> as the end product by other worker<sup>2</sup>. The stoichiometry can be represented by the equation:



**Bismuth(V) dependence:** The concentration of Bi(V) was varied from  $0.4 \times 10^{-3}$  -  $4.4 \times 10^{-3}$  mol dm<sup>-3</sup> at fixed concentration of oxalic acid ( $1.1 \times 10^{-2}$  mol dm<sup>-3</sup>). The initial rate were computed by plan mirror method<sup>3</sup>. The plot of initial rate *vs.* Bi(V) yielded straight line passing through the origin indicating first order in Bi(V). The values of second order rate constant (k) calculated from initial rates are given in Tables 2-4.

**Oxalic acid dependence:** The concentration of oxalic acid was varied in the range  $0.4 \times 10^{-2}$  -  $1.2 \times 10^{-2}$  mol dm<sup>-3</sup> at a fixed concentration of Bi(V) *i.e.*  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> and also at fixed concentration of [HClO<sub>4</sub>] = 1.0 mol dm<sup>-3</sup> and [HF] = 1.5 mol dm<sup>-3</sup> (Tables 2-4). Initial rates were calculated by plan mirror method<sup>4</sup>. The plot of the initial rate *vs.* the concentration of oxalic acid has zero intercept on the ordinate yielding a straight line. The order with respect to oxalic acid was found to be one.

**Hydrogen ion dependence:** [H<sup>+</sup>] was varied by changing the concentration of HClO<sub>4</sub> ( $1.1$  mol dm<sup>-3</sup> -  $2.25$  mol dm<sup>-3</sup>) at a fixed concentration of Bi(V) ( $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>), oxalic acid ( $1.1 \times 10^{-2}$  mol dm<sup>-3</sup>) and also at fixed ionic strength (L = 2.50 m) adjusted with requisite quantity of LiClO<sub>4</sub> solution. It was assumed that at the high concentration of HClO<sub>4</sub> there was no contribution of HF towards [H<sup>+</sup>] *i.e.* H<sup>+</sup> ion concentration was due to the contribution by HClO<sub>4</sub> only. The reaction rates remained unaffected by changing [H<sup>+</sup>].

TABLE-1  
STOICHIOMETRIC RESULTS OF OXIDATION OF OXALIC ACID  
WITH Bi(V) IN HClO<sub>4</sub> (1.0 M)-HF (1.5 M) MIXTURE AT 20°C

[Bi(V)] × 10 <sup>3</sup> M	[Oxalic acid] × 10 <sup>3</sup> M	[ΔBi(V)]/[Oxalic acid]
2.1	1.0	1.10
2.7	1.5	1.10
3.5	1.5	1.10
4.1	2.0	1.11
5.0	2.0	1.15

TABLE-2  
PSEUDO-FIRST ORDER (k<sup>o</sup>) AND SECOND ORDER RATE  
CONSTANT (k) FOR REACTION BETWEEN Bi(V) AND OXALIC  
ACID IN HClO<sub>4</sub> (1.0 M)-HF (1.5 M) MIXTURE AT 20°C

[Bi(V)] × 10 <sup>3</sup> M	[Oxalic acid] × 10 <sup>3</sup> M	(i.r.) × 10 <sup>6</sup> M s <sup>-1</sup>	k × 10 <sup>2</sup> M <sup>-1</sup> s <sup>-1</sup>
0.4	11	0.27	
0.8	11	0.55	
1.2	11	0.74	
1.6	11	0.98	
2.0	11	1.20	
2.4	11	1.46	
3.0	11	1.80	
3.6	11	2.16	
4.0	11	2.40	
4.4	11	2.64	6.2
2.0	11	1.20	
2.0	4	0.44	
2.0	5	0.54	
2.0	6	0.66	
2.0	7	0.76	
2.0	8	0.88	
2.0	9	0.98	
2.0	10	1.08	
2.0	12	1.30	

**Ionic strength dependence:** Ionic strength changed in the range (1.0-2.58 mol dm<sup>-3</sup>) adjusted by adding LiClO<sub>4</sub> solution. The reaction rates decreased with the increase in ionic strength indicating that reacting species are ion (BiF<sub>6</sub><sup>-</sup>) and neutral molecules (oxalic acid)<sup>5</sup>.

**Effect of HF and F<sup>-</sup>:** The reaction kinetics were followed by changing [HF] in the range (0.75-2.0 mol dm<sup>-3</sup>) [NaF] in the range (0.1-0.5 mol dm<sup>-3</sup>). In each case the reaction rates remained unchanged. As the reaction rates were independent of [HF] and [NaF] it is suggested that reactive species are (BiF<sub>6</sub><sup>-</sup>) in the mixture of HClO<sub>4</sub> and HF as has also been assumed in the reaction of Bi(V) with hypophosphorus acid<sup>6</sup>, phosphorus

acid<sup>7</sup> and aspartic acid<sup>8</sup>. Such an assumption is also strengthened by like complexes of Sb(V) in HCl medium<sup>9,10</sup>.

TABLE-3  
SECOND ORDER RATE CONSTANT (k) FOR REACTION BETWEEN  
Bi(V) AND OXALIC ACID IN HClO<sub>4</sub> (1.0 M)-HF (1.5) MIXTURE AT 25°C

[Bi(V)] × 10 <sup>3</sup> M	[Oxalic acid] × 10 <sup>3</sup> M	(i.r.) × 10 <sup>6</sup> M s <sup>-1</sup>	k × 10 <sup>2</sup> M <sup>-1</sup> s <sup>-1</sup>
0.4	11	0.38	
0.8	11	0.72	
1.2	11	1.14	
1.6	11	1.44	
2.0	11	1.80	
2.4	11	2.16	
3.0	11	2.68	
3.6	11	3.22	
4.0	11	3.58	
4.4	11	3.94	8.6
2.0	11	1.80	
2.0	4	0.68	
2.0	5	0.82	
2.0	6	0.98	
2.0	7	1.14	
2.0	8	1.30	
2.0	9	1.48	
2.0	10	1.68	
2.0	12	1.96	

**Effect of Bi(III):** The concentration of Bi(III) was varied from  $2.5 \times 10^{-3}$  -  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> at fixed concentration of Bi(V) =  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>, [oxalic acid]  $1.1 \times 10^{-2}$  mol dm<sup>-3</sup>. The rate of reaction remains unchanged with the changing concentration of Bi(III) indicating that the Bi(III) is not involving in any equilibrium proceeded by the rate determining step in the reactions mechanism.

**Temperature dependence:** The rate of the reaction was calculated at three temperature 20, 25 and 30°C. The energy of activation and other parameters were also calculated. Energy of activation (E<sub>a</sub>) was calculated for the plot of log k vs. 1/T (Table-5).

The reaction rates are independence of (NaF) and (HF), it is obvious that the ultimate fluoro species of Bi(V) are involved and as such there appears to be non-involvement of NaF and HF in any equilibrium step proceeded by the rate determining step. A detailed information about the fluoro species of Bi(V) in HClO<sub>4</sub>-HF mixture is lacking and it has been assumed that Bi(V) exist as BiF<sub>6</sub><sup>-</sup> and protonated from HBiF<sub>6</sub>.

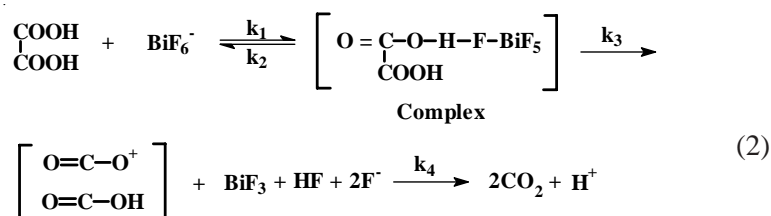
TABLE-4  
SECOND ORDER RATE CONSTANT (k) FOR REACTION BETWEEN Bi(V)  
AND OXALIC ACID IN HClO<sub>4</sub>(1.0 M)-HF (1.5 M) MIXTURE AT 30°C

[Bi(V)] × 10 <sup>3</sup> M	[Oxalic acid] × 10 <sup>3</sup> M	(i.r.) × 10 <sup>6</sup> M s <sup>-1</sup>	k × 10 <sup>2</sup> M <sup>-1</sup> s <sup>-1</sup>
0.4	11.0	0.45	
0.8	11.0	0.90	
1.2	11.0	1.36	
1.6	11.0	1.82	
2.0	11.0	2.27	
2.4	11.0	2.70	
3.0	11.0	3.36	
3.6	11.0	4.04	
4.0	11.0	4.48	
4.4	11.0	4.92	10.3
2.0	2.0	2.27	
2.0	2.5	2.82	
2.0	3.0	3.38	
2.0	3.5	3.94	
2.0	4.0	4.48	
2.0	4.5	5.05	
2.0	5.0	5.60	
2.0	5.5	6.16	
2.0	6.0	6.72	

TABLE-5  
TEMPERATURE DEPENDENCE OF OXIDATION REACTION OF  
OXIALIC ACID WITH Bi(V) IN HClO<sub>4</sub> - HF MIXTURE

Temp. (°C)	3 + log k	10 <sup>3</sup> × 1/T
20	1.79	3.41
25	1.93	3.6
30	2.01	3.30

Considering BiF<sub>6</sub><sup>-</sup> and oxalic acid as reactive species in the reaction. A plausible mechanism in conformity with the above experimental facts may be suggested as follows:



Applying steady state approximation, the rate law has been derived as

$$-\frac{d[\text{Bi(V)}]}{dt} = \frac{k_1 k_3 k_4}{k_2 + k_3 k_4} = k[\text{Oxalic acid}][\text{Bi(V)}]$$

$$k^{\circ} = \frac{k_1 k_3 k_4}{k_2 + k_3 k_4} = k[\text{Oxalic acid}]$$

where  $k^{\circ}$  = psuedo first order rate constant (observed) and  $k$  = observed second order rate constant.

Plot of  $k^{\circ}$  vs. [Oxalic acid] was linear passing through the origin in conformity with the rate law. The constant  $k$  was calculated from the slope ( $k = 6.2 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). Intermediate complex with hydrogen bonding assists in bringing Bi(V) in close proximity of O-atom for facile transference of electron to Bi(V). The kinetics investigation were carried out at 20, 25 and 30°C and calculated second order rate constant ( $k$ ) are found to be  $(6.2 \pm 2) \times 10^{-2}$ ,  $(8.6 \pm 0.31) \times 10^{-2}$  and  $(10.3 \pm 0.12) \times 10^{-2} \text{ mol}^{-2} \text{ dm}^3 \text{ s}^{-1}$ , respectively. The thermodynamic parameters were calculated in a conventional method. The energy of activation ( $E_a$ ) and entropy of activation ( $\Delta S^*$ ) are found to be  $(45.19 \pm 0.34) \text{ KJ mol}^{-1}$  and  $(-113.92 \pm 2) \text{ J K}^{-1}$ , respectively at 20°C (Table-6). The low value of energy of activation but high negative value of entropy of activation may be ascribed to the hydrogen bonded intermeidate, which causes a facile electron transference from oxygen atom to Bi(V).

TABLE-6  
THERMODYNAMIC PARAMETERS OF OXIDATION REACTION  
OF OXALIC ACID WITH Bi(V) IN HClO<sub>4</sub>-HF MIXTURE AT 20°C

log A (s <sup>-1</sup> )	6.84
E <sub>a</sub> (KJ mol <sup>-1</sup> )	45.19
ΔG (KJ)	-5.6
ΔH (KJ)	42.75
ΔS (J K <sup>-1</sup> )	-113.92

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