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Kinetics and mechanism of oxidation of glycollic acid with Bi(V) in phosphoric acid medium

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Abstract

The kinetics and mechanism of Oxidation of glycollic acid with Bi(V) has been investigated in phosphoric acid medium.

The order with respect to substrate and oxidant each is one. The reaction rate is independent of $[H^+]$ ion as well as [Bi (III)]. The reaction rate decreases with increasing ionic strength indicating reactive species of opposite charge.

The simple rate law explained all the experimental observations. The mode of electron transfer from the substrate to Bi(V) has been indicated is a bridged outer sphere mechanism.

Introduction

In synthetic and analytical chemistry Bi (V) is being used since long[1-3]. The solution chemistry of Bi(V) is not well explored as yet. In recent year some workers[4-11] have studied the redox kinetics of Bi(V) using hydrogen fluoride and perchloric acid mixture. Since it is very risky to work with such solution no useful study in the solution chemistry has been done up till now. Further the prolong use of HF makes the apparatus unusable. More over, the estimation of Bi(V) in HF-$HClO_4$ mixture requires critical condition.

These are the reason the reference about the solution chemistry of Bi(V) is very scanty in literature. In preliminary test we have tried to dissolve the solid in phosphoric acid. The pink colour solution was tested for the presence of Bi(V). The solution of Bi(V) so obtained is fairly stable for long time when it is kept in refrigerator.

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The title project is under taken for investigation to elucidates the mode of electron transfer from the substrate to the oxidant Bi(V).

Experimental

All the chemicals were either of AnalaR or guaranted reagent grade. The kinetics of the reaction was monitored by estimating the remaining Bi(V) in an aliquot samples iodometrically at different interval of time.

The kinetics of oxidation of glycollic acid (GA) with Bi(V) were studied at three different temperatures 293K, 298K & 303K.

A known quantity of sodium bismuthate (BDH Anala R) was digested in a known volume of 3.0 M phosphoric acid (H_3PO_4) and filtered for undissolved salt. The filtrate was the pink colour solution containing Bi(V). 5.0 ml Bi(V) solution was added to 5.0 mL KI (0.1 mL dm^{-3}) solution and pH of the solution was adjusted between 2 – 3 by adding 1 mol. dm^{-3} NaOH. Solution. A slight appearance of turbidity in solution indicating suitable pH of the solution. After adding 5.0 mL EDTA (0.001 mol. dm^{-3}) solution, it was titrated with thiosulphate using starch indicator. Every time freshly prepared Bi(V) solution was used[12,13].

Reaction were conducted in a Teflon bottle immersed in a water bath thermostated at desire temperature. The kinetic of the reaction were monitored by withdrawing an aliquot of 5.0 mL at different interval of time and estimating the remaining Bi(V) iodometrically stated above. Kinetic investigation were carried out under pseudo-first order condition taking glycolic acids in excess over the oxidant Bi(V).

Stoichiometry :

The stoichiometry of the reaction was determined by taking an excess of Bi(V) concentration over that of glycollic acid (GA) at fixed concentration of phosphoric acid 3.0 mol dm^{-3}. These reaction mixtures were kept in a thermostated water bath at 293K and the excess of Bi(V) was determined iodometrically[4] after ensuring the completion of the reaction after twelve hours. The stoichiometry of the reaction was found to be 1:1 *i.e.*, one mole of Bi(V) reacted with one mole of glycollic acid. The stoichiometry ratio which is greater than this ratio account for the decomposition of Bi(V).

Therefore more Bi(V) is consumed than required by glycollic acid. The stoichiometry indicate the formation of aldehyde as the end product and can be represented as follows:

$$CH_2(OH)COOH+Bi^{+5}\rightarrow CH_2O+CO_2+Bi^{+3}+2H^{+}$$

The oxidation product formaldehyde was detected by spot test.[5]

The evolution of CO_2 gas was detected by conventional method.

Rate law :

$$\frac{-d[Bi(V)]}{dt}=k[GA][Bi(V)]$$

Where Bi(V) is the total gross concentration of all phosphato species of Bi(V)

[GA] is the equilibrium concentration of glycollic acid.

Results

Bismuth (V) dependence :

The concentration of Bi(V) was varied from 0.4x10^{-3} to 2.0 x 10^{-3} mol dm^{-3} at fixed concentration of glycollic acid 1.0x10^{-2} mol dm^{-3}. and phosphoric acid 3.0 mol dm^{-3}.

The initial rate were calculated by plane mirror method[14]. The plot of initial rate (ir) versus Bi(V) is linear passing through the origin showing first order in Bi(V). Concentration of Bi(V) greater than 2.0x10^{-3} was not taken for the study as the decomposition of Bi (V) becomes significant. The values of second order rate constant (k) were calculated. The initial rates are given in (Table -1, Graph-1).

Glycollic acid dependence :

The concentration of glycollic acid was varied in the range (0.4-2.0)x10^{-2} mol dm^{-3} at a fixed concentration of Bi(V) at 1.2x10^{-3} mol dm^{-3} and also at fixed concentration 3.0 mol dm^{-3} of phosphoric acid.

The initial rates (i.r.) were calculated by plane mirror method[14] and plot of initial rate (i.r.) versus the concentration of glycollic acid has zero intercept on the ordinate yielding a straight line. Thus the order with respect to glycollic acid was found to be one. (Table -1, Graph-2).

Hydrogen ion dependence :

The concentration of hydrogen ion was varied by changing the concentration of perchloric acid ($HClO_4$) from 1.0 to 2.0mol. dm^{-3} at the fixed ionic strength of 2.4 mol. dm^{-3} adjusted with lithium perchlorate and also a fixed concentration of [Bi(V)] = 1.2x10^{-3} mol dm^{-3}. The reaction remained unchanged.

Ionic strength dependence :

The ionic strength of the reaction mixture was changed by varrying the concentration of lithium perchlorate at fixed concentration of Bi(V) =1.2x10^{-3} mol dm^{-3}, phosphoric acid 3.0 mol dm^{-3}. The reaction rates decreases with the increase in ionic strength indicating reactive species of opposite charges[15] (Table -2).

Effect of Bi (III):

The concentration of Bi(III) was varried from 2.5x10^{-3} to 1.0x10^{-2} mol. dm^{-3} at fixed concentration of [Bi(V)]= 1.2x10^{-2} mol.dm^{-3} [GA]= 1.0x10^{-2} mol. dm^{-3}, phosphoric acid [H_3PO_4]=3.0 mol. dm^{-3}. The rate of reaction remain unchanged with the changing concentration of Bi(III) indicating that the Bi(III) is not involving in any equilibrium preceeded by the rate determining step in the reaction mechanism.

Temperature dependence :

The rate of the reaction was calculated at three temperatures 293K, 298K, and 303K. The energy of activation and other parameters were calculated using the following standard equations.

$$\log K = \log A + Ea/2.303RT$$

Energy of activation (Ea) was calculated from the plot of log K Vs 1/T. The slope of curve gives the value of (Ea/2.303 RT). log A was calculated after substituting the value of logK and Ea so obtained. Entropy of activation (ΔS^*) was calculated after substituting the value of logA in the equation.

$$\Delta S^* = 2.303\ R\ (\log A - \log RT/Nh).$$

Similarly enthalpy of activation (ΔH) and free energy of activation (ΔG) was calculated using following equations

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = \Delta Ea - RT$$

The results are given in the. (Table 3 & 4)

Discussion

The speciation of phosphato bismuth (V) species in the solution can neither kinetically nor spectrally be ascertained. Since the concentration of phosphoric acid in the reaction is significantly high.

However, useful information related to phosphato bismuth (V) species can be obtained on the pattern of fluoroantimony(V) species in the solution only on the basis of their group affinity in periodic table.

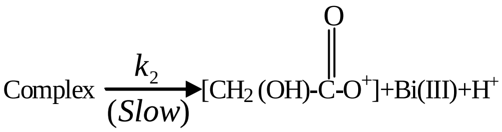
The trend of increasing cationic character is exhibited by the heavier elements, such as antimony and bismuth. Although electron gain to achieve electronic structure of the next noble gas is conceivable, a considerable amount of energy is involved in such a process.

The reactive form of bismuth (V) in phosphoric acid medium should be anionic such as $Bi(PO_4)_n^{(5-n)}$- in view of the large concentration of phosphoric acid. This species is therefore, has been written as Bi(V) for simplicity in analysis.

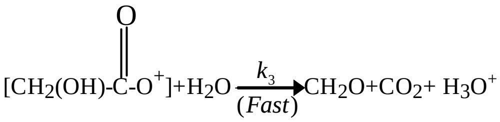
K.K, Banerji *et. al.*[16] established the fact that oxidation of α- hydroxy acid is one electron oxidation reaction. They confirmed it by kinetic isotope effect. The cleavage of α- C-H bond is the rate determining step. Other workers also observed this fact.[17]

Considering anionic phosphato-bismuth (V) species as the reactive species with glycollic acid ($CH_2(OH)\ COOH$), a probable reaction mechanism consisting of steps 1, 2, 3 can be envisaged as follow:

$$CH_2(OH)COOH + Bi\ (V) + H^+ \underset{k^{-1}}{\overset{k}{\rightleftarrows}} \text{complex} \quad (1)$$



$$\text{Complex} \xrightarrow[(Slow)]{k_2} [CH_2(OH)\text{-}C(=O)\text{-}O^+] + Bi(III) + H^+ \quad (2)$$



$$[CH_2(OH)\text{-}C(=O)\text{-}O^+] + H_2O \xrightarrow[(Fast)]{k_3} CH_2O + CO_2 + H_3O^+ \quad (3)$$

Applying steady state treatment the rate law is derived as

$$-d\,[Bi(V)]/dt = K \,.\, k_2 \cdot k_3\ [Bi(V)]\ [GA]$$

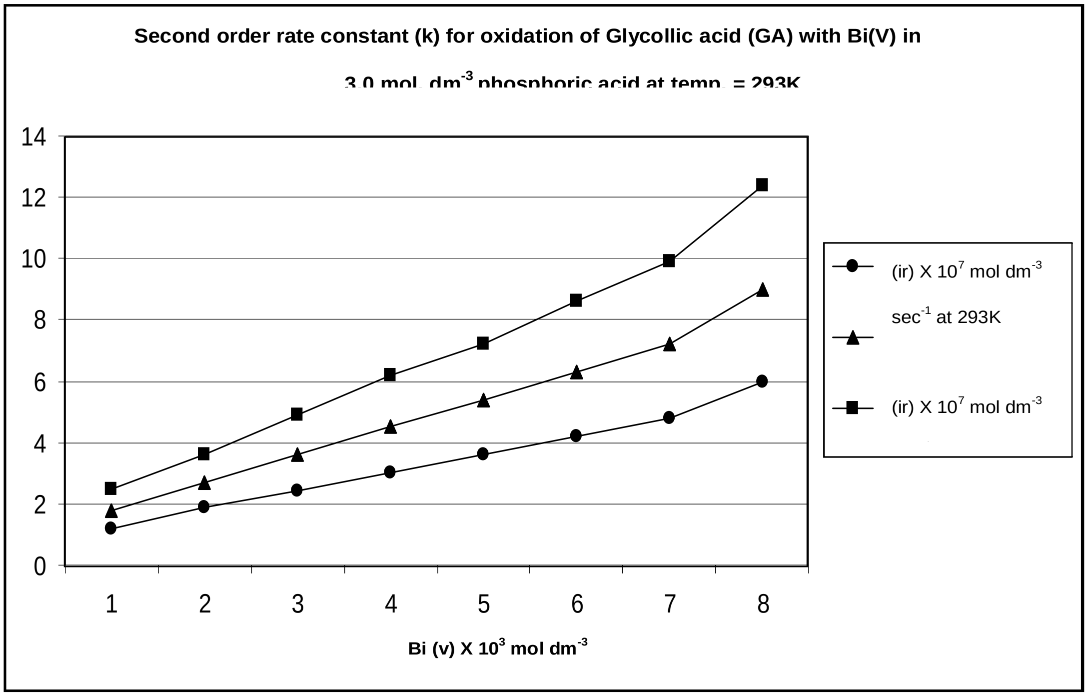
where $k_1/k_2 = K$

$$-d\,[Bi(V)]/dt = k\ [Bi(V)]\ [GA]$$

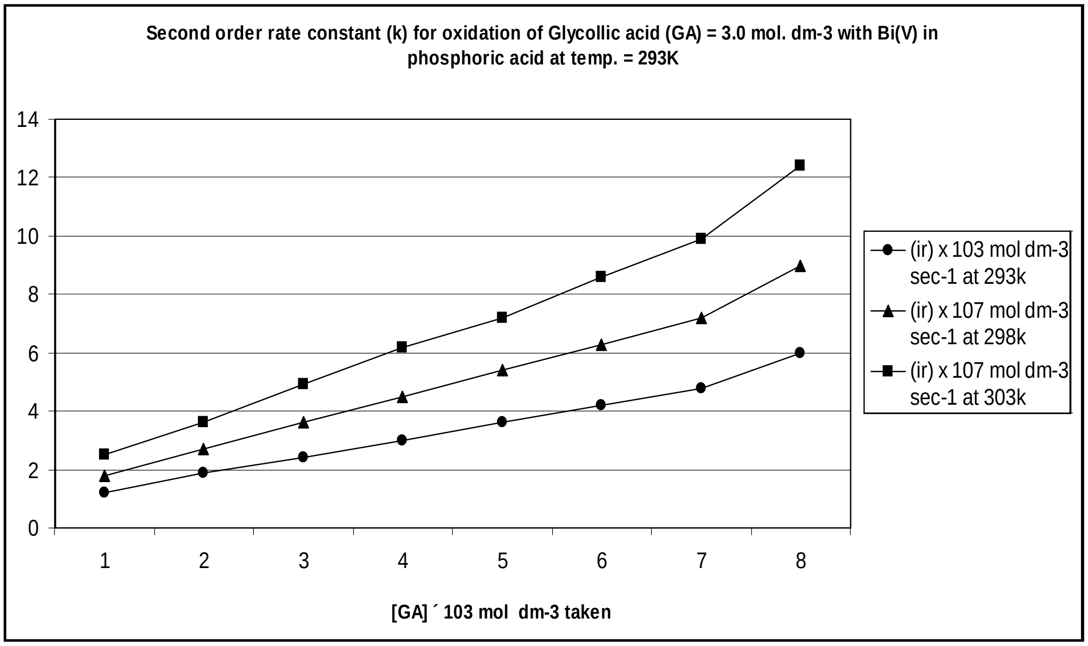
where $k = K\ k_2 \cdot k_3$

= observed second order rate constant

The kinetic investigation were performed at 293K, 298K and 303K and value of second order rate constant (K) were found as $3.01\text{x}10^{-2}$ $dm^3\ mol^{-1}$, sec^{-1}, $4.5\text{x}\ 10^{-2}\ dm^3\ mol^{-1}\ sec^{-1}$ & $6.2\ \text{x}\ 10^{-2}\ dm^3\ mol^{-1}\ sec^{-1}$ respectively.



Graph-1



Graph-2

Table 1. Second order rate constant (k) for oxidation of glycollic acid (GA) with Bi(V) in 3.0 mol. dm^{-3} phosphoric acid at temp. = 293K

[Bi(v)x10^3 mol dm^{-3} taken	[GA]x 10^3 mol dm^{-3} taken	(ir) x10^3 mol dm^{-3} sec^{-1} at 293K	(ir) x10^7 mol dm^{-3} sec^{-1} at 298K	(ir) x10^7 mol dm^{-3} sec^{-1} at 303K
1	2	3	4	5
0.4	10	1.2	1.8	2.5
0.6	10	1.9	2.7	3.6
0.8	10	2.4	3.6	4.9
1.0	10	3.0	4.5	6.2
1.2	10	3.6	5.4	7.2
1.4	10	4.2	6.3	8.6
1.6	10	4.8	7.2	9.9
2.0	10	6.0	9.0	12.4
1.2	4	1.4	2.5	3.0
1.2	6	2.2	3.8	4.5
1.2	8	2.9	5.0	5.9
1.2	10	3.6	6.3	7.2
1.2	12	4.3	7.6	8.9
1.2	14	5.1	8.8	10.4
1.2	16	5.8	10.0	11.9
1.2	20	7.2	-	14.9
Calculated Value of kx$10^2$$dm^3$$mol^{-1}$ sec^{-1}		3.01	4.5	6.2

The thermodynamic parameters were calculated in a conventional manner. The energy of activation (Ea) and entropy of activation, (ΔS^*) were calculated to be 57.44 kJ mol^{-1} and -77.92J K^{-1} respectively, at 293K.

The low value of activation energy (Ea) and negative value of entropy of activation (ΔS^*) suggested that the degree of freedom of intermediate complex is less than that of the reacting molecules and the intermediate complex permit a facile electron transfer from the substrate to Bi(V).

The formation of moderately stable complexes is supported by the value of thermodynamic parameter also. The complex formation is favoured by the enthalpy term but there is loss of entropy indicating the formation of a rigid structure.

The mechanism supports the formation of an intermediate in a rapid pre- equilibrium rate determining step in the form of a cation.

The observed negative entropy of activation[18-23] also supports the mechanism. As the charge separation takes place in the transition state of rate determining step, the charge ends are highly solvated. This results is an immoblisation of large number of solvent molecules reflected in loss of entropy[24].

Table 2.Ionic strength dependence of oxidation of [GA] with Bi(V) in phosphoric acid medium.

[GA] = 1.0 x 10^{-2}mol. dm^{-3}, [Bi(V)]=1.2x10^{-3} mol. dm^{-3}, [H_3PO_4]=3.0 mol.dm^{-3} Temperature = 293K

Ionic Strength	(ir) x 10^7 mol dm^{-3} sec^{-1}
1.4	6.5
1.6	6.0
1.8	5.8
2.0	5.6
2.4	5.3

Table 3. Temperature dependence of oxidation reaction of [GA] with Bi(V) in phosphoric acid medium

3+logK	10^3x1/T
1.45	3.41
1.61	3.36
1.79	3.30

Table 4. Thermodynamic parameters of oxidation reaction of [GA] with Bi(V) in phosphoric and medium at temperature 293K.

log A(S^{-1})	8.72
ΔEa(kJ mol^{-1})	57.44
ΔG(kJ)	77.84
ΔH(kJ)	55.00
ΔS (JK^{-1})	-77.92

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