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

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Abstract

The kinetics and mechanism of oxidation of Mandelic 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.

Keywords: α-Hydroxy acid, Mandelic acid, Bismuth, Phosphoric acid, Rate of reaction, Order of reaction.

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 apparatuses unusable. More over, the estimation of Bi(V) in HF–$HClO_4$ mixture requires critical condition.

These are the reason the references 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.

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

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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 Mandelic acids (MA) with Bi(V) were studied at three different temperatures 293K, 298K & 303K.

A known quantity of sodium bismuthate (BDH AnalaR) 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 desired temperature. The kinetics 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. Kinetics investigation were carried out under pseudo-first order condition taking Mandelic 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 Mandelic acid (MA) 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 Mandelic 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 Mandelic acid. The stoichiometry indicate the formation of aldehyde as the end product and can be represented as follows :

$$Ph–CH(OH)COOH + Bi^{+5} — Ph–CHO + CO_2 + Bi^{+3} + 2H^+$$

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

The evolution of CO_2 gas was detected by conventional method.

Rate law :

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

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

[MA] is the equilibrium concentration of Mandelic acid.

Results :

Bismuth (V) dependence :

The concentration of Bi(V) was varied from 0.4×10^{-3} to 2.0×10^{-3} mol dm^{-3} at fixed concentration of Mandelic acid 1.0×10^{-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 2.0×10^{-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).

Mandelic acid dependence :

The concentration of Mandelic acid was varied in the range (0.4–2.0) $\times 10^{-2}$ mol dm^{-3} at a fixed concentration of Bi(V) at 1.2×10^{-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 Mandelic acid has zero intercept on the ordinate yielding a straight line. Thus the order with respect to Mandelic acid was found to be one. (Table-1, Graph-2).

Hydrogen ion dependence :

The concentration of hydrogen ion was varied by changing the concentration pf perchloric acid ($HClO_4$) from 1.0 to 2.3 mol dm^{-3} at the fixed ionic strength of 2.6 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 varying the concentration of lithium perchlorate at fixed concentration of Bi(V) = 1.2×10^{-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 varied from $2.5x10^{-3}$ to $1.0x10^{-2}$ mol. dm^{-3} at fixed concentration of [Bi(V)]= $1.2x10^{-2}$ mol.dm^{-3} [MA]= $1.0x10^{-2}$ 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 preceded 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.

$$\text{Log } A = \log K + Ea/2.303\ RT$$

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 log K and Ea so obtained. Entropy of activation (ΔS^*) was calculated after substituting the value of log A 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 phosphate 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 phosphate 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 phosphate- bismuth (V) species as the reactive species with Mandelic Acid Ph–CH(OH)COOH a probable reaction mechanism consisting of steps 1, 2, 3 can be envisaged as follow

$$\text{Ph–CH(OH) COOH} + \text{Bi(V)} + \text{H}^+ \underset{k^{-1}}{\overset{k}{\rightleftharpoons}} \text{complex} \quad (1)$$

$$\text{Complex} \underset{\text{(slow)}}{\overset{k_2}{\rightarrow}} [\text{PhCH(OH)–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–O}^+] + \text{Bi(III)} + \text{H}^+ \quad (2)$$

$$[\text{Ph–CH(OH)–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–O}^+] + \text{H}_2\text{O} \underset{\text{Fast}}{\overset{k_3}{\rightarrow}} \text{Ph–CHO} + \text{CO}_2 + \text{H}_3\text{O}^+ + \ldots \quad (3)$$

Applying steady state treatment the rate law is derived as

$$-d[\text{Bi(V)}]/dt = K\, k_2k_3\, [\text{Bi(V)}]\, [\text{MA}]$$

where $k_1/k_2 = K$

$$-d[\text{Bi(V)}]/dt = k\, [\text{Bi(V)}]\, [\text{MA}]$$

where $k = K\, k_2k_3$= 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 $2.57\text{x}10^{-2}$ $dm^3\, mol^{-1}$, sec^{-1}, $3.47\text{x}10^{-2}$ $dm^3\, mol^{-1}\, sec^{-1}$ & $5.13\text{x}10^{-2}$ $dm^3\, mol^{-1}\, sec^{-1}$ respectively.

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

[Bi(V)] x 10^3 mol dm^{-3} taken	[MA] x 10^3 mol dm^{-3} taken	[ir]x10^7 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	1.03	1.39	2.05
0.6	10	1.54	2.08	3.08
0.8	10	2.06	2.78	4.10
1.0	10	2.67	3.47	5.13
1.2	10	3.28	4.28	6.16
1.4	10	3.60	4.86	7.18
1.6	10	4.11	5.55	8.21
2.0	10	5.14	6.94	10.26
1.2	4	1.23	1.94	2.46
1.2	6	1.85	2.91	3.69
1.2	8	2.47	3.89	4.92
1.2	10	3.08	4.86	6.16
1.2	12	3.70	5.83	7.39
1.2	14	4.32	6.80	8.62
1.2	16	4.93	7.78	9.85
1.2	20	6.17	9.72	12.31
Calculated value of kx$10^2$$dm^3$ mol^{-1} sec^{-1}		2.57	3.47	5.13

Table 2.
Ionic strength dependence of oxidation of [MA] with Bi(V) in phosphoric acid medium.
[MA] = 1.0 x 10^{-2} mol dm^{-3}, [Bi(V)] = 1.2 x 10^{-3} mol dm^{-3}, [H_3PO_4] = 3.0 mol dm^{-3}, Temperature = 293 K.

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 [MA] with Bi(V) in phosphoric acid medium.

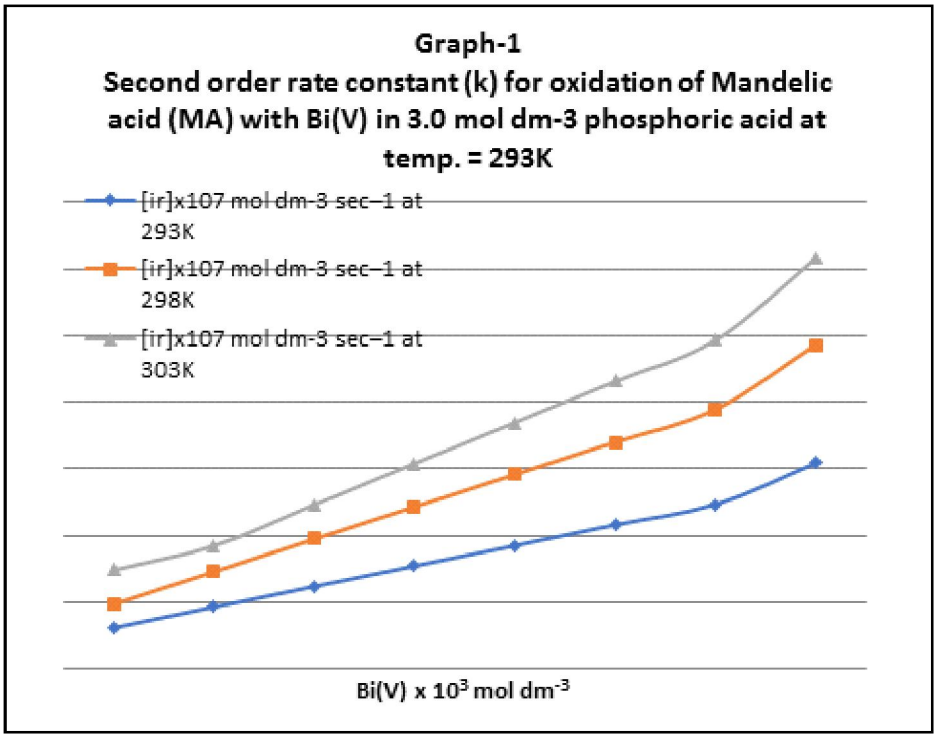
3+logK	10^3 x 1/T
1.41	3.41
1.54	3.36
1.71	3.30

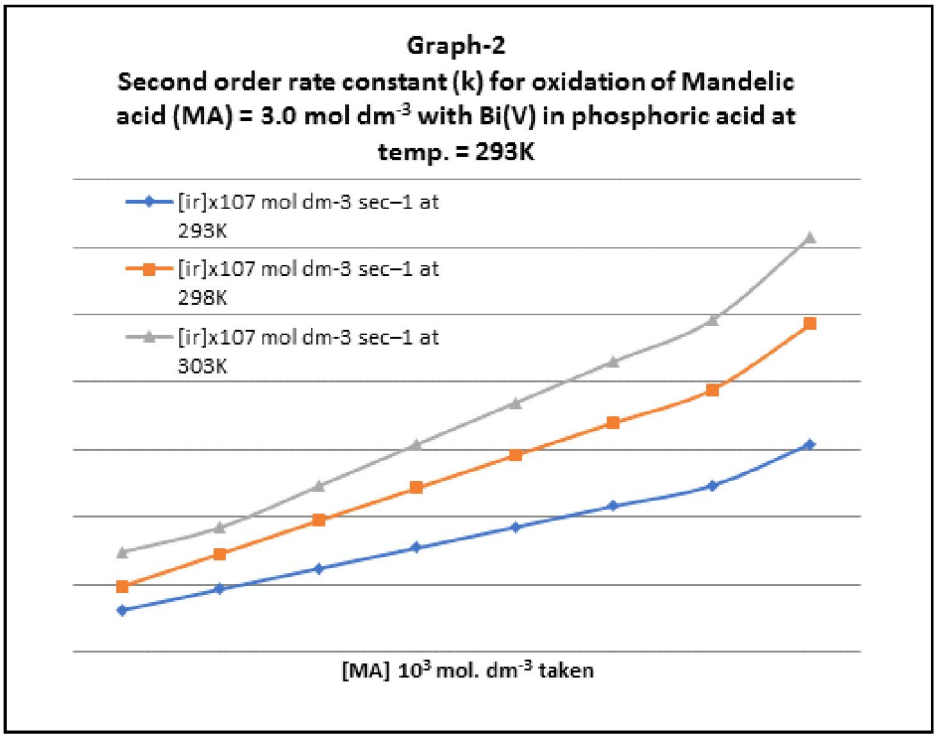
Table 4.
Thermodynamic parameters of oxidation reaction of [MA] with Bi(V) in phosphoric acid and medium at temperature 293K.

logA(S^{-1})	7.80
ΔEa(kJ mol^{-1})	52.66
ΔG(kJ)	78.20
ΔH(kJ)	50.22
ΔS(JK^{-1})	–99.56

Table 5.
Table of abbreviation and its respective name.

Bi(V)	Bismuth in +5 oxidation state
EDTA	Ethylene diamine tetraacetate
i.r.	Initial rate
MA	Mandelic acid
Ea	Activation energy
ΔS	Entropy
ΔH	Enthalpy
ΔG	Gibb's energy
A	Pre-exponential factor


Graph-1
Second order rate constant (k) for oxidation of Mandelic acid (MA) with Bi(V) in 3.0 mol dm-3 phosphoric acid at temp. = 293K
[ir]x107 mol dm-3 sec−1 at 293K
[ir]x107 mol dm-3 sec−1 at 298K
[ir]x107 mol dm-3 sec−1 at 303K
Bi(V) x 10³ mol dm⁻³


Graph-2
Second order rate constant (k) for oxidation of Mandelic acid (MA) = 3.0 mol dm⁻³ with Bi(V) in phosphoric acid at temp. = 293K
[ir]x107 mol dm-3 sec−1 at 293K
[ir]x107 mol dm-3 sec−1 at 298K
[ir]x107 mol dm-3 sec−1 at 303K
[MA] 10³ mol. dm⁻³ taken

The thermodynamic parameters were calculated in a conventional manner. The energy of activation (Ea) and entropy of activation, (ΔS^*) were calculated to be 52.65 kJ mol^{-1} and –99.56 JK^{-1} mol^{-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 intermediated complex is less than that of 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 or entropy indicating the formation of a rigid structure.

The mechanism supports the formation of an intermediate in a rapid pre-equilibrium in the rate determining step form 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 because highly solvated. This result is an unmoblisation of large number solvent molecule reflected in loss of entropy.[24]

Conclusion

Although, it was observed that rate of reaction was first order with respect to concentration of the mandelic acid only upto the lower range of the concentration of mandelic acid. However, at higher concentration of mandelic acid, the rate reaction became independent of the concentration of the mandelic acid. Thus the rate of reaction was observed as complex with respect to the concentration of the mandelic acid.

Further, the effect of ionic strength on the rate of reaction was also studied. It was found that rate of reaction increases with increase of ionic strength, which indicates that the formation of ionic intermediate. As ionic intermediate is stablised by the ionic medium so, activation energy decreases. It increases the rate of reaction.

Furthermore, the effect of acidic medium i.e. the concentration of H^+ ion (i.e pH of the reaction mixture) on the rate of reaction was also studied. It was found that rate of reaction decreases with increase of pH of the reaction mixture.

Scope of future work :

This work will give opportunity to future scholar to strengthen the field of kinetics and mechanism of oxidation of different α-hydroxy acid with Bismuth(V) phosphate complex.

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