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Kinetic Studies of Oxidation of Lactose with Biv Oxidizing Agent

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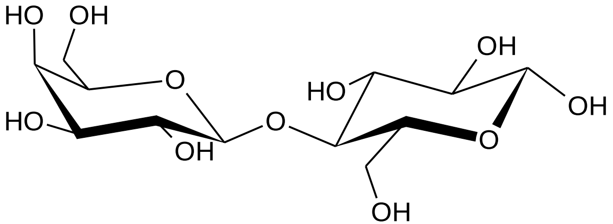
ABSTRACT

The present research work has explained the effect of concentration of lactose and effect of the concentration of BiV. The rates of reactions were studied at three different temperatures at 298 K, 308 K and 318 K of disaccharide sucrose. The research work has confirmed that the rate of reaction was first order with respect to the oxidant in the whole range of the concentration of bismuthate ion.

Keywords : Disaccharide, lactose, Bismuth, Rate of reaction, Order of Reaction

I. INTRODUCTION

Latose is a disaccharide[1-5]. It is a sugar composed of galactose and glucose subunits and has the the following structure.



Lactose

Lactose makes up around 2-5% of milk[6].

The most common oxidation states of bismuth are: III and V. Due to the inert pair effect, bismuth in V oxidation state is less stable and hence in this state, element has tendency to convert readily into III or elemental form. So, in this state, bismuth acts as strong oxidizing agent.

II. MATERIALS AND METHODS

The requisite quantities of various components of the reaction mixturewere taken in glass stoppered Erlenmeyer flasks, which were then suspended in a water bath thermostated at the desired temperature ±0.1 ^{0}C. The reaction was initiated by adding the requisite solution into the reaction mixture and the time of initiation was recorded when half of the contents from the pipette were released. Aliquot samples (5 to 10 cm^3) were withdrawn at different intervals of time and then quenched in an ice-cold KI (10%) solution; the liberated iodine was titrated against thisulphate solution using starch as an indicator. Measurements in triplicate without any intereference from the ingredients of the reaction mixture were in agreement to within ±5%.

Initial rates were computed employing plane mirror method[7]. Pseudo-first order plots were also made wherever reaction conditions permitted. Since the

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kinetics is not affected by the light, no further precautions were taken to exclude light from the reaction mixtures.

KINETICS OF LACTOSE WITH BI^V:

The kinetics of oxidation of lactose with Bi (V) in phosphoric acid medium was studied at three different temperatures say 298 K, 308 K, 318 K. The order with respect to oxidant is one. It is complex one with respect to maltose. Rate law may be expressed as:

$$Rate\ law = -\frac{d[Bi^V]}{dt}$$

$$-\frac{d[Bi^V]}{dt} = \frac{kK[Bi^V][Lact]}{1+K[Lact]}.\frac{1}{1+K_p[H^+]}$$

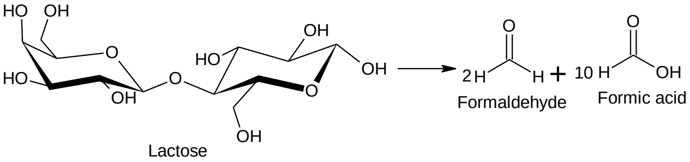
$$k^I = \frac{kK[Lact]}{1+K[Lact]}.\frac{1}{1+K_p[H^+]}$$

Where, [Bi^V] is the total gross concentration of all phosphate species of Bi (V) and [Lact] is the equilibrium concentration of lactose.

STOICHIMETRY:

The stoichimetry of the reaction was determined by taking an excess of Bi (V) concentration over thatof Lactose (Lactt) at fixed concentration of phosphoric acid (3.0M). The reaction mixtures wee kept in a thermostated water bath at desired temperature and the excess of Bi (V) was determined iodomerically[8] 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 lactose.

The stoichiometric ratio, which is greater than this ratio account for decomposition of Bi (V), therefore more Bi (V) is consumed than required by lactose. The stoichimetry indicates the formation of these products as the end products and can be represented as follows:



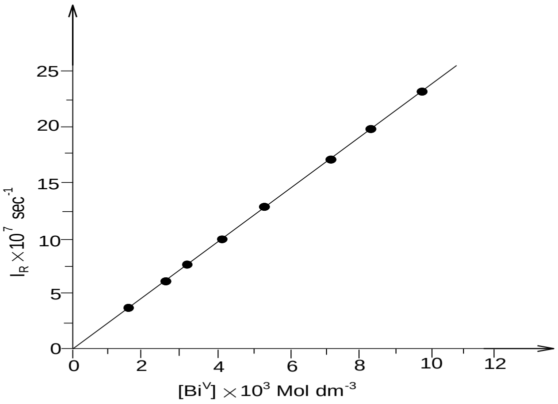
The oxidation product of formaldehyde and formic acid were detected by spot test[9]. The results are recorded in table:-1

Table:-1

[Lact] = 5.0×10^{-3} mol dm^{-3}, Temp.= 308 K

[H$_3$PO$_4$]= 3.0 mol dm^{-3}, Aliquot= 5mL

[Bi^V]×10^{-3} mol dm^{-3}	[Lact]×10^{-3} mol dm^{-3}	[I$_R$]×10^{7}Sec^{-1}
1.5	5.0	4.0
2.5	5.0	6.33
3.3	5.0	7.8
4.16	5.0	10.0
5.4	5.0	12.8
7.35	5.0	17.2
8.2	5.0	19.2
9.8	5.0	23.0



Graph : A PLOT OF I_R vs [Bi^V] AT FIXED CONCENTRATION OF LACTOSE AT 308 K FOR OXIDATION OF LACTOSE

Bi (V) DEPENDENCE:

The concentration of Bi (V) was varied from 1.5×10^{-3} to 9.8×10^{-3} mol dm^{-3} at fixed concentration of lactose 5.0×10^{-3} mol dm^{-3}. The initial rates (I_R) were computed by plane mirror method[10]. These results are recorded in table:-2

Table:-2

$[Bi^V] = 1.63\times10^{-3}$ mol dm^{-3}, Temp.= 298 K $[H_3PO_4]$= 3.0 mol dm^{-3}, Aliquot= 5mL

$[Lact]\times10^{-3}$ mol dm^{-3}	$[Bi^V]\times10^{-3}$ mol dm^{-3}	$[I_R]\times10^7$ Sec^{-1}	$K_0\times10^4$ Sec^{-1}
2.0	1.63	1.16	4.0
3.0	1.63	1.58	6.33
4.0	1.63	1.83	7.8
5.0	1.63	2.00	10.0
6.0	1.63	2.11	12.8
8.0	1.63	2.16	17.2

The plot of initial rates (I_R) vs Bi (V) yielded straight line pasing through the origin indicating first order with respect to Bi (V) oxidant.

LACTOSE DEPENDENCE:

The concentration of lactose was varied in the range of 2.0×10^{3} mol dm^{-3} to 8.0×10^{3} mol dm^{-3} at fixed concentration of Bi (V) i.e. 1.63×10^{-3} mol dm^{-3} and also at fixed concentration of phosphoric acid 3.0 mol dm^{-3} at 298 K. The results are in table:-3.

Table:-3

$[Bi^V] = 1.63\times10^{-3}$ mol dm^{-3}, Temp.= 308 K $[H_3PO_4]$= 3.0 mol dm^{-3}, Aliquot= 5mL

$[Lact]\times10^{3}$ mol dm^{-3}	$[Bi^V]\times10^{-3}$ mol dm^{-3}	$[I_R]\times10^7$ Sec^{-1}	$K_0\times10^4$ Sec^{-1}
1.0	1.63	1.66	1.66
2.0	1.63	2.66	1.33
3.0	1.63	3.33	1.11
4.0	1.63	4.33	1.08
5.0	1.63	5.00	1.00
6.0	1.63	5.50	0.91
7.0	1.63	6.00	0.86

The concentration of lactosewas varied in the range of 1.0×10^{3} mol dm^{-3} to 7.0×10^{3} mol dm^{-3} at fixed concentration of Bi (V) i.e. 1.63×10^{-3} mol dm^{-3} and also at 308 K. The results are in table:-4.

Table:-4

$[Bi^V] = 1.63\times10^{-3}$ mol dm^{-3}, Temp.= 318 K $[H_3PO_4]$= 3.0 mol dm^{-3}, Aliquot= 5mL

$[Lact]\times10^{3}$ mol dm^{-3}	$[Bi^V]\times10^{-3}$ mol dm^{-3}	$[I_R]\times10^7$ Sec^{-1}	$K_0\times10^4$ Sec^{-1}
2.0	1.63	4.66	2.33
4.0	1.63	10.66	2.60
6.0	1.63	20.12	3.30
10.0	1.63	24.00	2.40
15.0	1.63	32.00	2.10
20.0	1.63	40.10	2.00

The concentration of lactosewas varied in the range of 2.0×10^{3} mol dm^{-3} to 20.0×10^{3} mol dm^{-3} at fixed concentration of Bi (V) i.e. 1.63 $\times 10^{-3}$ mol dm^{-3} and also at 318 K. The results are in table:-5.

Table:-5

$[Bi^V]$ = 1.6×10^{-3} mol dm^{-3}, Temp.= 308 K
[Lact]= 5.0 $\times10^{-3}$ mol dm^{-3}, Aliquot=5mL
H_3PO_4 = 3.0 mol dm^{-3}

1 mol dm^{-3}	$[I_R]\times10^7 Sec^{-1}$
1.4	5.35
1.6	5.75
1.8	6.00
2.0	6.40
2.4	7.00
2.6	7.35

The initial rates were calculated by plane mirror method[11]. The plot of initial rate (I_R) vs concentration of lactosegave a curve line. Thus the order with respect to sugar seemed to be complex one.

IONIC STRENGTH DEPENDENCE:

Investigations were carried out at different ionic strength in the range of 1.4mol dm^{-3} to 2.6mol dm^{-3}. The reaction rates increases with increasing ionic strength. The table:-6 shows the results.

Table:-6

$[Bi^V]$ = 1.6×10^{-3} mol dm^{-3}, Temp.= 308 K
[Lact]= 5.0 $\times10^{-3}$ mol dm^{-3}, Aliquot=5mL
H_3PO_4 = 3.0 mol dm^{-3}

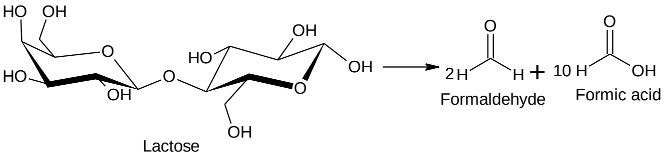
$[HClO_4]$1 mol dm^{-3}	$[I_R]\times10^7 Sec^{-1}$
0.50	9.20
0.90	7.50
1.00	7.10
1.25	6.00
1.50	5.30
1.75	5.00
2.00	4.83

H^+ ION DEPENDENCE:

The H^+ ion concentration was varied from 0.5 to 2.0 mol dm^{-3} by adding $[HClO_4]$ at constant ionic strength. The reaction rate decreases with increasing H^+ ion concentration.

III. RESULTS AND DISCUSSION

The oxidation of lactose by sodium bismuthate was carried out, which gave two equivalents of formaldehyde and ten equivalents of formic acid in acidic medium (pH = 3). The titration curves suggested the formation of following oxidative products as:



Effect of Bismuthate:

The plot of initial rates (I_R) vs Bi (V) yielded straight line pasing through the origin indicating first order with respect to Bi (V) oxidant as observed in table:-2. It was observed that the rate law equation with respect to bismuthate ion may be written as:

$$Rate \propto [\,Bismuthate] \ldots\ldots\ldots\ldots..(1)$$

Effect of Concentration of Lactose:

The initial rates were calculated by plane mirror method[1]. The plot of initial rate (I_R) vs concentration of maltose was yieled a curve line. Thus the order with respect to lactose seemed to be complex one.

The concentration of lactose was varied in the range of 1.0×10^3 mol dm^{-3} to 20.0×10^3 mol dm^{-3} at fixed concentration of Bi (V) i.e. 1.63 $\times10^{-3}$ mol dm^{-3} and also at fixed concentration of phosphoric acid 3.0 mol dm^{-3}. The investigations were carried out at three difrent temperatures i.e. 298 K, 308 K, 318 K. The results are shown in Tables:-3, 4 and 5 and their respective graphs.

The graph at 298 K shows that at lower concentration of the lactose, rate linearly varies with the concentration of the sugar exhibiting first order say about 4.0×10^{3} mol dm^{-3} concentration of the lactose. However, as concentration exceeds this value, rate became independent or more clearly it remains constant.

The graph at 308 K remains almost same as at 298 K. it shows that at lower concentration of the lactose say about 6.0×10^{3} mol dm^{-3} concentration of the lactose, rate linearly varies with the concentration of the lactose exhibiting first orde. However, as concentration exceeds this value, rate became constant.

The graph at 318 K was found to be more complex. The plot of initial rate (I_R) vs concentration of lactose was yieled a curve lines and different from the graphs obtained at 308 K and 318 K. Thus the order with respect to lactose seemed to be complex one.

Hence, the rate law equation with respect to lactose is difficult to express. The overall rate may be pseudofirst order say first order with respect to the [bismuthate] and remains independent from [Lactose].

Effect of Ionic Strength:

Investigations were showed reaction rates increases with increasing ionic strength shown in table:-6.

The variation of rate of reaction with ionic strength indicates that formation of ionic intermediate, which is stabilized by ionic medium, during the course of reaction. Since ionic intermediate is stabilized by ionic medium, which decreases the activation energy. Hence rate of reaction increases with increase of ionic strength.

Effect of [H+]:

The concentration of H^+ ion was varied from 0.5 to 2.0 mol dm^{-3} by adding [$HClO_4$] at constant ionic strength. The reaction rate decreases with increasing H^+ ion concentration. The observation at 308 K has been given in table:-7. It is obvious thatthe rate of reaction decreases with increasing H^+ ion concentration i.e rate decreases with decreasing pH.

Reaction Mechanism:

Considering all these observations and also accounting for the experimental findings a probable reaction mechanism can be proposed as follows:

$$Bi(PO_4)_6^- + H^+ \rightarrow^{K_P} HBi(PO_4)_6 \dots\dots\dots.(1)$$

$$Bi(PO_4)_6^- + Lactose \rightarrow^{K}\ Complex \dots\dots\dots.(2)$$

$$\text{Complex} \xrightarrow[\text{Slow}]{k} \text{Product} \ldots\ldots\ldots\ldots\ldots(3)$$

By using the Eq.1, Eq.2 and Eq.3, the rate law equation may be derived as:

$$-\frac{d[Bi^V]}{dt} = \frac{kK[Bi^V][Lact]}{1+K[Malt]}.\frac{1}{1+K_P[H^+]} \dots\dots\dots..(4)$$

$$or,\quad \frac{-\frac{d[Bi^V]}{dt}}{[Bi^V]} = \frac{kK[Lact]}{1+K[Lact]}.\frac{1}{1+K_P[H^+]}$$

$$or,\quad K^I = \frac{kK[Lact]}{1+K[Lact]}.\frac{1}{1+K_P[H^+]} \dots\dots\dots(5)$$

$Where,$
$K^I\ =\ observed\ first\ order\ rate\ constant,$

$[Lact]$
$=\ Equilibrium\ concentration\ of\ maltose$

$$[Bi^V] = total\ gross\ concn.\ of\ all\ phosphato\ species\ of\ Bi^V$$

$$\frac{1}{K^I} = \left\{\frac{1+K[Lact]}{kK[Lact]}\right\}.\{1+K_P[H^+]\} \ldots\ldots\ldots\ldots(6)$$

$$or, \quad \frac{1}{K^I} = \left\{\frac{1}{kK[Lact]}+\frac{1}{k}\right\}.\{1+K_P[H^+]\}$$

$$or, \quad \frac{1}{K^I} = \left\{\frac{1+K_P[H^+]}{kK[Lact]} + \frac{1+K_P[H^+]}{k}\right\} \ldots\ldots\ldots(7)$$

A plot of $1/K^I$ vs 1/[lactose] at constant $[H^+]$ ion concentration was constructed from the equation. A straight line with non-zero intercept was obtained as below:

Taking different concentrations of lactoseat three different temperatures 298 K, 308 K and 318 K, the value of 'k' was calculated to be ~95, ~65 and ~20 at 298 K, 308 K and 318 K, respectively.

A plot of $1/[k^I]$ vs 1/[lactose] at different concentration of $[H^+]$ ion yield a straight line as below:

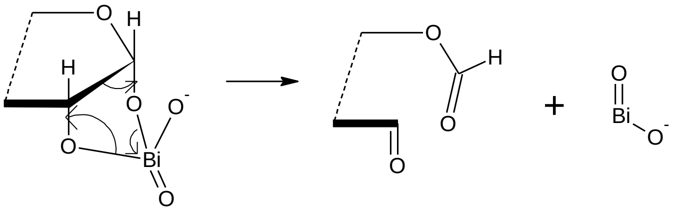
The plot of intercept $\frac{1+K_P[H^+]}{k}$ and gradient $\frac{1+K_P[H^+]}{kK}$ against $[H^+]$ were further constructed.

The value of k and K_P were calculated from the ratio of intercept and gradient as 4.3 $dm^3\ mol^{-1}$ and 1.4 $dm^3 mol^{-1}$.

Further, K^I was calculated from the values of k, K and K_P by the help of respective equations.

The mode of electron transfer is through an intermediate to be formed in two equivalent steps taking oxidative cleavage.

The oxidation of lactose with sodium bismuthate in phosphoric acid medium takes place via the formation of bismuthic acid followed by the formation of cyclic intermediate, which readily decomposes to form carbonyl compounds. It may be shown as:



Oxidation kinetics of lactose has been studied by some researchers[12,13] and it has been observed that oxidation of of sugar by sodium busmuthate takes place almost similar to that of lead tetracetate[14-16]. Such oxidative cleavage had been also observed[17].It is remarkable that the side reactions are also observed[18,19].The oxidation products of lactose have also been found as formaldehyde and formic acid by other workers[20].

IV. CONCLUSION

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

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.

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