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Kinetics and mechanism of oxidation of Maltose by Potassium Permanganate in Sulphuric acid medium

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Abstract

The oxidation kinetics of maltose has been measured spectrophotomatrically. Oxidation behaviour of potassium permanganate is proved in case of sugar maltose and first order kinetics is obtained. According to changing the reaction condition it has been found that when concentration of maltose, potassium permanganate, sulphuric acid increases, then the rate of reaction also increases while the variation of concentration of salt does not affect the rate of reaction which indicates the molecular species has been involved during the reaction. A plot of [maltose] verses K was found to be linear and also plot of log [maltose] verses logK gave straight line with unity slope indicates the first order kinetics. Carboxylic acid group formed as a main product of oxidation by MnO_4^-. These products are formed due to the cleavage of c-c bond of sugar by permanganate ion. Rate law equation, stoichiometry and mechanism of the reaction is determined.

The kinetic and mechanistic study of oxidation of carbohydrates specially the monosaccharides and disaccharides have been largely responsible for the great interest due to its biochemical and biophysical importance. These kinetic studies have occured under different reaction conditions such as changing the concentration of ionic strength, temperature, p^H. Literature survey reveals that various kinetic studies have been done for the oxidation of different mono and disaccharides by several oxidants such as Potassium heptaoxodichromate (VI)[13], Vanadium (V)[12,14], Ruthenium(III)[6], Potassium Ferrate(VI)[13], etc. and so many results were found. K.K. Gupta and U. Chatterjee described that the oxidation of D-glucose 6 phosphate by hexachloroiridate (IV) and tetrachloroaurate (III)[15] at constant concentration of sugar, acid and temperature. The first order rate constant was found and rate was enhanced by increasing sodium chloride concentration. In spite of these works it has been observed that very less work has been done in acidic medium. Hence the

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present work is taken for the investigation and selected for kinetics and mechanism of oxidation of maltose by potassium permanganate in acidic medium.

In this research work, efforts have been made for the determination of order of reaction, establishment of reaction mechanism and rate law, formation of acid derivative which can be helpful for understanding the oxidising capacity of potassium permanganate.

2. Experimental

(a) Stock solutions :

Analytical grade chemicals is used for the analysis of present work and stock solutions of maltose (0.1 M), potassium permanganate (0.01M), potassium nitrate (0.1M), sulphuric acid (0.1M) were freshly prepared using doubly distilled water.

(b) Spectrophotometer :

Systronic UV/Visible Spectrophotometer–105 is used for recording kinetic data at 545nm wavelength. During the oxidation reaction of maltose with potassium permanganate the colour of the solution turns purple to brown. Optical density of potassium permanganate is recorded as a function of time. First order reaction is determined and according to beer lamberts law rate constant is recorded by the slope of graph plotting between log A Vs time (t).

(c) Stoichiometry and product analysis :

In this section reaction mixture of maltose and oxidant were allowed to kept for 72 hours at room temperature and residual [$KMnO_4$] is determined. According to the analysis 4 moles of the potassium permanganate is required for the oxidation of 1 mole of the maltose. Requisite volume of the maltose and the permanganate is taken in the reaction vessel and 0.5 ml of the sulphuric acid is added in it and allowed to kept overnight and by using conventional method -COOH group is determined in the main product of oxidation of maltose[10].

Effect of variation of concentration of oxidant :

The rate of reaction was increased by increasing the concentration of oxidant. This experiment was done at constant concentration of maltose, salt, and acid. Oxidant concentration was varying from 1x 10^{-3}mol dm^{-3} to 5 x 10^{-3} mol dm^{-3}. First order rate constant was calculated from the slope of graph plotted log A verses time (t) (Figure 1). The value of rate constant was presented in the Table 1. It was observed that the plot of K verses [MnO_4^-] has been found linear indicates first order dependence on permanganate ion (Figure 2)[10].

Effect of variation of concentration of substrate :

It was found that rate of oxidation of maltose was increased by increasing the concentration of maltose from 1x 10^{-2} mol dm^{-3} to 5 x 10^{-2} mol dm^{-3}, while keeping constant other parameters and first order kinetics is determined. K is obtained by graph plotting between log A and time (Table 2 & Figure 3) and also a plot of K verses [maltose] (figure 4) gives straight line showing the first order rate of oxidation reaction[12,13].

Effect of variation of concentration of sulphuric acid :

It has been seen that rate of reaction increases by increasing the concentration of sulphuric acid by changing it’s concentration from 1×10^{-1} mol dm^{-3} - 5×10^{-1} mol dm^{-3} (Table 3 & Figure 5) indicates that reactive species of oxygen produced during the oxidation reaction of the maltose by permanganate ion. The plot of K against $[H^{+}]$ (figure 6) which was linear indicates that hydrogen ion involved in the rate determining step of the oxidation reaction[15].

Effect of variation of concentration of salt:

It has been recorded that by changing the concentration of salt $[KNO_3]$ does not affect on the rate of reaction. This result shows that the reacting species of oxidation reaction are non-ionic or in molecular in nature[12].

Mechanism and rate law :

Potassium permanganate produces permanganate ion and nascent oxygen in acidic medium. Maltose has one free hemiacetal group. In aqueous solution of maltose three forms α, β and aldehydo exist as an equilibrium mixture and forms carboxylic acid (*e.g.* maltonic acid) on oxidation[14].

$$C_{12}H_{22}O_{11} + [O] \longrightarrow \text{maltonic acid} \quad ....(2)$$

$$C_{12}H_{22}O_{11} + MnO_4^{-} + H_3O^{+} \underset{\mathbf{K''}}{\overset{\mathbf{K'}}{\rightleftharpoons}} \underset{\text{Complex}}{[C_{12}H_{22}O_{11}.......\ MnO_4^{-}]} \quad ....[1]$$

$$\underset{\text{Complex}}{[C_{12}H_{22}O_{11}.......\ MnO_4^{-}]} \xrightarrow[\text{slow}]{\mathbf{K'''}} [\text{ Corresponding Product}] \quad ....[2]$$

Since,

$$\underset{\text{complex}}{[C_{12}H_{22}O_{11}.......\ MnO_4^{-}]} = \frac{\mathbf{K'}\,[C_{12}H_{22}O_{11}]\,[MnO_4^{-}]}{\mathbf{K'} + \mathbf{K'''}} \quad ....(3)$$

Since,

$$\text{Rate} = \frac{\mathbf{K'}\,\mathbf{K'''}\,[C_{12}H_{22}O_{11}]\,[MnO_4^{-}]}{\mathbf{K'} + \mathbf{K'''}} \quad ....(4)$$

and

$$\frac{-\,d\,[MnO_4]}{dt} = \frac{\mathbf{K}^{'}\,\mathbf{K}^{'''}\,[C_{12}H_{22}O_{11}]\,[MnO_4^-]}{\mathbf{K}^{'} + \mathbf{K}^{'''}} \quad \text{.....................[5]}$$

With the help of mathematical rearrangement of the equations following equation of first order reaction is predicted for the present oxidation reaction.

$$\frac{-\,d\,[MnO_4]}{dt} = \frac{\mathbf{K}^{'}\,\mathbf{K}^{'''}\,[C_{12}H_{22}O_{11}]\,[MnO_4^-]}{\mathbf{K}^{'} + \mathbf{K}^{'''} + \mathbf{K}^{'}\,[C_{12}H_{22}O_{11}]}$$

The value of $\mathbf{K}^{'} + \mathbf{K}^{'''} >>> \mathbf{K}^{'}$ [maltose], so above equation can be written as follows:

$$\frac{-\,d\,[MnO_4]}{dt} = \mathbf{K}\;[C_{12}H_{22}O_{11}]\,[MnO_4^-]$$

$$\text{Where}\quad \mathbf{K} = \frac{\mathbf{K}^{'}\,\mathbf{K}^{'''}}{\mathbf{K}^{'} + \mathbf{K}^{'''}}$$

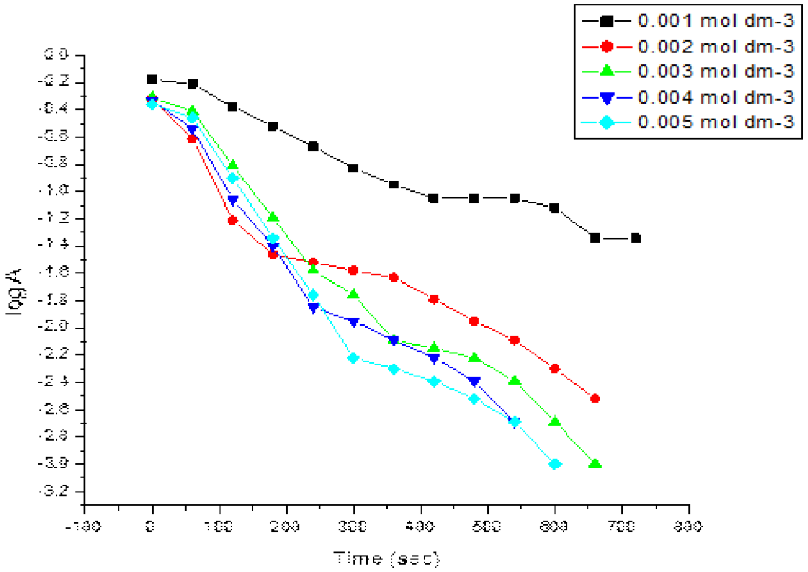

Figure 1 : Plot of logA versus Time (sec) for effect of variation of [$KMnO_4$]

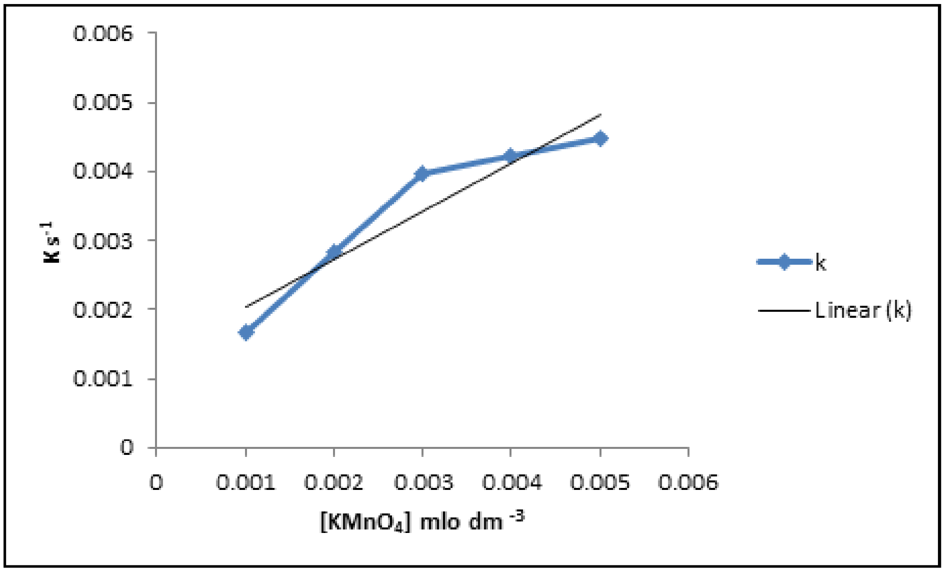

Figure 2 : Plot of K (s^{-1}) versus [$KMnO_4$] mol dm^{-3} for effect of variation of [$KMnO_4$]

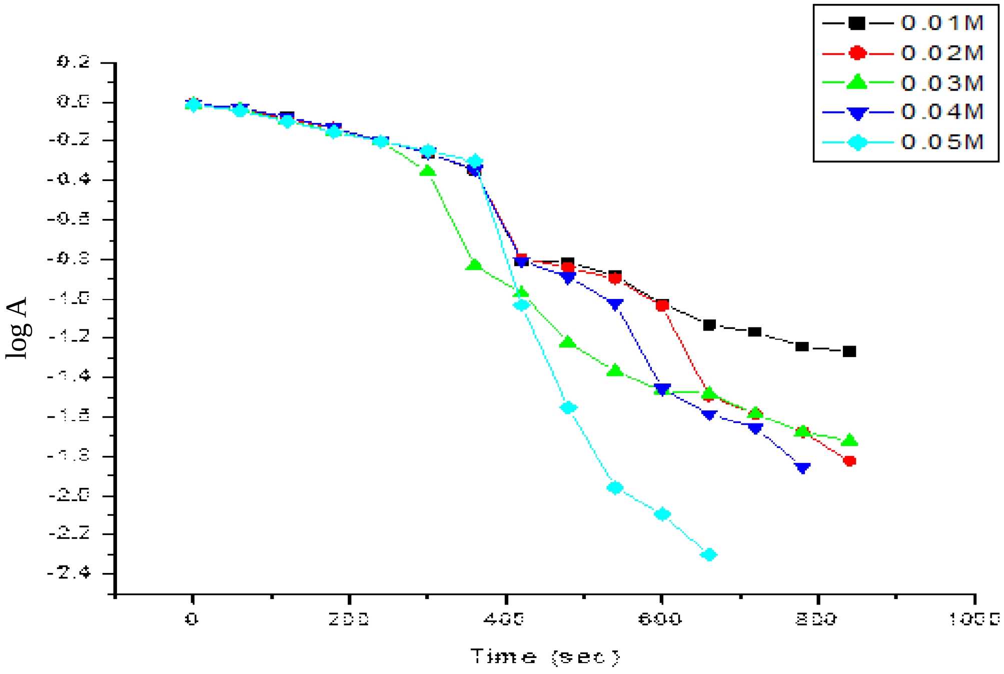

Figure 3 : Plot of logA versus Time (sec) for effect of variation of [maltose]

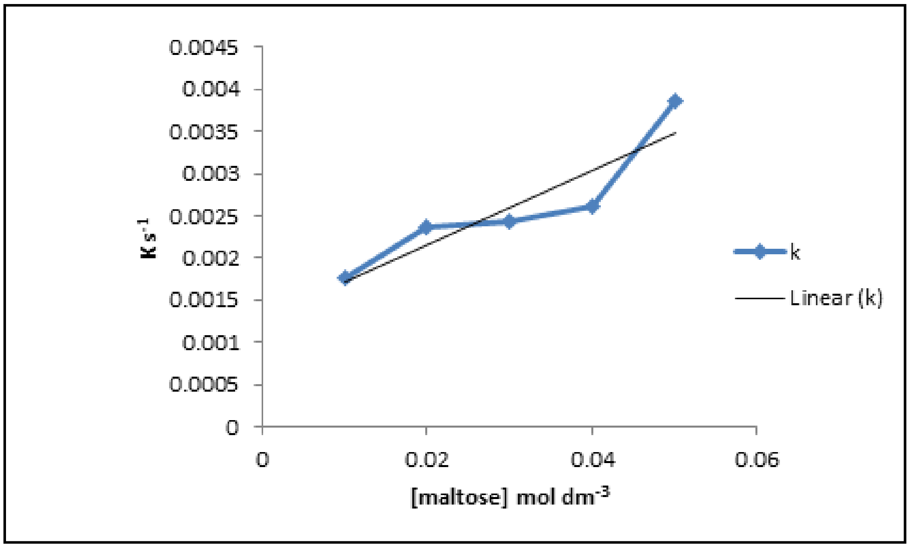

Figure 4 : Plot of K (s^{-1}) versus [maltose] mol dm^{-3} for effect of variation of [maltose]

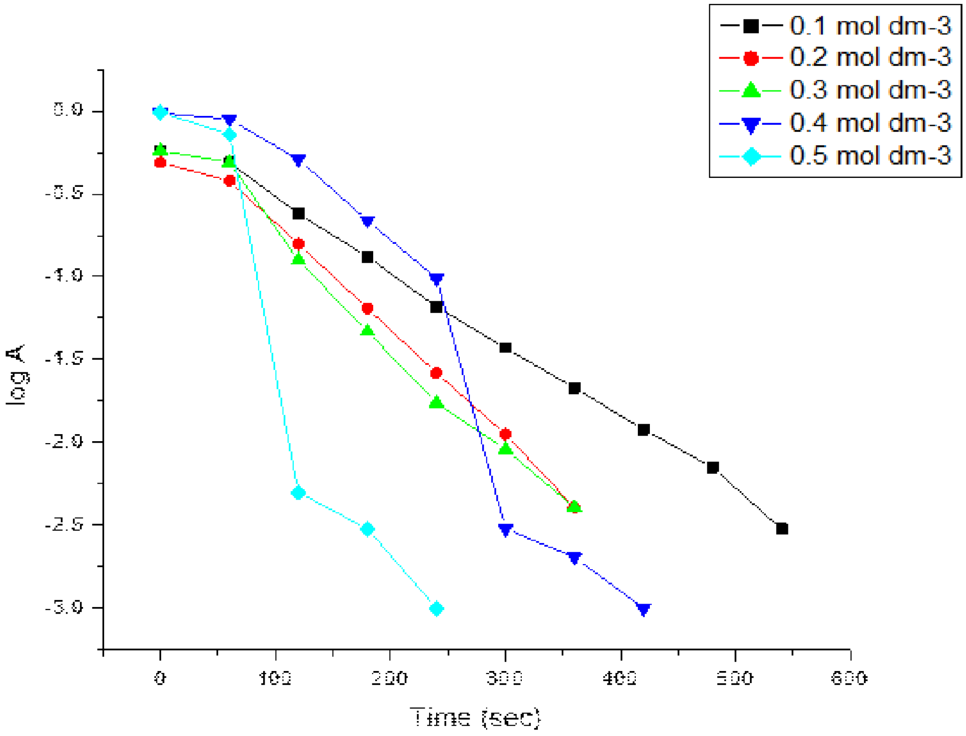

Figure 5 : Plot of logA versus Time (sec) for effect of variation of [H_2SO_4]

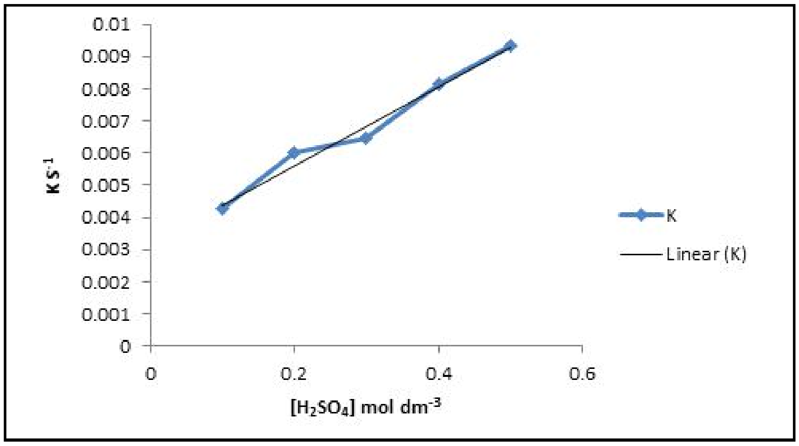

Figure 6 : Plot of K (s^{-1}) versus [maltose] mol dm^{-3} for effect of variation of [H_2SO_4]

Table-1. Observed value of k on varying the concentration of oxidant
[maltose] = $4x10^{-2}$ mol dm^{-3}, [H_2SO_4] = $1x10^{-1}$ mol dm^{-3}, [KNO_3] = $3x10^{-1}$ mol dm^{-3}

[$KMNO_4$] x 10^3 mol dm^{-3}	K x 10^3
1	1.68
2	2.84
3	3.98
4	4.21
5	4.47

Table-2. Observed value of k on varying the concentration of substrate
[$KMnO_4$] = $1x10^{-3}$ mol dm^{-3}, [H_2SO_4] = $1x10^{-1}$ mol dm^{-3}, [KNO_3] = $3x10^{-1}$ mol dm^{-3}

[maltose] x 10^2 mol dm^{-3}	K x 10^3
1	1.77
2	2.37
3	3.42
4	2.61
5	3.85

Table-3. Variation of rate constant k with concentration of H_2SO_4 at 30° C
[$KMnO_4$] = $1x10^{-3}$ mol dm^{-3}, [maltose] = $4x10^{-2}$ mol dm^{-3}, [KNO_3] = $3x10^{-1}$ mol dm^{-3}

[H_2SO_4]x 10(mol dm^{-3})	kx 10^3(s^{-1})
1	4.28
2	6.00
3	6.47
4	8.16
5	9.35

On the basis of above experimental data, it is proved that very less concentration of potassium permanganate gives fast reaction and reduces the sugar immediately. First order kinetics is obtained in present research work and four moles of potassium permanganate is used for the one mole of maltose. Concentration of salt does not affect the rate of reaction indicates the presence of non-ionic or molecular species in rate determining step. Mechanism and rate law of the present oxidation is determined and useful for further investigation by using different sugars and oxidants and also it is useful for pharmacologists. Oxidation behaviour of potassium permanganate is explained on the basis of present study.

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