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(1.) TITLE :-

KINETIC STUDY OF OXIDATION OF SOME SUGARS BY POTASSIUM PERMANGANATE IN ACIDIC MEDIUM

(2.) INTRODUCTION

A carbohydrate is an organic compound with the general formula $C_m (H_2O)_n$ that consist only of carbon, hydrogen and oxygen, the last two in the ratio 2:1 atom ratio. Carbohydrates can be viewed as hydrates of carbon, hence their name (Flitsch and Uliju, 2003)[1]. They can be classified as monosaccharrides, disaccharides, oligosaccharides and polysaccharides. Thus monosaccharides and disaccharides are referred to as “sugar”. Polysaccharides serve for the storage of energy (that is, starch and glycogen) and structural components (that is cellulose in plants and chitin in anthropods, while the monosaccharide is the simplest carbohydrates in that they cannot be hydrolized to smaller carbohydrates (Maton, et al.1993)[3].

Carbohydrates perform numerous roles in living things and they are sources of energy for vital metabolism processes. They are also constituents of cellular substances such as nucleic acids and are enzyme co-factors and structural components of cell walls and cell membranes. Carbohydrates, simple or compound are one of the major food components. Present in the wide range of them are usually refined foods such as white sugar, white bread or cola. (Donald and George, 1977)[4].

Potassium permanganate is widely used as an oxidizing agent in synthetic as well as in analytical chemistry and also as a disinfectant Sheltar et al.(2005)[9] and Hiremath et al.(1995)[10].It has been used in the determination of content of pharmaceutical formulation, ( Kanakapura and Okram, and Wassecf et al.2010)[11, 12] as oxidizing agent for removal of organic molecules and heavy metals from the nuclear wastes (Maqsood et al.2009)[13] and in the estimation of ascorbic acid (Murti et al.1944)[14]. During oxidation by permanganate, it is evident that the Mn(VII) in permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Consequently, the mechanism by which this multivalent oxidant oxidizes a substrate depends not only on the substrate but also on the medium (Rahamatalla et al.2003)[15] . In acidic medium it exists in different forms as $\text{HMnO}_4$, $\text{H}_2\text{MnO}^+$, $\text{HMnO}_3$, $\text{Mn}_2\text{O}_7$ and depending on the nature of the reductant
Despite much work already done on the oxidation of sugars, very little attention was given to the use of permanganate anion. The present study is therefore undertaken to clarify the mechanism of oxidation of D-glucose, D-mannose, D-xylose, D-sucrose and D-maltose by permanganate anion in acidic medium.

(3.) A BRIEF REVIEW OF THE WORK ALREADY DONE IN THE FIELD

The study of carbohydrate is one of the most exciting field of organic chemistry. Vast literature is available on the kinetics of oxidation of carbohydrates by various organic and inorganic oxidants. One of the thoroughly investigated reactions of saccharides is oxidation. There are more than one hydroxyl groups for oxidation. Further in aqueous solution a reducing sugar can exist in aldehydic, hydrated, pyranose or furanose form. Thus the nature of reducing sugar as well as the nature of oxidant species greatly influences the kinetic and mechanistic features of particular oxidation reaction.

The selective oxidation of aldose and aldonic acid to 2-ketoaldonic acid with oxygen and air at 55°C in water using Pt/C catalyst (Pierre et al. 1986) [16]. After oxidation of reducing group, if available, the primary hydroxyl group is preferentially oxidised using an unmodified catalyst. Addition of a lead(III) salt changes the preference dramatically towards oxidation at the position α to the carbonyl group provided that oxygen transfer to the liquid phase is carefully controlled in order to prevent deactivation of the catalyst 2-ketoaldonic acids can be prepared in high yields.

Okeola et al. (2012)[17] were studied the kinetics of catalytic oxidation of D-glucose and D-galactose by potassium heptaoxodichromate (VI) in alkaline buffer and in the presence of Fe(III) spectrophotometrically under pseudo-first order condition, temperature of 308K-328K and pH of 9.6-11.0. The reaction was first order with respect to oxidant and sugar concentration. The rate of oxidation increased with increase in substrate and oxidant concentration, temperature, ionic strength and pH of the reaction medium. Kinetic and mechanistic study of oxidation of salicylic acid hydrazide by thallium (III) in acidic medium (Mhatre et al. 2011) [18]. They investigated that free radicals does not produced during oxidation. It gives an idea that the reaction proceeds with two electron transfer step. The order of Thallium (III) was found to be unity and fractional order is found for hydrazide. Thermodynamic parameters are evaluated and mechanism is predicted.
Oxidation of Sugar by Halogens and Halogen Derivatives:

The kinetics and mechanism of Ruthenium(III) catalyzed oxidation of lactose and maltose by potassium bromate (KBrO₃) have been investigated in alkaline medium in the presence of mercuric acetate as a scavenger in the temperature range 300 – 450°C (Srivastava and Chaudhary, 2008)[19]. The reaction follows identical kinetics. The reaction exhibits first order kinetics with respect to KBrO₃ and catalyst Ru(III) while zero order kinetics with respect to substrates (Lactose & Maltose). Increase in [Cl⁻] showed negative effect while acetic acid (AcOH) showed positive effect on the rate of reaction. Negligible effect of [OH⁻], mercuric acetate and ionic strength of the medium were observed. Ruthenium (III) chloride has been reported to give a number of possible chloro species depending on the pH of solution. The reactive species of Ru(III) in alkaline medium is [RuCl₂(H₂O)₃(OH)] under the experimental pH range. A suitable mechanism in conformity with the kinetic observation has been proposed. The various activation parameters such as energy of activation (ΔE*), Arrhenius factor (A), entropy of activation (ΔS*) were calculated from the rate measurements at 300, 350, 400, and 450°C. A rate law has been derived on the basis of obtained data.

Oxidation by Transition Metals:

(1.) Copper (Cu)

Singh R. S. (1997) [20] reported the oxidation of maltose and lactose by Cu (II) in the presence of ammonium hydroxide. The reaction exhibits zero order with respect to Cu (II) and first order with respect to the substrate and hydroxide ion concentration.

(2.) Vanadium (V)

Odeburummi et al. (2010)[21] reported the kinetics of oxidation of D-Arabinose and D-xylose by vanadium (V) in the presence of Mn(II) as homogeneous catalyst was studied spectrophotometrically. The reaction rate was first order with respect to substrate and [H⁺] at low concentration but zero at higher concentration and first order with respect to Mn(II). The effect of Cl⁻ concentration was found to be negligible. The reaction rate increases with increasing ionic strength.
(3.) CHROMIUM (Cr)

Odebunmi and Owalude (2005)[22] were suggested the kinetics and mechanism of oxidation of sugars by chromic (VI) in perchloric acid medium that the reaction was first order with respect to substrate and Cr(VI) while the order with respect to [H+] was complex. The order of reactivities of different sugars is fructose > maltose > glucose > sucrose. Thermodynamic parameters were evaluated and mechanism was predicted.

(4.) MANGANESE (Mn)

The kinetics and mechanism of oxidation of D-glucose, D-mannose, D-fructose and L-sucrose by trivalent manganese Mn(III) in aqueous sulphuric acid media has been studied by Reddy et al. (2012)[23]. The reaction exhibit first order kinetics with respect to sugar concentration and fractional order with respect to oxidant concentration.

(5.) CERIUM (Ce)

The kinetics of uncatalysed and catalysed oxidation of D-galactose by Cerium (IV) has been studied in acidic medium by Rajput and Choubey (2012)[24]. This experiment was studied at the temperature range 303-338 K. The reaction has been found to be first order with respect to [D-galactose]. The rates follow first order kinetics with respect to [Ir(III)] for catalysed oxidation reaction. The increase in ionic strength of the medium decreases the rate of uncatalysed reaction while increases catalysed reaction. A1:2 stoichiometry is observed in the oxidation. From the effect of temperature on the reaction rate, the Arrhenius and activation parameters were calculated. A suitable mechanism was proposed and a rate law explaining the experimental results is derived.

(6.) OSMIUM (Os)

The kinetics and mechanism of oxidizing reducing sugars by osmium tetraoxide in alkaline medium (Singhet al. 1998)[25]. It was suggested that the oxidation reaction of reducing sugars pentoses, hexoses and disaccharides by OsO₄ in alkaline medium each reaction exhibits pseudounimolecular kinetics with respect to OsO₄ are first order with respect to lower [sugar] and [OH⁻], but tend towards zeroth order with respect to both higher [sugar] and [OH⁻].
POTASSIUM PERMANGANATE (KMnO₄) AS AN OXIDANT

Chemical formula of potassium permanganate is KMnO₄. It contains potassium and permanganate ions. The Mn is in the +7 oxidation state. It is also known as permanganate of potash and condy’s crystal. Manganese (VII) is best known in the form of salts of the permanganate ion, MnO₄⁻ of which the potassium salt is by far the commonest, being used as a laboratory oxidising agent.

The manganate ion is stable only in very basic solution. In basic solution permanganate functions as a powerful oxidising agent [6]:

\[
\text{MnO}_4^- + 2\text{H}_2\text{O} + 3e \rightarrow \text{MnO}_2(s) + 4\text{OH}^- \quad E^\circ = +1.23\text{V}
\]

In very strong base and with an excess of MnO₄⁻, however, manganese ion is produced:-

\[
\text{MnO}_4^- + e \rightarrow \text{MnO}_4^{2-} \quad E^\circ = +0.56 \text{V}
\]

In acid, neutral or only slightly basic solutions it readily disproportionate according to the equation :-

\[
3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + 2\text{H}_2\text{O}
\]

In acid solution permanganate is reduced to Mn²⁺ by an excess of reducing agent :-

\[
\text{MnO}_4^- + 8\text{H}^+ + 5e \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad E^\circ = +1.51 \text{V}
\]

But because MnO₄⁻ oxidises Mn²⁺

\[
2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2(s) + 4\text{H}^+ \quad E^\circ = +0.46 \text{V}
\]

The product in presence of an excess of permanganate is MnO₂.

Permanganate is a versatile oxidizing agent and is used for studying the oxidation kinetics of many organic substrates. The mechanisms for different organic substrates suggested by various authors are not similar, indicating that a variety of mechanisms are possible, depending upon the nature of the reactive manganese species, the reaction environment and the nature of the substrate.

The kinetics of oxidation of glucose, galactose, fructose, maltose and sucrose by alkaline permanganate anion has been studied by Odebunmi and Owalude, (2008)[26].
reactions studied spectrophotometrically over a wide range of experimental conditions show that the rate of the reactions is enhanced by increase in pH, ionic strength, and temperature as well as the reactant concentrations. The mechanism has been proposed to proceed via the formation of enediol intermediate complexes and the order of reactivities of the sugars is fructose > glucose ≈ galactose > maltose > sucrose. The activation parameters were evaluated and lend further support to the proposed mechanism.

4) OBJECTIVES

The biological, biochemical and economic importance of the carbohydrates and especially the mono and disaccharides has been largely responsible for the great interest for the study of their bio and physicochemical properties and reactivities. These reactivities and properties depend largely on their redox behaviour.

Present proposed work covers following objectives:
(1.) To determine the kinetics of oxidation of sugars by using potassium permanganate spectrophotometrically.
(2.) To determine the effect of concentration of KMnO₄ on the rate of oxidation of sugars with KMnO₄.
(3).To determine the effect of concentration of sugars on the rate of oxidation of sugars with KMnO₄.
(4.) To determine the effect of concentration of H₂SO₄ on the rate of oxidation of sugars with KMnO₄.
(5) To determine the effect of ionic strength on the rate of oxidation of sugars with KMnO₄.
(6.) To determine the effect of temperature on the rate of oxidation of sugars with KMnO₄.
(5.) To study the kinetics of the oxidation of sugars in acidic medium with the variation of concentration of sugars, oxidants [H⁺], ions salt and effect of variation of temperature.
(6.) To evaluate thermodynamic parameters activation energy (Eₐ), enthalpy (ΔH*), free energy (ΔG*), and entropy (ΔS*) to establishment of reaction mechanism of oxidation of sugars by KMnO₄ in acidic medium.
(7.) Establishment of reaction mechanism of oxidation of sugars.
(5.) NOTEWORTHY CONTRIBUTION IN THE FIELD OF PROPOSED WORK

The oxidation of sugars especially the monosaccharides and di-saccharides have been the subject of extensive research and several reviews already exist on it. Sugar oxidation occurs under different conditions of pH, temperature, ionic strength giving products that depends on the reaction conditions used. Noteworthy contribution in the field of proposed work is as follows.

The kinetics and mechanism of oxidation of sugar and sugar alcohols by KMnO₄ in hydrogen/ NaOH buffer were studied spectrophotometrically by Okaro and Odeburgmi, (2009)[27]. The pseudo first order rate constant were determined against substrate concentration. The rate of reaction increased with an increase in substrate concentration but marginal decrease in reaction rate was observed in the case of sorbitol as a substrate. The first order rate constant were obtained with respect to oxidant KMnO₄. The rate of reaction increased as the pH, ionic strengths, temperature, as well as concentration of KMnO₄ increased. The relative reactivity of the sugar and sugar alcohols are sorbitol > maltose > glucose > fructose > sucrose > mannitol. It was suggested that disaccharides are more reactive than monosaccharides and for the sugar alcohols sorbitol is more reactive than mannitol. The Arrhinius activation energy and other thermodynamic parameters were evaluated and mechanism were reported.

The kinetics of oxidation of D-glucose and D-sorbitol is by potassium permanganate in sodium hydrogen carbonate and sodium hydroxyl buffer and hexachloroiridate in sodium acetate and acetic acid buffer have been investigated spectrophotometrically by Odeburgmi and Marufu (1999)[28]. pH range of 9.2 to 11.3 in NaHCO₃ / NaOH alkaline buffer and 3.60 to 5.60 in sodium acetate and acetic acid buffer. The disappearance of KMnO₄ or Ir(IV) with time uniformly followed pseudo first order kinetics in each run. Rao and Rao (2004)[29] discussed the kinetics of oxidation of some monosaccharide viz., D-ribose, D-xylose, D-arabinose, D-glucose, D-fructose, D-galactose, 2- deoxyglucose, and α-methyl glucopyranoside by MnO₄⁻ in aqueous alkaline medium. The rate of oxidation has been found to be first-order both with respect to [oxidant] and [sugar]. The effect of ionic strength is negligible on the rate. Activation energy and other thermodynamic parameters and mechanism of the reaction were suggested.

Odeburgmi et al. (1999)[30] have been studied “The kinetics and mechanism of oxidation of D-mannose and D-mannitol by KMnO₄ in sodium hydrogen carbonate and sodium hydroxide buffer and disodium hexachloroiridate (IV) in sodium acetate and acetic acid
buffer spectrophotometrically under pseudo-first conditions and over a wide range of experimental conditions. The oxidation rate is in the order D-mannose > D-mannitol in both acidic and alkaline media and is accelerated by increase in the pH of the reaction mixture and increase in salt concentration. The formation of free radical intermediates and formic acid as one of the reaction product has been demonstrated.

The kinetics and mechanism of the oxidation of methylene blue by permanganate ion has been studied in aqueous acidic medium by Osunlaja et al. (2012)[31]. Experiment has been studied by colorimeter. The rate of the oxidation reaction was found to be first order with respect to oxidant and reductant. The rate of reaction decreased with increase in ionic strength of the medium.

On the basis of review many data are exist on the kinetics and mechanism of the sugars but correlation of data is difficult because of wide variations of reaction conditions were used. Since KMnO$_4$ based reactions have been found relatively rare application in oxidation of sugars in acidic medium and so D-glucose, D-mannose, D-xylose and D-sucrose and D-maltose is chosen for the oxidation by potassium permanganate in sulphuric acid medium.

(6.) PROPOSED METHODOLOGY

The kinetics and mechanism of oxidation of D-Glucose, D-Mannose, D-xylose, D-Sucrose, and D-maltose by potassium permanganate in sulphuric acid medium will be done spectrophotometrically.

There are many methods of following a reaction with time. Some of them are changes with pressure, absorbance, pH, refractive index, thermal conductivity electrical resistance and volume. Analysis by means of these physical properties that can be measured continuously without the removal of the sample from the reaction chamber minimizes the lack of precision in time measurement.

(1.) SPECTROPHOTOMETRIC ANALYSIS

This technique is useful particularly for organic compounds where a distinguishing band in the infrared region can often be employed. The relationship between the absorption and concentration of solution of interest is given below:-
\[ \log \frac{P}{P^0} = \varepsilon c l \]

Where

\( P^0 \) = The radiant power of incident light.

\( P \) = Transmitted radiant power.

The term \( P/P^0 \) is called the absorbance. \( \varepsilon \) is the molar absorptivity of the sample and \( c \) is the concentration. While \( l \) is the path length The relationship is called the beer-lamberts law. Researcher (Odeumni and Owalude,2008)[26] (Odeumni and murufu 1999)[28],(Osunlaja et al.,2012)[31] ; used this method to follow the kinetics and mechanism of sugars and the determination of other compound.

(2.) IONIC STRENGTH

The Ionic Strength \( (I_m) \) of a solution is a function of the concentration of all ions present in the solution. Ionic strength is the measure of the electric field existing in a given solution. According to following equation.

\[ I_m = 0.5 \varepsilon_{B=1} M_B Z_B^2 \]

Where, \( M_B \) is the concentration of ion B , \( Z_B \) is the charge number of that ion and the sum is taken overall in the solution. Ionic Strength plays a central role in the Debye Huckel theory that describes the strength deviations from ideality typically encountered in ionic solution. In the study of solution, reaction kinetics it is often describe to change the concentration of an active species without changing the ionic strength because the latter affects the value of the rate constant \( K \). It has been reported by the several researchers that sugar oxidation may depend on ionic strength(Odebunmi et al. 1999) [30].

The effect of ionic strength on the rate of oxidation of sugars by KMnO\(_4\) in acidic medium will be investigated by varying KNO\(_3\) concentration by keeping concentration of sugar concentration of KMnO\(_4\) and temperature constant. The values of rate constant will be calculated from the slope of \( \ln A_0-A_{\infty}/A_t- A_{\infty} \) Vs time. Which will indicate effect on the reaction (Osunlaja and Iyun, 2012)[31].
(3.) CONCENTRATION OF SUGAR

It has been discovered that at a higher concentration, molecules collide faster for reaction to occur, thereby increasing the reaction rate, but at a lower concentration the collision will be reduced, this is due to the low amount of molecules present in the system.

(4.) CONCENTRATION OF OXIDANT (KMnO₄):-

Oxidants are substances which help in alteration of the rate of sugar oxidation reaction; oxidants can decrease, increase or have no effect on the reaction rates depending on the substrate

(5.) TEMPERATURE

Molecules will collide faster at a higher temperature than when the temperature is low. The Arrhenius Equation shows the relationship between the rate constant of a reaction, Activation Energy and Temperature.

The oxidation of different sugars by potassium permanganate in sulphuric acid medium will be carried out spectrophotometrically at different temperature but at constant initial concentration of the substrate and oxidant, constant pH, and constant ionic strength. The activation parameters will be calculated. The activation energy (Ea) will be evaluated with the help of Arrhenius equation.

\[ k = A e^{\frac{-E_a}{RT}} \]

or

\[ \log k = \log A - \frac{E_a}{2.303RT} \]

The slope of the plot of log k vs 1/T will give the value of Ea. Other thermodynamic parameter like enthalpy (ΔH*) and entropy of activation (ΔS*) can be calculated with the help of following equation;

\[ \log k/T = \log k/h + (\Delta S^*/R) - (\Delta H^*/R).1/T \]

Value of ΔH* can be calculated by the slope plotted logk/T vs 1/T and ΔS* from the interception. Free energy of activation ΔG* can be calculated by the following equation (Okeola et al.2012)[17].
\[ \Delta G^\# = \Delta H^\# - T \Delta S^\# \]

(6.) pH

The pH (Odebunmi and Owalude 2008)[26] is defined as a measure of the acidity or alkalinity of a solution. The pH of a solution is the negative logarithm to base ten of the molar hydrogen ion concentration i.e.:

\[ \text{pH} = - \log [H^+] \]

(7.) POLYMERIZATION TEST

If gel is formed by the addition of 20% acrylamide to various reaction mixtures of sugars and oxidant and polyacrylamide is precipitated on further addition of methanol then these results indicates that the free radicals are formed during the reaction. (Odebunmi and Marufu, 1999) [28].

(8.) STOICHIOMETRY OF THE RACTION

The procedure is adapted from that used by Sircar and Saika (1991) [32]. An excess of the permanganate solution is added to the sugar solution and allowed to react for several hours. Then the excess permanganate is then determined. Blanks is prepared without addition of sugar solution for each set of the experiment. If the volume of the primary standard (Fe\(^{2+}\)) consumed by blanks are always find to be greater than the corresponding reacting species and consequently the consumption ratio, i.e. the number of moles of the permanganate consumed per mole of the sugars will be estimated by assuming that all the sugars is totally consumed under the reaction conditions.

(9.) PRODUCT ANALYSIS

CHROMOTROPIC ACID TEST

If violet pink colour is obtained by addition of chromotropic acid (1, 8-dihydonaphthalene-3,6-disulfonic acid) to the various reaction mixtures of both the substrates and the permanganate anion then these results indicates the formation of carboxylic acid. (Odebunmi and Marufu, 1999) [28].
(7) EXPECTED OUTCOME OF THE PROPOSED WORK

Carbohydrates are the “staff of life” for the most of the organisms. In the form of sugar and starch they represent a major part of the total caloric intake for humans and for most animal life. Numerous enzymes occurring in living cells catalyse the oxidation of carbohydrates and are important in their metabolism. Hence the chemical oxidation of such compounds which are found in biological system has its own advantage as the process may help in understanding the step of oxidation.

Further these compounds are polyfunctional compounds having aldehydic, ketonic, primary alcoholic, secondary alcoholic and lactone ring also. Interaction amongst these functional groups and competing reactions frequently occur, hence carbohydrate chemistry appears to be an interesting chemistry posing a challenge to the scientists. In aqueous solution a saccharide exist as equilibrium mixture of two cyclic forms (the aldehyde form and its hydrate) and atleast four cyclic forms (two furanose and two pyranose). Conversion of these forms into one another depends on pH of the medium and structure of saccharide and hence makes the oxidation further complicated. In the light of above description present proposed work can be expected in many ways like.

(1.) Oxidation of carbohydrates by potassium permanganate with different buffer, alkaline and acidic medium can be done to extend the present proposed work.
(2.) New mechanism will be developed for establishing the reaction kinetics of oxidation of different sugars by potassium permanganate.
(3.) New organic and inorganic oxidants and transition metal using as a catalyst will be used to extend the present proposed work.
(4) Different reducing and non reducing sugars can be carried out for the comparative study with KMnO₄ to extend the present proposed work.
16. Pierre C.C. Smits, Ben F.M. kuster, Kees Vender Wile and Hessel S. Vander Baan, 
17. Okeola O. Fatai, Odebunmi E.O. and Okoye A. Grace, *International Research 
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