

ISSN 1996-5052

Current Research in
Chemistry

Homogeneous Catalytic Oxidation of Some Sugars: A Review

¹E.O. Odebunmi and ²A.S. Ogunlaja

¹Department of Chemistry, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria

²Department of Chemical Sciences, Bells University of Technology, P.M.B. 1015, Ota, Ogun State, Nigeria

Corresponding Author: A.S. Ogunlaja, Department of Chemical Sciences, Bells University of Technology, P.M.B. 1015, Ota, Ogun State, Nigeria Tel: +2348056514663

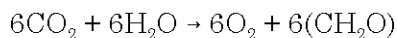
ABSTRACT

The study of carbohydrates is one of the most exciting fields of organic chemistry. Carbohydrates serve as the chief fuel of biological system, supplying living cells with usable energy. Carbohydrates are the body's primary source of energy. Energy is stored in the complex molecular structure of the carbohydrates when we metabolized the complex compounds, the atoms arrange themselves back into simple compounds and in the process, release their stored energy for our use. Carbohydrate must be burned or oxidized if energy to be released. An oxidation study of monosaccharide by different oxidizing agents is of special importance due to their biological relevance. The catalyzed oxidation provides a mild reaction condition and also gives an understanding of carbohydrate mechanism, because they can undergo a wide variety of reactions and give rise to different products. A brief report on some oxidation studies was also reported.

Key words: Carbohydrates, mechanism, oxidation, oxidizing agent

INTRODUCTION

Carbohydrates: Organic compound that are related to the simple sugars are called carbohydrates. Photosynthesis is the most important bio-synthesis and it represents the process whereby plants containing pigment chlorophyll absorb light energy and utilize it to convert atmospheric carbon (IV) oxide in the presence of water to carbohydrates (Francis, 2000; Cole and Coles, 1964):



Carbohydrates are divided into three main classes; these are the monosaccharide, disaccharide and polysaccharides. Classification of monosaccharides has been shown in Fig. 1.

The monosaccharide, being the simplest carbohydrates, cannot be hydrolyzed into simpler carbohydrates (Keilin and Hartree, 1952).

Aldoses are the most abundant in nature than the ketoses. The most important are ribulose and fructose.

The disaccharide is a carbohydrate composed of two units of monosaccharide joined together by a glycoside link, this link is called 1, 4- β link depending of the stereochemistry of the glycoside carbon. Figure 2 shows the 1,4- β glycosidic link.

Examples of disaccharides include maltose, cellobiose, lactose and sucrose.

The polysaccharides are compounds whose molecules contain many units of monosaccharide joined together by glycosidic linkages. Poly saccahrides are cellulose. Figure 3 shows the structure of cellulose.

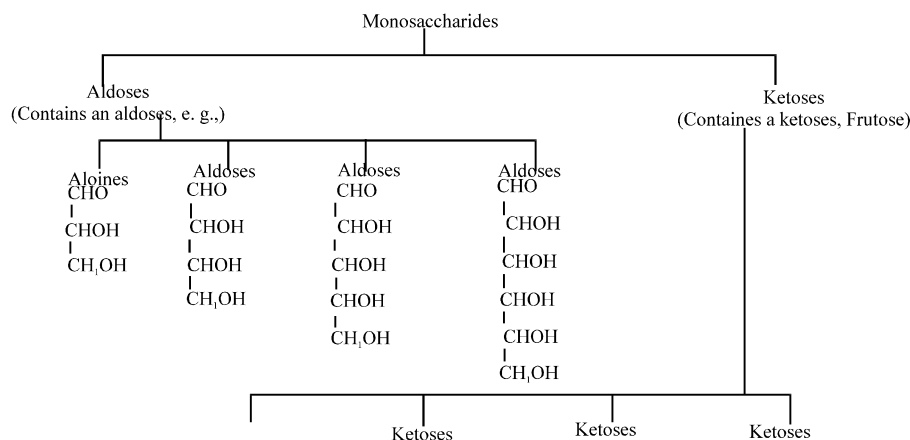


Fig. 1: Classification of monosaccharide

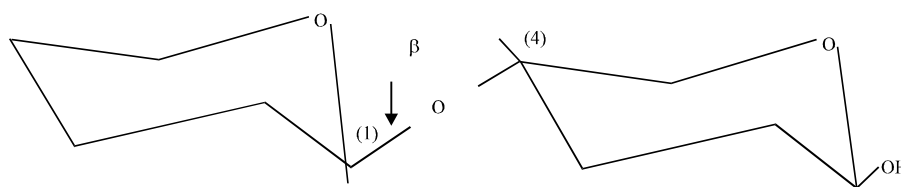


Fig. 2: 1,4- β glycosidic link (Morrison and Boyd, 1987)

Sugars undergo several reactions some of which are oxidation to form its respective acids, isomerization, ether and ester formation, mutarotation etc. Sugars can also be used as a sweetener, preservation of many food products. The additions of sugar to jams and fellies for example inhibit microbial growth and subsequent spoilage, having the ability to absorb water, sugar withdraws moist are from micro-organisms. As a result micro organisms become dehydrated and cannot multiply and cause food spoilage (Kitts, 1998). Yeast in baking and brewing industries use sugars as food to produce ethanol, carbon dioxide and water through the process of fermentation (Clarke, 1997; Kathiresan and Manivannan, 2006). Sucrose has been reported to exhibit antioxidant properties which help to prevent the deterioration of textures and flavours in canned fruits and vegetables (Kitts, 1998). Sugar is valued in cough syrups for its solubility and bodying effect. Sugar also functions as diluents, to control the concentration of active ingredients in tablets and as a binder to hold ingredients together (Clarke, 1997). By dissolving sugars in the tissues of an open wound, sugar produces an environment in which bacteria cannot grow (Kitts, 1998). Bioplastics refer to the production of natural biodegradable plastics produced by microorganisms. Sucrose has been noted as a preferred carbon source for various bacterial species that produce biodegradable plastics as storage materials synthesized and accumulated within their cells (Murano, 2003).

The oxidation of sugars has been enhanced with the use of catalyst also known as catalysis; which is the alteration in the rate of a chemical reaction by means of a substance called a catalyst.

A catalyst is a substance, which alters the speed of a chemical reaction without undergoing any chemical change and can be recovered at the end of the reaction. A catalyst provides an alternative route of reaction where the activation energy is lower than the original chemical reaction. There are many different kinds of catalyst and many different mechanisms by which catalyst operates have been proposed (Sharma and Sharma, 2004).

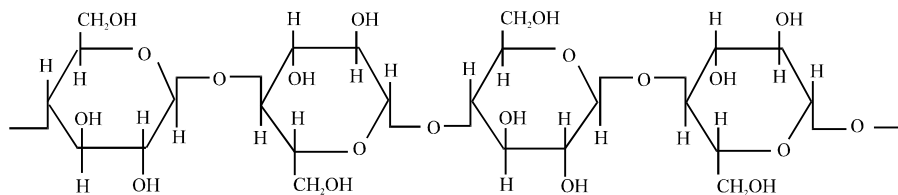


Fig. 3: Structure of cellulose (Morrison and Boyd, 1987)

There are generally three types of catalysis: Homogeneous catalysis, Heterogeneous catalysis and Enzyme catalysis. In homogeneous catalytic system, the catalyst is present in the same phase as the reactants, while the heterogeneous catalytic system, the catalyst constitutes a separate phase from the reactions (Chari *et al.*, 2007). Enzyme catalysis lies in between the homogenous and heterogeneous catalysis. The enzymes are complex organic compounds (proteins) of very high molecular weights and are not very stable.

General characteristics of catalyzed reactions: Although there are various types of catalyzed reactions, but in spite of their many differences, they show the following characteristics properties (Francis, 2000).

- A catalyst remains unchanged in chemical composition at the end of the reaction: The amount of the catalyst recovered at the end of the reaction is found to be the same as the amount taken at the start of the reaction. Hence, a catalyst does not undergo any chemical change although; its physical form may change completely
- Only a small amount of the catalyst is required to bring about a reaction: There are many cases known where a very small amount of the catalyst is sufficient to convert large quantities of the reactants into the products
- A catalyst is specific in action: This implies that a given catalyst can catalyze only particular reaction and cannot be used to bring about another reaction. For example, bromine water will catalyze the oxidation of a monosaccharide to aldonic acid and will not catalyze other reactions. Similarly enzymes are specific in action
- Catalyst have an optimum temperature: The temperature at which the catalysts are most active
- A catalyst is poisoned by the presence of small quantities of certain substances called catalytic poison: Some of the most powerful catalytic poisons are arsenic oxide, hydrogen cyanide and carbon monoxide. The presence of these substances makes the catalyst inactive
- A catalyst does not alter the final position of equilibrium in a reversible reaction and hence does not modify the value of the equilibrium constant. A catalyst accelerates equally the rates of both forward and reversible reactions and helps to establish equilibrium quickly

CATALYTIC OXIDATION OF SUGARS

The biological and economic importance of carbohydrates has been largely responsible for the interest in the study of their bio-chemical and physiochemical properties and reactivities. Studies have been carried out on the structural elucidation, chemical degradation and oxidation reactions. The catalytic oxidation of sugars has been carried out both in acidic and alkaline media using such oxidants as transition metal ions, inorganic acids, organo metallic complexes and enzymes (Gupta *et al.*, 1979; Odebunmi and Marufu, 1999; Neyhart *et al.*, 1995; Singh *et al.*, 1991;

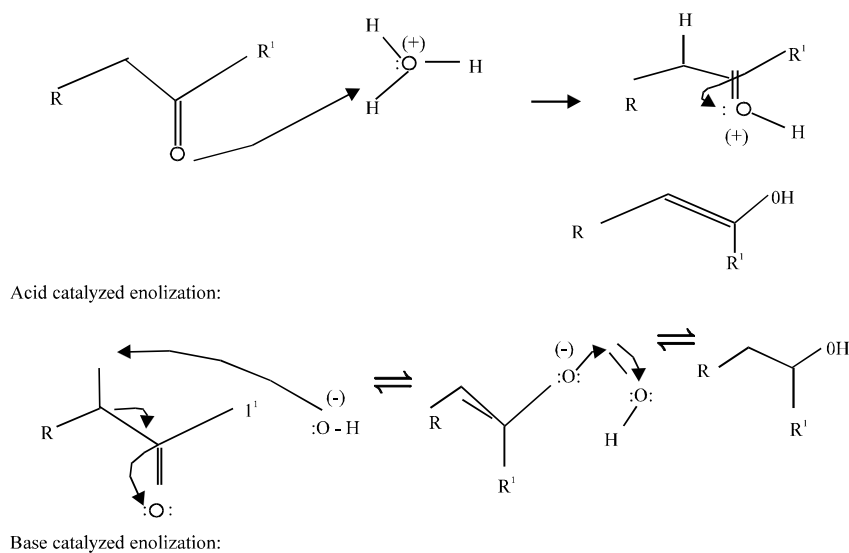
Weibel and Bright, 1971; Gupta *et al.*, 1998). The literature on the oxidation of sugars shows that interest has been largely on how varying the following factors; concentration of the sugars, concentration of the various oxidants, pH, ionic strength and temperature will affect the rate of oxidation of the various sugars used.

Oxidation either means addition of oxygen to the substrate. Wide variety of agents available for the oxidation of organic compounds probably the most widely used is potassium permanganate and derivatives of hexavalent chromium. Permanganate and derivatives of heptavalent manganese are very powerful oxidant. Its reactivity depends to a great extent on whether they are used for acid, neutral or basic conditions (Carruthers, 2003). In recent years, several oxidizing agents, specific and selective to varying species have been added to the literature of organic chemistry. Selenium dioxide, aluminium alkoxide, osmium tetroxide, organic per-acid and potassium ferricyanide have greatly enhanced the skill of the organic chemist in introducing and attaching particular groups to large molecules. Ferric sulphate, ammoniacal silver nitrate, Fehling's solution and potassium ferricyanide all fall into the same class of oxidizing agents (Carruthers, 2003).

Mechanism of catalysed oxidation of sugars: The oxidation of aldose with strong oxidizing reagents e.g., nitric acid (and under suitable conditions) produces dicarboxylic acid already discussed under the properties of sugars. Aldoses are reducing sugars, since they possess an aldehyde function in their open chain form. Which mechanism involves the formation of an enediol as the intermediate product.

Acidic and Basic medium for the catalyzed enolization reaction (scheme 1), for the acid catalyzed enolization, delocalization of the double bond of the carbonyl group resulting in the transfer of electron from the positive site from the negative site of the compound to the positive site of the hydrogen ion, while the base catalyzed enolization, dehydrogenation takes place, resulting to double bond followed by the transfer of base (-OH) to the empty site formally occupied by the hydrogen atom (Isbell and Pigman, 1968).

The catalytic oxidation of sugars has been carried out both in acidic and alkaline media using such oxidants as transition metal ions, inorganic acids, organo-metallic complexes and enzymes (Odeunmi *et al.*, 2006; Gupta and Chatterjee, 1984; Castellan, 1983).



Scheme 1: Mechanism for Enediol formation (Isbell and Pigman, 1968)

EXPERIMENTAL MEASUREMENT AND FACTORS AFFECTING THE OXIDATION RATE OF SUGARS

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 (Castellan, 1983). 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.

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:

$$\text{Log } p_0/p = \epsilon cl$$

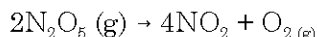
Where:

p_0 = The radiant power of incident light

P = Transmitted radiant power

The term p_0/p is called the absorbance. ϵ 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 (Strobel, 1962). Researchers (Odebunmi *et al.*, 2006; Ogunlaja *et al.*, 2009; Odebunmi and Owalude, 2005; Perez-Benito and Arias, 1993; Dinelli *et al.*, 2010; Sangshetti *et al.*, 2007; Sangshetti *et al.*, 2008) used this method to follow the kinetics and mechanism of oxidation of sugars and the determination of other compounds.

Manometric analysis: A reaction in the gaseous phase might result in a change pressure and so its progress may be monitored by recording the change in pressure as a function of time. An instance of this is the decomposition of nitrogen (V) oxide according to the equation below:



For every mole of N_2O_5 destroyed, 5/2 mole of gaseous product is formed and so the pressure of the system increases during the course of the reaction. The reaction is inappropriate for reactions that leave the overall pressure unchanged for reactions in solution (Atkins, 1978). Keilin and Hartree (1952) used this method to study the oxidation of glucose in differential manometer at 20°C.

Polarimetric method: This is based on the measurement of angle of rotation of plane polarized light by passing it through a solution. The degree of rotation of this light depends upon the substance in solution, their concentration and the length of path through the solution. When the specific rotation of the reactants differs from the products, the course of the reaction may be followed in this way (Swayer *et al.*, 1984).

Colorimetric method: This method is used to study colour change in reactants, a reaction can be followed colorimetrically provided the presence of other coloured substance does not obscure colour

change (Matthews, 1977). Krishna and Prakash used this method to study the kinetics and mechanism of oxidation of some reducing sugars by diperiodatoargentate (III) in alkaline medium.

Electrical methods: When a reaction changes the number or nature of ions present in a solution, monitoring the conductivity of the solution may follow its course. A very important class of these reactions consists of those occurring at electrodes (Atkins, 1978). Other methods for studying a reaction change include conductometry, mass spectrometry and chromatography (Dursun and Taniguchi, 2004).

The literature on the oxidation of sugars shows that interest has been largely on how varying the following factors; concentration of the sugars, concentration of the various oxidants, pH, Ionic Strength and Temperature will affect the rate of oxidation of the various sugars used.

- **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 electrical field existing in a given solution. According to the following the equation below:

$$I_m = 0.5 \sum_{B=1} M_B Z_B^2$$

where, M_B is the concentration of ion B, Z_B is the charge number of that ion and the sum is taken over all ions in the solution. Ionic strength plays a central role in the Debye Huckel theory that describes the strong deviations from ideality typically encountered in ionic solutions. In the study of solution, reaction kinetics it is often desirable 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 several researchers that sugar oxidation may depend on ionic strength (Shukla and Kesarwani, 1984; Fadnis and Shrivastava, 1982)

- **Concentration of sugars:** 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
- **Concentration of the various oxidants:** 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 (Odebunmi *et al.*, 2006; Ogunlaja *et al.*, 2009)
- **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

$$K = A e^{-E_a/RT}$$

A is the pre-exponential factor; E=Activation energy; K=Rate constant, T= temperature

From the logarithmic plot of the above equation, the activation energy, entropy, enthalpy, Gibbs free energy of the system can be calculated. All these parameters have helped in reporting the rate determining step of the reaction. Shukla and Kasawani reported that a positive entropy of activation indicates a rate determining step involving ions of opposite charges (Shukla and Kesarwani, 1984), while Odebunmi and Marufu reported that a negative entropy value indicates that a reaction occur between ions of the same charge (Odebunmi and Marufu, 1999).

- **pH:** The pH 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.,:

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

At certain conditions, enzymes activities are high mostly at the alkaline and neutral condition (Weibel and Bright, 1971). Gupta and co-workers, while studying the effect of HClO_4 on the rate of oxidation of some aldoses, reported that the rate of oxidation of the aldoses increased with the increase in acid concentration (Gupta and Chatterjee, 1984). The Zucker Hammet plot (Zucker and Hammet, 1939) $\log K_{\text{obs}}$ against $\log (\text{HClO}_4)$ was linear indicating that the reactions were acid catalyzed.

Odebunmi *et al.* (2006) reported the kinetics of oxidation of fructose, sucrose and maltose in potassium permanganate in alkaline buffer and of fructose and sucrose by hexachloroiridate (IV) in acidic buffer which was measured spectrophotometrically at a maximum absorbance of 488 nm and 525 nm for Ir(IV) and KMnO_4 respectively. The reaction was done at a pH range of 9.2 to 11.8 for KMnO_4 and a pH range of 3.6 to 5.6 for Ir(IV), from their work it was also shown that KMnO_4 has greater reactivity than IrCl_2^+ , because IrCl_2^+ is a one electron transfer oxidant. The rate of oxidation of the sugars follow the order maltose>fructose>sucrose (Odebunmi *et al.*, 2006).

Ogunlaja *et al.* (2009) reported the kinetics and mechanism of oxidation of D-arabinose and D-xylose by acidic solution of Chromium (VI) in the presence of Mn (II). First-order dependence of the reaction rate was observed on sugars, HClO_4 at low concentrations and a zero-order observed for sugars at a higher concentration. First-order kinetics with respect to Mn (II) throughout its variation was observed in the oxidation of both sugars. The Cl^- and ionic strength effect was found to be negligible.

Formic acid and Erythronic acid were reported as the product of oxidation for both sugars.

The rate of oxidation of the sugars follow the order xylose>arabinose (Ogunlaja *et al.*, 2009).

The kinetics of oxidation of epimeric aldo and D-(L) keto sugars, namely D-glucose, D-mannose, D-fructose and L-sucrose by trivalent manganese in aqueous sulphuric acid media has been studied. The experimental data indicate a first order dependence on sugar concentration and fractional order dependence on oxidant. Variation of $[\text{HSO}_4^-]$, $[\text{SO}_4^{2-}]$, $[\text{F}^-]$, $[\text{P}_2\text{O}_7^{4-}]$, $[\text{ClO}_4^-]$, $[\text{Cl}^-]$ or $[\text{NO}_3^-]$ hold hardly any effect on the rate of oxidation (Reddy *et al.*, 1996).

The kinetics of oxidation of D-glucose 6-phosphate by hexachloroiridate (IV) and tetrachloroaurate (III), but at constant [substrate], [acid] and temperature was investigated. The pseudo-first order rate constant was found to be independent of [oxidant] it was also reported that the reaction rate was enhanced when sodium chloride was added to the reaction mixture. It was discovered that the rate of the oxidation of D-glucose 6-phosphate increased with the increase in pH (3.72-4.63). The free radical in the sugar undergoes fast oxidation by a unit of Iridium (IV) to yield Lactones (Gupta and Chatterjee, 1984).

The oxidation of ketohexose by Chromium (VI) and vanadium (V), was reported to be first order with respect to [oxidant]. The reactions were first order with respect to both [fructose] and [sorbitol] in chromium (IV) oxidations (Gupta *et al.*, 1981) it was reported that the main difference is that the major product of chromium (VI) is formic acid, whereas oxidation by vanadium (V) gives formaldehyde.

In another recent report on the kinetics and mechanism of the Ir(III) -catalyzed oxidation of xylose and maltose by potassium iodate in aqueous alkaline medium, for the first time, the Ir(III) catalysis of the iodate oxidation of xylose and maltose in aqueous alkaline medium was confirmed. The reactions exhibit first order kinetics with respect to lower $[\text{IO}_3^-]$ and $[\text{OH}^-]$ and show zero order kinetics at their higher concentrations. The main oxidation products for maltose are formic acid and arabinoic acid while xylose is formic acid and threonic acid as oxidation products (Singh *et al.*, 2007a).

The kinetics and mechanism of oxidation of some reducing sugars including D-glucose, D-galactose, D-fructose, D-ribose, D-arabinose, D-xylose and 2-deoxy D-glucose by Diperoiodatoargentate (III) (DPA) in alkaline medium has been reported. They found that the order of the reaction with respect to [DPA] is unity while the order with respect to [sugar] is <1 over the concentration range studied. The rate increases with an increase $[\text{OH}^-]$, No significant dependence on ionic strength was found, but the rate increases with increasing dielectric constant. Formic acid and aldonic acids were detected as the main products of the oxidation (Krishna and Prakash Rao, 1995).

The kinetics and mechanism for oxidizing reducing sugars (pentoses, hexoses and disaccharides) by OsO_4 in alkaline medium was investigated (Singh *et al.*, 1991; Singh *et al.*, 1998a). The reactions exhibit pseudo-unimolecular kinetics with respect to OsO_4 , are first order with respect to lower [sugar] and $[\text{OH}^-]$, but tend towards zero order with respect to both higher [sugar] and $[\text{OH}^-]$. These results suggest the formation of an activated complex between the enediol and Osmium tetroxide. On the basis of the experimental results, the following scheme for the oxidation of sugars in alkaline medium was proposed.

The kinetics of Pd(II) catalysed oxidation of Arabinose, Xylose and Galactose by N-bromosuccinimide (NBS) in acidic medium has been studied using $\text{Hg}(\text{OAc})_2$ as a scavenger for the Br^- ion. The reaction data show that first-order kinetics in each pentose and hexose at low concentrations tends to zero-order at high concentration. First-order kinetics with respect to NBS and Pd(II) and inverse fractional order, i.e., decreasing effect of $[\text{H}^+]$ and $[\text{Cl}^-]$, were observed, whereas ionic strength, $\text{Hg}(\text{OAc})_2$ and succinimide did not influence the oxidation rate (Singh *et al.*, 1999).

Kinetics of oxidation of D-glucose and D-fructose by potassium iodate has been studied for the first time in alkaline medium using Ru (III) as homogeneous catalyst. The linear dependence of the reaction rate at lower $[\text{IO}_3^-]$ and $[\text{OH}^-]$ tends towards zero-order at their higher concentrations. Experimental results also show that the order with respect to $[\text{Ru(III)}]$ is unity and the order with respect to [reducing sugar] is zero in the oxidation of both glucose and fructose. Variation in $[\text{Cl}^-]$ and ionic strength (i) of the medium does not affect the oxidation rate. The species, $[\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2]^-$ and IO_3^- , were found to be the reactive species of Ru(III) chloride and potassium iodate in alkaline medium, respectively. The formation of activated complex is very well supported by the spectrophotometric evidence, observed kinetic data and also by the negative entropy of activation observed for the oxidation of both glucose and fructose. Arabinonic acid and formic acid were identified as the main oxidation products of the reactions (Singh *et al.*, 2007b).

Kinetics and mechanism of Ru(III)-catalyzed and Hg(II) co-catalyzed oxidation of D-arabinose and d-mannose by acidic solution of N-bromoacetamide (NBA). First-order dependence of the reaction on both NBA and sugar at low concentrations shifts to zero-order at their higher concentrations. First-order kinetics with respect to $[\text{Ru(III)}]$ throughout its variation was observed in the oxidation of both arabinose and mannose. A positive effect on the oxidation rate is observed

for [Hg(II)] and [Cl⁻] whereas a negative effect is observed for [H⁺] and [acetamide]. Ionic strength does not influence the oxidation rate. The decrease in the rate of reaction with the increase in dielectric constant (D) of the medium was observed in the oxidation of both reducing sugars. Formic acid and erythronic acid for arabinose and formic acid and arabinonic acid for mannose were identified as main oxidation products of the reactions (Singh *et al.*, 2007c).

Ruthenium complexes have also been used for the oxidation of sugar. The ruthenium complex (Ru(azpy)₂(H₂O)₃)²⁺ has been used as a catalyst in the oxidation of several sugars by sodium bromate. The activity and selectivity of the reaction are strongly dependent on the structure of the sugar substrate (Timmanagoudar *et al.*, 1997). In a similar manner, the kinetics and mechanism of oxidation of sugars and Nucleotides by oxoruthenium (IV) and the oxidation of D-ribose, 2-deoxy-D-ribose by Ru (tpy) (bpy)O²⁺ were measured at pH 7 phosphate buffer (tpy = 2,2;2''-terpyridine, bpy = 2,2-bipyridine). The complex Ru (tpy) (bpy) O²⁺ oxidizes organic substrates by hydride abstraction or oxo transfer (Neyhart *et al.*, 1995).

The oxidation of pentoses in alkaline solution with oxygen as the oxidant has also been investigated (Gleason and Barker 1976).

The reaction of pentoses with oxygen in dilute aqueous potassium hydroxide was studied by determining the initial rate of oxygen uptake and the rate of disappearance of the reducing sugar. The pentose reactivity was found to decrease in the order D-xylose>D-ribose>L-arabinose>D-lyxose. The products formed were identified by paper chromatography, isolation and NMR spectroscopy. The oxygen uptake by glucose in aqueous sodium hydroxide begins immediately and is first order.

Other kinetics of the oxidation of D-glucose by some other metal ion oxidants have also been reported by Shukla and Kesarwani (1984). The Mn (II) catalyzed oxidation of glucose by peroxodisulphate ions occurs via a radical-chain mechanism (Kislenko *et al.*, 1997). Similarly, oxidation of Ketoses and aldoses by manganese (IV) in sulphuric acid media have a first order dependence on sugar and fractional-order dependence on oxidant (Reddy *et al.*, 1996).

Mechanistic studies of oxidation of reducing sugars have been made by different workers using N-halo compounds (Iyengar *et al.*, 1990; Rangappa *et al.*, 1998a, b), Cu(II) (Singh *et al.*, 1978), ammoniacal Ag(I) (Singh *et al.*, 1975) and Nessler's reagent (Singh *et al.*, 1980) in acidic/alkaline medium. Gupta *et al.* (1998) have described in their study that mechanism for the oxidation of some aldoses by Cr(VI), V(V) (Khan *et al.*, 2004), Ce(IV), Mn(III), Ir(IV), Au(III) and periodic acid has been investigated in acidic media. A study of the kinetics of periodates oxidation on a series of dextran oligomers and polymers has been reported recently (Tiziani *et al.*, 2003).

Kinetic studies regarding catalyzed oxidations of reducing sugars by various oxidants, viz., N-bromoacetamide (NBA), N-bromosuccinimide (NBS) and sodium metaperiodate in acidic or alkaline medium using transition metal ions, viz., Os(VIII) (Tripathi and Upadhyay, 2004), Pd(II) (Singh *et al.*, 2006, 1998b), Ru(VIII) (Singh *et al.*, 1992), Ru(III) (Singh *et al.*, 2007b), ruthenate ion (Singh *et al.*, 2005) and Ir(III) (Singh *et al.*, 2004), as homogeneous catalysts.

CONCLUSION

Various studies using different metal and metal complexes as catalysts have been used to carryout the oxidation of different sugars; it has also been observed that from the literature different metal catalyst give rise to different products (White *et al.*, 1963). Trace amount of some transition metals are present in human bodies which helps in catalyzing the oxidation of carbohydrates (sugars) taken into the body.

Metal such as Vanadium is present as vanadium III in the blood cells of certain marine invertebrates which is formed as a reduction of Vanadium V (Kustin and Toppen, 1973).

Sugars such as fructose plays an important role in mammalian metabolism and the recent tendency to use it as a substitute for sucrose, because of its nutritive qualities and without risk has led to the investigation of its physicochemical properties in solution (Gupta and Chatterjee, 1984).

Further research on sugar oxidation should be encouraged going by its biological importance.

REFERENCES

- Atkins, P.W., 1978. Physical Chemistry. 1st Edn., Oxford University Press, London, pp: 849-852.
- Carruthers, E., 2003. Modern Methods of Organic Synthesis. 3rd Edn., University Press, Cambridge, pp: 345-347.
- Castellan, G.W., 1983. Physical Chemistry. 3rd Edn., Addison Wiley Publishing Company, London, pp: 832-839.
- Chari, M.A., D. Shobha, T.K. Kumar and K. Syamasundar, 2007. Polymer (PVP) supported ferric chloride as a heterogeneous catalyst for selective deprotection of aldoximes and hydrazone. Trends Applied Sci. Res., 2: 80-84.
- Clarke, M.A., 1997. Sugar in food processing: A wide range of valuable properties for baking and confectionary. Int. Sugar. J., 99: 114-126.
- Cole, R.H. and J.S. Coles, 1964. Physical Chemistry. W.H. Freeman and Company, USA., pp: 733-736.
- Dinelli, L.R., T.M.S. Bezerra and J.J. Sene, 2010. A kinetic study of the reaction between *trans*-[CoCl₂(en)₂]Cl and the amino acids alanine and valine. Curr. Res. Chem., 2: 18-23.
- Dursun, Z. and I. Taniguchi, 2004. Catalytic effect of ad-atoms modified Au(100) on d-glucose oxidation in alkaline solution. Proceedings of the Adnan Menderes University, 4th AACD Congress, Sept. 29-Oct. 3, Kusadasi-Aydin, Turkey, pp: 1-3.
- Fadnis, A.G. and S.K. Shrivastava, 1982. Kinetics of oxidation of aldoses by thallium(III) in acid perchloric medium. Carbohydrate Res., 102: 23-29.
- Francis, A.C., 2000. Organic Chemistry. 4th Edn., McGraw-Hill Higher Education, New York, pp: 223.
- Gleason, W.B. and R. Barker, 1976. Oxidation of pentose in alkaline medium. Can. J. Chem., 49: 1425-1432.
- Gupta, K.K., S.S. Gupta and S.N. Basu, 1979. Kinetics and mechanism of oxidation of some aldoses by chromic acid in perchloric acid medium. Carbohydr. Res., 71: 75-84.
- Gupta, K.K., S.N. Basu and S.S. Gupta, 1981. Kinetics and mechanism of oxidation of D-Fructose and L-Sorbose by chromium(IV) and Vanadium(V) in perchloric acid medium. Carbohydr. Res., 97: 1-9.
- Gupta, K.K. and U. Chatterjee, 1984. Kinetics of oxidation of D-glucose 6-phosphate by hexachloroiridate (IV) and hexachloreaurate (III). Carbohydr. Res., 126: 321-325.
- Guptal, K.K.S., B.A. Begum and B. Pal, 1998. Reactivity of some sugars and sugar phosphate towards gold (III) in sodium acetate-acetic acid buffer medium. Carbohydr. Res., 309: 303-310.
- Isbell, H.S. and W. Pigman, 1968. Muarotation of sugars in solution: Part I: History, basic kinetics and composition of sugar solutions. Adv. Carbohydr. Chem., 23: 11-57.

- Iyengar, T.A., Puttaswamy and D.S. Mahadevappa, 1990. Oxidation of some aldopentoses by chloramine-B in alkaline medium: A kinetic and mechanistic study. *Carbohydr. Res.*, 204: 197-206.
- Kathiresan, K. and S.M. Anivannan, 2006. Glucose isomerase production by *Penicillium fellutanum* isolated from mangrove sediment. *Trends Applied Sci. Res.*, 1: 524-528.
- Keilin, D. and E.F. Hartee, 1952. Specificity of glucose oxidase (notation). *Biochem. J.*, 50: 331-340.
- Khan, Z., P.S.S. Babu and Kabir-ud-Din, 2004. Kinetics and mechanism of the oxidation of D-fructose by vanadium(V) in H₂SO₄ medium. *Carbohydr. Res.*, 339: 133-140.
- Kislenko, V.N., A.A. Berlin and N.V. Litovchenko, 1997. Kinetics of oxidation of glucose by persulfate ion in the presence of Mn(II) ion. *Kinetics Catal.*, 38: 359-364.
- Kitts, D.D., 1998. Functional Role of Sugars in Food. Canadian Sugar Institute, Toronto-Ontario, Canada.
- Krishna, K.V. and P.J.P. Rao, 1995. Kinetics and mechanism of oxidation of some reducing sugars by diperiodatoargentate (III) in alkaline medium. *Trans. Met. Chem.*, 20: 344-346.
- Kustin, K. and D.L. Toppen, 1973. Reduction of vanadium(V) by L-ascorbic acid. *Inorg. Chem.*, 12: 1404-1407.
- Matthews, P., 1977. *Advanced Chemistry*. Cambridge University Press, Cambridge, pp: 459-479.
- Morrison, R.I. and R.N. Boyd, 1987. *Organic Chemistry*. 5th Edn., Allyn and Bacon Inc., Boston, USA., pp: 1052.
- Murano, P., 2003. *Understanding Food Science and Technology*. Thomson/Wadsworth, C.A., USA.
- Neyhart, G.A., C.C. Cheng and H.H. Thorp, 1995. Kinetics and mechanism of the oxidation of sugars and nucleotides by oxoruthenium(V): Model studies for predicting cleavages patterns in polymeric DNA and RNA. *J. Am. Chem. Soc.*, 117: 1463-1471.
- Odebunmi, E.O. and R. Marufu, 1999. Kinetics and mechanism of oxidation of D-glucose and D-sorbitol by KMnO₄ and hexachloroiridate IV. *Nig. J. Sci.*, 33: 133-143.
- Odebunmi, E.O. and S.O. Owalude, 2005. Kinetics and mechanism of oxidation of sugars by chromium (VI) in perchloric acid medium. *J. Chem. Soc. Nig.*, 30: 191-197.
- Odebunmi, E.O., S.A. Iwarere and S.O. Owalude, 2006. Kinetics of oxidation of fructose, sucrose and maltose by potassium permanganate in NaHCO₃/NaOH buffer and Iridium (IV) complex in sodium acetate/acetic acid buffer. *Int. J. Chem.*, 16: 167-176.
- Ogunlaja, A.S., E.O. Odebunmi and S.O. Owalude, 2009. Kinetics and mechanism of Mn (II) catalyzed oxidation of D-arabinose and D-xylose by chromium (VI) ions in perchloric acid medium. *Pacific J. Sci. Technol.*, 10: 451-461.
- Perez-Benito, J.F. and C. Arias, 1993. A kinetic study on the reactivity of chromium (IV). *Can. J. Chem.*, 71: 649-655.
- Rangappa, K.S., H. Manjunathaswamy, M.P. Raghavendra and D.C. Gowda, 1998a. Oxidation of threose-series pentoses and hexoses by sodium N-chloro-p-toluenesulfonamide. *Carbohydr. Res.*, 307: 253-262.
- Rangappa, K.S., M.P. Raghvendra, D.S. Mahadevappa and D.C. Gowda, 1998b. Kinetics and mechanism of oxidation of erythro-series pentoses and hexoses by N-Chloro-p-toluene sulphonamide. *Carbohydr. Res.*, 306: 57-67.

- Reddy, M.K.R., K. Nagi, K.C. Ragama and P.K. Saiprakash, 1996. Oxidation of epimeric aldo and D L-Keto sugars by trivalent manganese in sulphuric acid media A kinetic approach. *Oxidation Commun.*, 19: 381-389.
- Sangshetti, J.N., P.A. Kulkarni and D.B. Shinde, 2007. Spectrophotometric determination of didanosine in bulk and tablet formulation. *Trends Applied Sci. Res.*, 2: 71-75.
- Sangshetti, J.N., P.R. Mahaparale, S. Paramane and D.B. Shinde, 2008. spectrophotometric estimation of donepezil hydrochloride in bulk and tablet formulation. *Trends Applied Sci. Res.*, 3: 109-112.
- Sharma, K.K. and L.K. Sharma, 2004. *A Textbook of Physical Chemistry*. 4th Edn., Viska Inc., New Delhi, India, pp: 570.
- Shukla, S.N. and R.N. Kesarwani, 1984. The kinetics and mechanism of oxidation of maltose and lactose by Ti(III) in acidic media. *Carbohydr. Res.*, 133: 319-323.
- Singh, M.P., H.S. Singh, S.C. Tiwari, K.C. Gupta, A.K. Singh, V.P. Singh and R.K. Singh, 1975. In organic oxidants such as Cu(II) in oxidation of sugars in alkaline media. *Ind. J. Chem.*, 13: 819-822.
- Singh, M.P., A.K. Singh and V. Tripathi, 1978. Kinetics and mechanism of oxidation of D-fructose and L-sorbose by copper(II) in the presence of ammonium hydroxide. *J. Phys. Chem.*, 5: 1222-1225.
- Singh, M.P., R.K. Singh, A.K. Singh and A. Srivastava, 1980. Quinoxalines derived from D-glucose and O-phenylenediamine in acidic media. *Ind. J. Chem.*, 19A: 547-549.
- Singh, H.S., B. Singh and A.K. Singh, 1991. Mechanism of oxidation of reducing sugar by osmium tetroxide in alkaline medium by the stopped flow technique. *Carbohydr. Res.*, 211: 235-243.
- Singh, A.K., A. Singh, R. Gupta, M. Saxena and B. Singh, 1992. Kinetics and mechanism of Ru (III) and Hg (II) Co-catalysed oxidation of D-mannose and D-maltose by acidic solution of N-bromoacetamide. *Trans. Met. Chem.*, 17: 413-416.
- Singh, A.K., D. Chopra, S. Rahmani and B. Singh, 1998a. Kinetics and mechanism of Pd(II) catalysed oxidation of D-arabinose, D-xylose and D-galactose by N-bromosuccinimide in acidic solution. *Carbohydr. Res.*, 314: 157-160.
- Singh, H.S., A. Gupta, A.K. Singh and B. Singh, 1998a. Kinetics and mechanism of oxidation of reducing sugars by osmium tetroxide in alkaline medium. *Trans. Met. Chem.*, 23: 277-281.
- Singh, A.K., D. Chopra, S. Rahmani and B. Singh, 1999. Kinetics and mechanism of Pd(II) catalysed oxidation of D-arabinose, D-xylose and D-galactose by N-bromosuccinimide in acidic solution. *Carbohydr. Res.*, 12: 26-32.
- Singh, A.K., S. Rahmani, B. Singh, R.K. Singh and M. Singh, 2004. Mechanism of Ir (III) catalysed and Hg (II) co-catalysed oxidation of reducing sugars by boromoacetamide in acidic medium. *J. Phys. Org. Chem.*, 17: 249-256.
- Singh, A.K., N. Chaurasia, S. Rahmani, J. Srivastava and A.K. Singh, 2005. Ruthenate ion catalysed oxidation of D-galactose and D-xylose by alkaline solution of sodium meta-periodate: A kinetic study. *J. Chem. Res.*, 2005: 304-310.
- Singh, A.K., J. Srivastava, S. Rahmani and V. Singh, 2006. Pd (II) Catalysed and Hg(II) Co-catalysed oxidation of D-glucose and D-fructose by N bromoacetamide in the presence of perchloric acid. *Carbohydr. Res.*, 341: 397-409.

- Singh, A.K., S. Srivastava, J. Srivastava and R. Singh, 2007a. Kinetic and mechanism of the Ir(III) catalyzed oxidation of xylose and maltose by potassium iodate in aqueous alkaline medium. *Carbohydr. Res.*, 348: 1078-1090.
- Singh, A.K., S. Srivastava, J. Srivastava, R. Srivastava and P. Singh, 2007b. Studies in kinetics and mechanism of oxidation of D-glucose and D-fructose by alkaline solution of potassium iodate in the presence of Ru(III) as homogeneous catalyst. *J. Mol. Catal. A Chem.*, 278: 72-81.
- Singh, A.K., J. Srivastava and S. Rahmani, 2007c. Mechanistic studies of oxidation of d-arabinose and d-mannose by acidic solution of N-bromoacetamide in presence of chloro-complex of Ru(III) as homogeneous catalyst. *J. Mol. Catal. A Chem.*, 271: 151-160.
- Strobel, H.A., 1962. *Chemical Instrumentation*. 1st Edn., Addison Wiley Publishing Company, London, pp: 150.
- Swyer, D.T., W.R. Heineman and J.M. Beebe, 1984. *Chemistry Experiment for Instrumental Methods*. John Wiley and Sons Inc., USA., pp: 90-108.
- Timmanagoudar, P.L., G.A. Hiremath and S.T. Nandibeoor, 1997. Permanganate oxidation of chromium (III) in aqueous alkaline medium: A kinetic study by the stopped-flow technique. *Trans. Met. Chem.*, 22: 193-196.
- Tiziani, S., F. Sussich and A. Cesaroi, 2003. The use of periodate in the non catalyzed oxidation of carbohydrate. *Carbohydr. Res.*, 338: 1083-1095.
- Tripathi, R. and S.K. Upadhyay, 2004. Kinetics of oxidation of reducing sugars by catalytic amount of osmium(VIII) in presence of periodate. *Int. J. Chem. Kinet.*, 36: 441-448.
- Weibel, M.K. and H.J. Bright, 1971. Insolubilized enzymes. Kinetic behaviour of glucose oxidase bound to porous glass particles. *Biochem. J.*, 124: 801-807.
- White, A., P. Handler, E.L. Smith and D.W. Stetten, 1963. *Principle of Biochemistry*. 2nd Edn., McGraw Hill, New York, pp: 380-445.
- Zucker, L. and L.P. Hammett, 1939. Kinetics of the iodination of acetophenone in sulphuric and perchloric acid solution. *J. Am. Chem. Soc.*, 61: 2791-2798.