SUMMARY

S U M M A R Y

Carbohydrates have contributed much to our knowledge of stereochemistry with the continued research activity in the field of carbohydrate chemistry. In recent times, interest has focussed on the conformations of sugar molecules and on the study of the mechanisms of reactions of such compounds. One of the basic reasons for research developments in carbohydrate chemistry is the need to understand the basic chemistry of carbohydrate molecules required in the investigation of more complex problems, especially biochemical processes.

In almost all living cells, the carbohydrates are the central pathway for supply of energy needed for mechanical work and chemical reactions. All sugars absorbed into the blood-stream are usually converted into glucose, which is then fed into the body tissues to provide energy. Excess glucose is converted either to glycogen and kept as an energy store until needed, or to reserve fatty tissue. Reserve energy depots, including fat and protein, are metabolized when needed to provide circulatory glucose. The ultimate fate of metabolizable carbohydrate is oxidation. The oxidation of glucose and the related monosaccharides thus constitutes a very important class of reactions which may help, though indirectly, in elucidation of many problems of biochemistry. Hence, an attempt has been made here to study the oxidation of D-ribose and D-arabinose by potassium bromate in alkaline medium. The kinetics has been followed under different conditions and the thermodynamic parameters have been calculated. The results have been explained on the basis of conformations of sugars. The mechanism is suggested which satisfactorily accounts for the experimental results.

97

Chapter I includes a brief account of structural representations of monosaccharides followed by an extensive review of the oxidation reactions of monosaccharides in acidic as well as alkaline media. Action of alkali on monosaccharides has been outlined briefly with a special reference to 'Lobry de Bruyn-Alberda van Ekenstein transformation'. Oxidation reactions of many aldoses and ketoses by various oxidising agents like Br_2 water, Ce(IV), V(V), chromic acid, dichromate, pyridine chloro-chromate, bromate ion, N-bromoscuccinimide, Mn(III), Ir(IV), Au(III) and IO_4^- ions etc. in acidic media and oxidation by hexacyanoferrate ion, Cu(II), iodine, chlorine, chloromine-T, bromamine-T, silver nitrate, sodium peroxide, etc. in alkaline media have been extensively reviewed. The chapter is concluded with the discussion of the scope and a brief outline of the work proposed.

Chapter-II is devoted to experimental procedures. These include the purification of chemicals used, preparation of solutions, the method of following kinetics, identification of end products, etc. The kinetics has been followed by analysing the reaction mixture iodometrically for unused BrO_3^- ion concentration. Methods of studying dependence of rate of reaction on [substrate], [oxidant], [OH⁻], ionic strength and temperature have been given. The methods of detection of free radicals and the identification of end-products have been described in detail. The end-products have been identified by paper chromatography.

Chapter-III deals with the results on the kinetics of oxidation of D-ribose and D-arabinose followed by discussion and conclusion.

Dependance of reaction rate on the following factors has been studied –

(i)   Variation of substrate concentration,

(ii)   Variation of oxidant concentration,

(iii)   Variation of OH⁻ ion concentration,

(iv)   Variation of ionic strength,
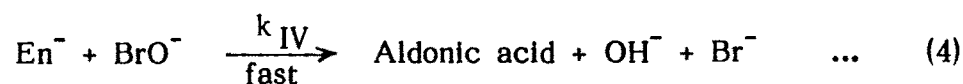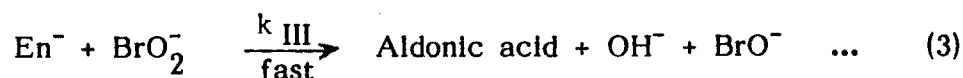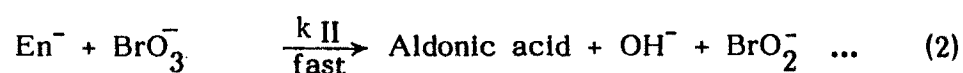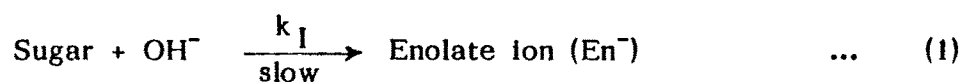
(v)   Variation of temperature.

The oxidation reaction shows zero-order dependence on [oxidant] while first order dependence on [substrate] and [OH⁻], for both the sugars. The oxidation seems to follow a general equation,

$$\frac{- d\,[BrO_3^-]}{dt} = k\,[Sugar]\,[OH^-]$$

The relative rates of oxidation of the sugars studied under similar conditions are observed to be D-ribose > D-arabinose. The rate of reaction seems to be independent of ionic strength (μ) showing that the reaction is of ion-molecule or molecule-molecule type. The reaction has been studied at four/five different temperatures in the vicinity of $333^{O}K$ in order to calculate temperature coefficient, frequency factor (A), energy of activation (Ea), enthalpy of activation ($\Delta H*$), entropy of activation ($\Delta S*$) and free energy of activation ($\Delta G*$). The Ea values of the two sugars are related as D-ribose < D-arabinose and $\Delta S*$ also shows a similar trend. But $\Delta S*$ of D-ribose is negative and that of D-arabinose is positive. The reaction does not involve any free radical as shown by acrylonitrile and allyl acetate tests. The end-product analysis shows that the sugar is oxidized to corresponding aldonic acid.

The results on the oxidation of D-ribose and D-arabinose by alkaline potassium bromate have been discussed on the basis of well-known

'Lobry de Bruyn-Alberda Van Ekenstein transformation' and the rate of oxidation has been shown to be the rate of enolization of sugar molecule in presence of OH^- ions. A four step mechanism has been suggested on the basis of formation of enolate ion and successive reduction of BrO_3^- ion to Br^- ion. The mechanism involves following steps –

$$Sugar + OH^- \xrightarrow[slow]{k_I} Enolate\ ion\ (En^-) \qquad ... \quad (1)$$

$$En^- + BrO_3^- \xrightarrow[fast]{k_{II}} Aldonic\ acid + OH^- + BrO_2^- \quad ... \quad (2)$$

$$En^- + BrO_2^- \xrightarrow[fast]{k_{III}} Aldonic\ acid + OH^- + BrO^- \quad ... \quad (3)$$

$$En^- + BrO^- \xrightarrow[fast]{k_{IV}} Aldonic\ acid + OH^- + Br^- \qquad ... \quad (4)$$

By considering step 1 i.e. the process of enolization as the rate determining step and the steps which follow it to be sufficiently fast in comparison, the following rate equation results –

$$\frac{-\,d\,[BrO_3^-]}{dt} = k_I\,[Sugar]\,[OH^-]$$

The suggested mechanism, thus agrees with the experimental observations in a convincing manner.

The differences in the oxidative behaviour and thermodynamic parameters of these sugars have been explained on the basis of their structures and the conformational analysis.

Further, the results of oxidation of these sugars have been compared with those of some selected sugars studied previously under similar conditions. It has been observed that Ea of D-ribose is not much different from that of D-xylose and D-glucose but much lower than that of D-arabinose and considerably greater than that of D-fructose. Similarly, ΔS^* values of D-ribose, D-xylose and D-glucose do not differ appreciably but ΔS^* of D-fructose is very low and that of D-arabinose is quite high and positive. The differences in behaviour of these sugars have been explained on the basis of their conformational analysis. Desolvation of sugar molecule prior to the formation of activated complex seems to be partially responsible for the relatively high value of ΔS^* for arabinose. By taking D-xylose (aldopentose) for comparison the order of reactivity is shown to be ribose > xylose > arabinose. Comparison with D-glucose (aldohexose) has lead to the order of reactivity glucose > ribose > arabinose whereas the order of reactivity is shown to be fructose > ribose > arabinose by taking fructose (ketohexose) for comparison.