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Note

The epimerisation of monosaccharides by γ-irradiation in frozen, aqueous solutions

N. K. KOCHETKOV, L. I. KUDRJASHOV, M. A. CHLENOV, AND T. YA. LIVERTOVSKAYA
N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences, Moscow (U. S. S. R.)
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An understanding of the radiation chemistry of carbohydrates is important because it can lead to an understanding, at the molecular level, of the effects of radiation on biological systems containing sugar components, such as immune systems, inter- and intra-cellular media, etc.

Carbohydrates are known to undergo the following primary processes under γ-irradiation: (*1*) scission into two-, three-, and four-carbon fragments[1], (*2*) radiation-induced hydrolysis of glycosidic bonds[2], (*3*) oxidation[3], (*4*) oxidation–reduction transformations with the formation of deoxy and deoxycarbonyl compounds[4].

We now report on a new type of radiation-induced carbohydrate transformation, namely the inversion of configuration at one or several asymmetric centres without cleavage of the carbon chain. This process occurs on irradiation of nitrogen-saturated, frozen, aqueous solutions of sugar at temperatures between -78 and $0°$.

A nitrogen-saturated D-ribose solution (10mM) was frozen at $-78°$ to the polycrystalline state and irradiated at the same temperature (^{60}Co-source, dose rate 0.6×10^{16} eV.ml^{-1}.sec^{-1}, total dose 1.5×10^{21} eV/ml). Paper chromatography [butanone–acetic acid–saturated, aqueous boric acid (9:1:1) and pyridine–1-butanol–water (4:6:3)] revealed the presence of arabinose, lyxose, and xylose, in addition to ribose. In blank experiments, no epimerisation was detected. The irradiated solution, after freeze-drying, was fractionated by preparative paper chromatography and, after removal of the major part of the D-ribose, the monosaccharides were isolated and conventionally acetylated with pyridine–acetic anhydride. The mass spectra of the tetra-acetates of arabinose, lyxose, and xylose established the identity of these compounds[5]. On the basis of optical rotatory dispersion measurements, it was found that the arabinose isolated after irradiation corresponded to the D series, and lyxose to the L series.

Irradiation of a frozen solution of D-arabinose, under the above conditions, gave only lyxose. Likewise, only arabinose was formed from D-lyxose. Preliminary experiments with hexoses revealed similar transformations. For example, after irradiation of frozen, aqueous solutions of both D-mannose and D-galactose, a product chromatographically identical with glucose was found.

A quantitative determination of the radiation-induced epimerisation process for D-ribose was carried out by paper chromatography[6]. The ($-G$)-value for ribose was found to be not less than 0.15 molecule per 100 eV (dose 1.5×10^{21} eV/ml) and the G-value for arabinose not less than 0.01 molecule. As the extent of ribose destruction and the yield of arabinose were determined only for one dose, these values should be regarded as minimal. Approximate determinations place the yields of lyxose and xylose almost equal to that of arabinose. Hence, the total yield of epimeric sugars is not less than 0.03 mol., which corresponds to a 20% transformation in relation to the ($-G$)-value of 0.15. Epimerisation is, therefore, one of the main processes occurring during γ-irradiation of frozen sugar solutions. The presence of a solid, aqueous phase at certain temperatures is a necessary condition for epimerisation. A more-detailed study of the irradiation of D-ribose shows that epimerisation occurs at $-78°$ and at $0°$, but does not take place at $-196°$. No epimerisation occurs when solid, crystalline D-ribose is irradiated or when aqueous solutions of D-ribose are irradiated at $20°$.

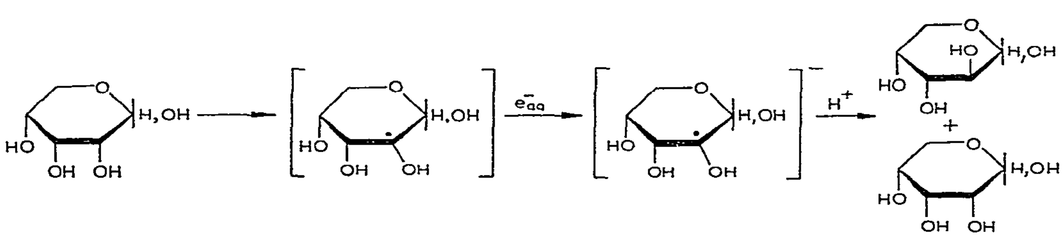
From e.s.r. data[7], signals corresponding to OH, e_{tr}^-, and primary ribose radicals produced by C–H bond scission were observed when frozen aqueous solutions of D-ribose were irradiated at $-196°$. After warming to $-78°$, the signals of e_{tr}^- and OH disappeared, and only sugar radicals remained. A similar pattern was observed after irradiation at $-78°$. It is possible that, at $-78°$, radiolysis products of water (OH and e_{tr}^-) become mobile and react with the carbohydrate trapped in the solid matrix at -78 to $0°$. Whereas OH radicals readily react with sugars[8] [Equation *1*; k (sugar+OH) $\sim 10^9$ mole^{-1}.sec^{-1}], e_{aq}^- has a low reactivity towards carbohydrates[9] [k (e_{aq}^-+sugar) $< 10^7$ mole^{-1}.sec^{-1}]. The electron could, nevertheless, react with the radical R· produced according to the reactions *1* and *2*.

$$RH + OH \rightarrow R\cdot + H_2O \qquad (1)$$

$$R\cdot + e_{aq}^- \rightarrow |R\cdot|^- \xrightarrow{H^+} RH \qquad (2)$$

where R is a sugar residue.

With such reactions, epimerisation at one or several asymmetric centres could occur. For example, the D-ribose → D-arabinose transformation could proceed according to the following scheme:



Such carbohydrate epimerisation is of interest for several reasons. First, the stereochemical aspects of γ-radiolysis have not been sufficiently studied, and carbohydrates could serve as a very convenient model for such investigations. On the other hand, a configurational change of carbohydrates and other biologically important substances on irradiation* could result in serious effects on the cell, either in relation to anomalous or "toxic" products formed, or with the production of abnormal units in polysaccharides. Such modification of polysaccharides could change the structure of inter- and intra-cellular media and lead, for example, to a change in gel-formation properties[11]. In conclusion, it should be noted that the epimerisation process takes place only in frozen solutions. If a necessary condition for epimerisation is the presence of a structured medium, such a transformation might take place in structured biological media, *e.g.* in gels.

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*It was shown that some α-amino acids also show inversion at the asymmetric centre during γ-irradiation of frozen solutions[10].