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Short Research Article

Study of the reactions of carbohydrates with tritium under solid-state catalytic hydrogenation condition†

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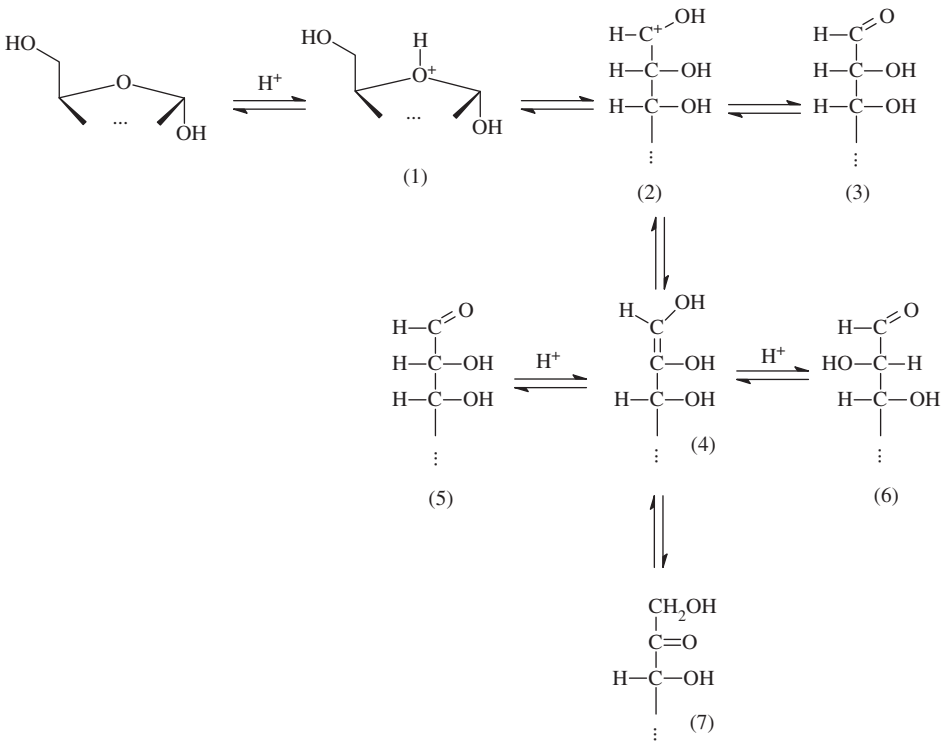
Introduction

The reaction of carbohydrates with tritium under solid-state catalytic hydrogenation conditions was investigated. D-ribose, D-glucose and lactulose were chosen as model compounds. The effects of temperature in the range of 90–140°C, catalysts, the composition of the solid-state and the surface area of support on the reaction of solid-state catalytic hydrogenation of model compounds with tritium were studied. Epimeric carbohydrates were found in the products of the reaction. A mechanism for the isomerization of carbohydrates in the solid state under the action of spillover hydrogen is proposed.



Scheme 1

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Results and discussion

We have investigated the reaction of solid-state catalytic hydrogenation of pentoses,[1] hexoses and disaccharides with tritium. Scheme 1 shows proposed mechanism of isomerization on the basis of our findings. In the scheme, spillover hydrogen in the form of protons associated with the oxygen of the oxidic cycle (1), subsequently (2) a carbocationic species is formed which then deprotonates to an enediol (4) with the double bond between the first and second carbon atoms. When a proton detached from the second carbonic atom, the enediol (4) with double bonds between first and second carbonic atom is formed. At the same time the chirality of second carbonic atom is lost. When a proton associates to second carbonic atom of enediol, re-protonation of the enediol can then take place from either face giving either the R or S configuration leading to isomerization. Conversely, protonation of the first carbon of the enediol can give rise to a ketose (7) whilst ketonization and/or protonation can give rise to the open chain aldehyde (3) or the carbocation (2).

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