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In the framework of a project devoted to the chemical transformation of monosaccharides from hemicelluloses into higher added value materials, the zinc-induced reductive elimination from 5-deoxy-5-iodo derivatives of D-xylose and L-arabinose was carried out. This study gave us the opportunity to observe surprising behaviors. In particular, the reaction strongly depends on structural parameters (protecting group pattern, configuration at C-4) and on the presence of Zn$^{2+}$ ions. Collaterally with the experimental work, water solvent PCM HF-DFT (MPW1K/LANL2DZ) computations were performed to obtain insight into the mechanism for the reductive part of the reaction sequence. Without Zn$^{2+}$, the zinc insertion reaction was found to proceed through a concerted but non-synchronous process involving a relatively large energy barrier (32 kcal mol$^{-1}$) that directly leads to the presumed organozinc intermediate. In the presence of Zn$^{2+}$, a three-step mechanism was identified in which the cation coordinates the anomeric and ring oxygen atoms and also the sugar iodine atom, causing an activating effect on the zinc insertion process by facilitating the homolytic rupture of the C–I bond. Complexes between zinc and Zn$^{2+}$ bound carbohydrates were characterized with large stabilization energies, suggesting that Zn$^{2+}$ might enhance the affinity of the organic compound with the zinc metal surface.

Introduction

The reductive elimination from halogeno sugars (Bernet–Vasella reaction) is a reaction sequence frequently used in carbohydrate chemistry. First reported by Vasella’s group with 6-deoxy-6-bromo-D-glucopyranose derivatives, the method was extended to 5-deoxy-5-halo-pentofuranosides (Scheme 1).

![Scheme 1](image)

The metal that is by far the most used to induce this reaction is zinc, even if other reducing systems such as indium$^3$ and Zn$^+$

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