



## Ab-initio and experimental study of pentose sugar dehydration mechanism in the gas phase



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### ABSTRACT

In this work pentose sugar (D-xylose, D-ribose and D-arabinose) gas phase dehydration reaction was investigated by means of mass spectrometric techniques and theoretical calculations. The ionic species derived from the dehydration reaction of protonated D-ribose and D-arabinose were structurally characterized by their fragmentation patterns and the relative dehydration energies measured by energy resolved CAD mass spectra. The results were compared with those recently obtained for D-xylose in the same mass spectrometric experimental conditions. Dehydration of C1-OH protonated sugars was theoretically investigated at the CCSD(T)/cc-pVTZ//M11/6-311++G(2d,2p) level of theory. Protonated pentoses are not stable and promptly lose a water molecule giving rise to the dehydrated ions at  $m/z$  133. D-xylose, D-ribose and D-arabinose dehydration follows a common reaction pathway with ionic intermediates and transition states characterized by similar structures. Slightly different dehydration energies were experimentally measured and the relative trend was theoretically confirmed. The overall dehydration activation energy follows the order arabinose < ribose < xylose. Gas-phase pentose sugar dehydration leads to the formation of protonated 2-furaldehyde as final product. Based on the experimental and theoretical evidence a new mechanistic hypothesis starting from C1-OH protonation was proposed.

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## 1. Introduction

The acid catalysed dehydration of sugars represents an important chemical transformation for the production of useful chemicals from biomass [1–3]. 2-Furaldehyde (2-FA) is the main product from pentose thermal acid catalysed dehydration, produced by the initial hydrolysis of hemicellulose, mainly composed by D-xylose [4–7]. World production of 2-FA is increasing year by year as this molecule represents a useful precursor of furfuryl, furyl and furfuryl compounds [8]. Owing to its industrial relevance, furfural production from pentose decomposition has been the focus of a number of studies aimed in particular at the optimization of its formation

through different acid and salt catalysed reactions [9,10]. At the same time the scientific interest has focused on the experimental and theoretical comprehension of D-xylose conversion into 2-FA mechanism but a debate still exists in literature on the effective reaction scheme [11–16]. The main degradation pathways proposed involve D-xylose acyclic and cyclic forms the latter one being the preferred structure in the gas phase. The cyclic mechanism is represented by two different acid-catalysed reaction sequences proceeding from the pyranose form of D-xylose protonated on the C1-OH or C2-OH oxygen atoms, respectively. Both reactions lead to a furanose ring structure after the loss of the first water molecule.

Previously reported theoretical calculations [13] strongly supported the degradation pathway starting from C2-OH protonation. Protonation at C1-OH was excluded due to the calculated high energy barrier for the subsequent ring contraction to the furanose intermediate (39.3 kcal mol<sup>-1</sup>). Besides conventional analytical applications, mass spectrometric techniques offer the possibility to study the mechanism of fundamental ionic reactions in the absence

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of solvation and counter ions allowing to clarify controversial hypotheses proposed in solution. The internal energy of the reactant ions can be increased by collision with a target gas thus allowing it to undergo energy controlled unimolecular endothermic reactions. The knowledge of the ion structures and of their dissociation energy barriers represent fundamental results that may validate the reaction mechanisms postulated by theoretical calculations.

Recently, this approach has been successfully applied to the gas phase dehydration reaction of protonated D-xylose, D-glucose and D-fructose [17–19].

Conversely to the previously reported theoretical evidence [13], mass spectrometric experiments demonstrated that in the gas phase the dehydration reaction of D-xylose involves protonation on the OH group bound at C1 position [17]. C1-OH protonated D-xylose is not stable and promptly loses the first water molecule in a process that seems to be characterized by a low energy barrier. In order to find a new mechanism that justifies these results, a comprehensive theoretical analysis of protonated D-xylose dehydration at the CCSD(T)/cc-pVTZ//M11/6-311++G(2d,2p) level of theory was performed. To confirm the experimental and theoretical results obtained for D-xylose, the same approach was used to study the dehydration of D-ribose and D-arabinose isomeric pentose sugars. Gaseous ionic species of interest, generated in the ESI source of an ion trap and of a triple quadrupole mass spectrometers, were structurally characterized by collisionally activated dissociation (CAD) mass spectrometry. The relative energy threshold values of the consecutive dehydration steps, derived by the energy resolved mass spectra of the ionic intermediates, were compared with dehydration energy barriers evaluated by theoretical calculations. The joint application of experimental and theoretical techniques allows a reasonable new dehydration mechanistic hypothesis starting from pentose C1-OH protonation to be proposed.

## 2. Experimental

### 2.1. Materials

All chemicals were obtained from commercial sources and were used as received. D-xylose, D-arabinose and D-ribose and methanol (LC/MS grade) were purchased from Sigma-Aldrich Ltd (St. Louis, Mo, USA). D-[1-<sup>18</sup>O]xylose, D-[1-<sup>18</sup>O]ribose and D-[1-<sup>18</sup>O]arabinose were purchased from Omicron Biochemicals Inc. (South Bend, IN, USA) with a stated purity of 99% and an isotopic enrichment  $\geq 90\%$ .

### 2.2. Mass spectrometry

Full scan and MS<sup>n</sup> mass spectra were acquired by using an Amazon SL ion trap instrument operating in the positive ion mode (Bruker, Bremen, Germany). Electrospray source conditions were as follows: capillary –4000/–4500 V, end plate offset –400/–450 V, nebulizer 5.0 psi, dry gas 2.5 L/min, dry temperature 200 °C. Mass spectra represent the average of 50 scans and were performed by direct infusion of 10<sup>–3</sup> M solutions of pure compounds in methanol/water (0.1% HCOOH) (1:1, V/V) with a 10  $\mu$ L/min flow rate. Full scan mass spectra were acquired from  $m/z$  50 to  $m/z$  500 and for the MS<sup>n</sup> experiments an activation time of 30 ms was used. CAD and energy resolved mass spectra were acquired using a TSQ700 triple stage quadrupole mass spectrometer from ThermoFinnigan Ltd. by introducing Ar in the triple quadrupole cell as the target gas at pressures of about 0.1 mTorr and at collision energies ranging from 0 to 40 eV (laboratory frame). An upper limit of 2 eV for the kinetic energy of the reactant ion at nominal collision energy of 0 eV (laboratory frame) and an ion-beam energy spread of about 1 eV can be estimated by using cut-off potentials. Laboratory ion energies ( $E_{\text{lab}}$ ) are converted to center-of-mass (ECM) energies by

using the formula  $\text{ECM} = E_{\text{lab}} m/(m + M)$ , where  $m$  is the mass of neutral reactant and  $M$  is the mass of the ionic reagent. Experimental cross sections,  $\sigma_{\text{tot}}$ , were determined by the relation  $I_{\text{R}}/I_{\text{tot}} = \exp(-\sigma_{\text{tot}} n l)$  where  $I_{\text{R}}$  is the intensity of the transmitted ion beam,  $I_{\text{tot}}$  is the total ions intensity,  $n$  is the number density of the neutral gas and  $l$  is the effective gas cell length. Individual product cross sections,  $\sigma_{\text{p}}$ , were calculated by  $\sigma_{\text{p}} = \sigma_{\text{tot}}(I_{\text{p}}/I_{\text{ptot}})$  where  $I_{\text{p}}$  represents the intensity of the product ion and  $I_{\text{ptot}}$  the total product ion intensities.

### 2.3. Theoretical calculations

All calculations were performed using NWChem 6.6[20] and GAMESS [21] (version Dec 5, 2014), both running on a six-node (8 Intel-Xeon E5520 2.27 GHz CPU and 24 GB DDR3 RAM each) cluster (48 CPU total) with a Debian GNU/Linux 8 “Jessie” operating system. A systematic conformational search was performed using Open Babel [22], with the MMFF94 force field. Only the best conformers were kept. Geometries optimization and harmonic frequencies calculations were performed at the M11/6-311++G(2d,2p) level of theory. M11 is a meta-GGA range separated M11 DFT functional [23] that gives an excellent accuracy-speed trade-off for this class of compounds [24]. The calculated frequencies were used to evaluate zero-point vibrational energies, kinetic contributions and to verify the nature of all the stationary points as either minima or transition states. Intrinsic reaction coordinate (IRC) calculations were carried out in order to confirm transition state geometries. CCSD(T)/cc-pVTZ [25] single point energy calculations were carried out on DFT optimized geometries in order to get electronic structure energies at higher level of theory. The potential energy surface (PES) of O1 protonated  $\beta$ -D-xylopyranose was also explored performing a quantum molecular dynamic simulation with the Car-Parrinello method (CPMD) [26] searching for feasible reaction pathways. CPMD was carried out with a time-step of 0.5 fs for 4 ps of total simulation time, at a temperature of 500 K, with an electron fake mass of 600 au, a wave function cut-off of 20 Ry, in aperiodic boundary conditions. Wave functions for valence electrons were linear combination of plane-wave basis functions. The hybrid PBE96 functional was used. Geometry optimization and CPMD simulation were performed using NWChem, while CCSD(T)/pVTZ single point energies with GAMESS. Three-dimensional (3D) structures were built using the Avogadro [27] and MacMolPlt software [28]. NWChem output files were graphically visualized by means of Jmol [29]. Cartesian coordinates for all the structures presented in this work and their M11 and CCSD(T) energies are reported in the [Supporting Information](#).

## 3. Results and discussion

### 3.1. Mass spectrometric results

The ionic species of interest were obtained in the ESI sources of an ion trap and a triple quadrupole mass spectrometers by the direct infusion of 10<sup>–3</sup> M solutions of the pentose monosaccharides. Ion-trap full scan ESI-MS spectrum of D-ribose, shown in Fig. 1a, is a representative example for the monosaccharides. As expected [17,30–32], the spectrum is dominated by the  $[M \cdot \cdot \text{Na}]^+$  ions at  $m/z$  173, whereas the ions at  $m/z$  151 corresponding to protonated D-ribose are present at very low intensity. Ionic species at  $m/z$  133 together with minor intensity of  $m/z$  115 and  $m/z$  97 ions, corresponding to the ionic intermediates and final product of pentose dehydration reactions, are also present.

In order to follow the dehydration reactions, we performed sequential ion trap MS<sup>n</sup> product ion experiments of selected precursor ions. Starting from the ion at  $m/z$  151, the loss of a water

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