A mass spectrometric study of the acid-catalysed D-fructose dehydration in the gas phase

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ABSTRACT

5-hydroxymethylfuraldehyde (5-HMF) and simpler compounds, such as levulinic acid (LA) and glyceraldehyde, are platform molecules produced by the thermal acid-catalyzed dehydration of carbohydrates coming from biomass. Understanding sugar degradation pathways on a molecular level is necessary to increase selectivity, reduce degradation by-products yields and optimize catalytic strategies, fundamental knowledge for the development of a sustainable renewable industry. In this work gaseous protonated D-fructose ions, generated in the ESI source of a triple quadrupole mass spectrometer, were allowed to undergo Collisionally Activated Decomposition (CAD) into the quadrupole collision cell. The ionic intermediates and products derived from protonated D-fructose dehydration were structurally characterized by their fragmentation patterns and the relative water-loss dehydration energies measured by energy-resolved CAD mass spectra. The data were compared with those obtained from protonated D-glucose decomposition in the same experimental conditions. In the gas phase, D-fructose dehydration leads to the formation of a mixed population of isomeric $[C_6H_6O_3]H^+$ ions, whose structures do not correspond exclusively to 5-hydroxymethyl-2-furaldehyde protonated at the more basic aldehydic group.

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1. Introduction

Nowadays, fossil fuels represents the source of more than three-quarters of the world's energy and petroleum is the feedstock used for the production of over 96% of the carbon-containing chemicals produced by the industries. With increasing consumption rate, the depletion of fossil fuels is becoming inevitable, and in less than two decades petroleum production will not be able to meet the growing energy demand.[1,2]

Biomass represents the most abundant carbon-rich renewable terrestrial biological resource that can be used directly as a fuel, fuel precursor or converted to useful chemicals. Carbohydrates are the main carbon source in lignocellulosic biomass.[3] Processes allowing the utilization of carbohydrates from lignocellulosic biomass as a renewable resource have received great attention over time.

Platform molecules, such as 5-hydroxymethylfurfuraldehyde (5-HMF) and 2-furaldehyde (2-FA) or simpler molecules such as levulinic acid (LA) and glyceraldehyde, are the products of the thermal acid-catalyzed dehydration of hexoses and pentoses.[4–7] These

compounds are important sustainable intermediates for the preparation of a great variety of chemicals, pharmaceuticals and furan-based polymers.

Research on fructose and glucose dehydration by homogeneous or heterogeneous catalyzed aqueous and organic systems has been recently reviewed.[8,9] By far, the highest 5-HMF yields were obtained from fructose, and the dehydration rate of glucose was found to be about 40 times lower than that of fructose. The mechanism, kinetics, and thermodynamics of fructose and glucose dehydration have been the subject of a wide number of experimental[10–17] and theoretical studies.[18–26] The two main reaction pathways proposed in solution start from the cyclic and open forms of the sugars. In particular the acyclic mechanism involves the formation of a 1,2-enediol postulated to be the intermediate in the glucose-fructose isomerization,[11] considered by many authors the key step of glucose conversion into 5-HMF in acidic aqueous solutions. This mechanism seems to account for the observation that 5-HMF is formed in higher yields from fructose.

However, the formation of cyclic intermediates from fructose dehydration in D_2O and the absence of deuterium incorporation in 5-HMF seems to suggest that the dehydration reaction in solution starts from the cyclic fructofuranose form.[27] Understanding sugar

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degradation pathways on a molecular level is necessary to increase selectivity, reduce degradation by-product yields, and optimize catalytic strategies, fundamental knowledge for the development of a sustainable renewable industry.

In the gas phase, computational studies can provide detailed information on the mechanism and the energetics of intramolecular conversion of protonated sugars in the gas phase. Based on protonation free energies of the various hydroxyl groups of the sugar, Assary et al.[19,20] predicts the relative reactivity of fructopyranose and fructo-furanose. As expected, fructo-furanose is more reactive toward the acid-catalyzed decomposition, predominantly due to the presence of the tertiary OH group having a higher proton affinity. The enthalpy surface for the acid-catalyzed fructose conversion to 5-HMF shows barriers for the dehydration in the range of 10—50 kcal mol^{-1} and the overall reaction is very exothermic. By comparing the results of more than 100 reaction pathways and over 400 different reaction intermediates, Yang et al. theoretically suggest the main acid-catalyzed dehydration channel for α-D-glucopyranose and β-D-fructofuranose.[26] A regioselectivity of the initial protonation site was observed, with the hydroxyl group at the anomeric carbon for both the sugars (O1H for glucose and O2H for fructose) markedly preferred over the other protonation sites due to the formation of a dehydrated carbocation stabilized by its oxonium resonance structure. According to these calculations, D-fructose protonation on the O2H initiates a facile reaction sequence leading to 5-HMF.

Experimental gas-phase studies on monosaccharide dehydration are almost non existent despite they can play a key role indicating the more likely reaction route occurring in the absence of solvent molecules, a benchmark for computational studies towards the understanding of solution mechanisms.

Recently, we reported gas-phase studies on the mechanism of D-xylose and D-glucose dehydration performed by a mass spectrometric approach.[28,29] The experimental results clearly demonstrate that D-xylose and D-glucose protonation occurs preferentially at the O1H group, and the ionic intermediates arising from the loss of the water molecules are characterized by a cyclic five-membered structure.

In this paper are shown the results of a gas-phase study on the fructose dehydration reaction performed by Electrospray Triple Quadrupole (ESI/TQ) mass spectrometry. As in our previous studies, this approach allowed us to identify and structurally characterize the ionic gaseous intermediates and products and to obtain mechanistic information on fructose dehydration reaction.

For comparison purposes, the experimental gas-phase data were compared with those relative to protonated D-glucose in order to demonstrate whether the two mechanisms follow a common reaction pathway.

2. Experimental

2.1. Materials

D-Fructose, D-Glucose, methanol (LC/MS grade), D$_2$O (99% grade), and all other chemicals were purchased from Sigma—Aldrich Ltd.

2.2. Mass spectrometry

Full-scan electrospray mass spectra were acquired using a Quattro Micro (Micromass, Manchester, UK) triple-stage quadrupole instrument operating in the positive-ion mode. Nitrogen was used as nebulisation and desolvation gas at flow rates of 40 and 300 L h^{-1}, respectively. Source and desolvation temperatures were set at 120 °C and 300 °C. Applied potential on the electrospray

capillary and on the cone ranged from 2.6 to 3.2 kV and from 15 to 50 V, respectively, and were optimized for each molecule.

All displayed mass spectra represent the average of 50 scans of 1 s duration and were performed by direct infusion of 10^{-3} M solutions of purified compounds in methanol/water (0.1% CH$_3$COONH$_4$) (1:1, V/V) with a 10 μL/min flow rate. H/D exchange experiments were performed by dissolving D-fructose in D$_2$O for about one hour and cleaning the ESI source with D$_2$O before recording mass spectra. Data acquisition and processing were carried out using the software MassLynx™ version 4.0 supplied with the instrument.

Collisionally activated dissociation (CAD) and energy-resolved (ERMS) mass spectra were acquired using a TSQ700 triple-stage quadrupole mass spectrometer from ThermoFinnigan Ltd. by introducing Ar as the target gas at pressures of about 0.1—0.5 mTorr and at collision energies ranging from 0 to 40 eV (laboratory frame). An upper limit of 3 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 (lab) are converted to center-of-mass (CM) energies by using the formula $E_{CM}=EL_{AB}$ m/(m+M), where m is the mass of neutral reactant and M is the mass of the ionic reagent. Experimental cross sections, σ_{tot}, were determined by the relation $I_R/It_{tot}=exp^{(\sigma nl)}$ where I_R is the intensity of the transmitted ion beam, I_{tot} is the total ion intensities, n is the number density of the neutral gas (3.5 10^{13} molecule/cm^3) and l is the effective gas cell length (12 cm). Individual product cross sections, σ_p, were calculated by $\sigma_p=\sigma_{tot}(I_p/Ip_{tot})$ where I_p represents the intensity of the product ion and I_{ptot} the total product ion intensities.

3. Results and discussion

3.1. D-Fructose protonation: the first dehydration step

In Fig. 1 the ESI mass spectrum of a CH$_3$OH/H$_2$O (1% CH$_3$COONH$_4$) (1:1) solution of D-fructose is reported. As previously described, the addition of ammonium acetate allows mild protonating conditions.[28]
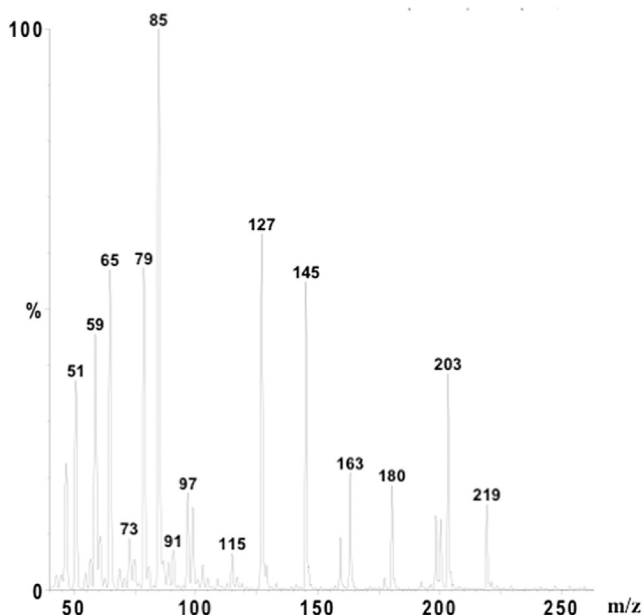

Fig. 1. ESI mass spectrum of a CH$_3$OH/H$_2$O (1% CH$_3$COONH$_4$) (1:1) solution of D-fructose.