



Insights into the isomerization of xylose to xylulose and lyxose by a Lewis acid catalyst



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ABSTRACT

We present electronic structure calculations on the isomerization and epimerization of xylose to xylulose and lyxose, respectively, by a zeolite Sn–BEA model at the MP2 and B3LYP theory levels. Benchmarking calculations at the CCSD(T) theory level are also presented. We show that lyxose is formed from a stable intermediate in the xylose–xylulose isomerization pathway. In agreement with experimental observations, we predict that xylulose is thermodynamically and kinetically favoured over lyxose. We find that the slowest step for both reactions involves hydrogen transfer from the C2 to the C1 carbon of the carbohydrate molecule and we characterize it using natural population analysis. We conclude that the hydrogen transfer does not take place as a hydride ion but rather as concerted neutral hydrogen–electron transfer that involves different centres for the hydrogen and electron transfer.

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1. Introduction

Xylose is the most prevalent pentose produced by acid hydrolysis of the hemicellulose fraction (~25–35% on a dry basis) of the lignocellulosic biomass. An approach to utilize xylose requires its thermochemical conversion to furfural, which is an industrial chemical with an annual production of more than 400,000 tons.¹ Furfural is envisaged as a platform chemical for the biofuel and biochemical industries. Furfural derivatives such as 2-methyl furan and 2-methyltetrahydrofuran have been reported as potential biofuel components.¹ Other furfural derivatives such as tetrahydrofuran (THF) are used as industrial solvents while furfuryl alcohol can be converted to levulinic acid,^{2,3} which has been marked as one of the twelve top value-added chemicals from biomass.⁴

Furfural is produced by the cyclodehydration of xylose using a homogeneous Brønsted acid catalyst in aqueous media and at high temperatures (>150°C).⁵ The current furfural processes are not only environmentally harsh but also quite inefficient, reaching only ~50% of the theoretical furfural yield. Recently, Choudhary et al. demonstrated xylose conversion to furfural in aqueous media at much lower temperatures through a sequence of cascade reactions involving heterogeneous Lewis acid-catalysed isomerization of xylose to xylulose and homogeneous Brønsted acid-catalysed dehydration of xylulose to furfural;⁶ the zeolite Sn–BEA was used

for the former and HCl or Amberlyst-15, a Brønsted acid, for the latter. It was also shown that Sn–BEA isomerizes xylose to xylulose and to the epimer lyxose; at 60% xylose conversion (in 15 min, at 100°C), the authors reported 27% yield for xylulose and 11% for lyxose. Furthermore, we recently compared the dehydration of various pentoses to furfural, using HCl in aqueous media, and the maximum furfural yields from xylulose, lyxose and xylose were, respectively, 65.7%, 28.9% and 28.8% at 418 K.⁷ Clearly, isomerization to xylulose is beneficial for furfural production; however, isomerization to lyxose does not add to the furfural yield and would probably open channels for side reactions.

The zeolite BEA with framework Sn Lewis acid centres has recently been demonstrated to isomerize others sugars as well: glucose to fructose and mannose, and erythrose to erythrulose.^{8–11} Prior to this recent discovery, Sn–BEA had successfully been employed as a catalyst in a number of reactions, including the Meerwein–Ponndorf–Verley (MPV) reduction of carbonyl compounds, the production of lactate derivatives from monosaccharides in methanol, and the conversion of trioses to alkyl lactates in the presence of alcohol.^{12–16} Using ¹H and ¹³C NMR spectroscopy of isotopically labelled glucose, Davis and co-workers revealed the mechanism of the Lewis acid-catalysed isomerization and showed that it is analogous to that of metalloenzymes such as xylose isomerase,^{9,17} a free energy profile was also calculated at the MP2 theory level and within the harmonic approximation for the thermal corrections,^{2,11} although the epimerization mechanism and its energetics were not explored in that work.

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The purpose of the present article is twofold: First, to explain how xylose is produced in the course of the xylose-xylulose isomerization by Sn-BEA, provide the mechanism and energetics of this epimerization and thus rationalize the experimental data of Choudhary et al.¹⁰ For completeness, we also provide the energetics of the xylose-xylulose isomerization. The mechanism of the latter is found to be the same as that reported by Deval et al. in the glucose-fructose case;¹⁷ the authors did not, however, investigate the mechanism and energetics of the epimerization (to mannose). Second, and given that Sn-BEA appears to be a broadly functioning catalyst for aldose-ketose isomerization in aqueous media, in the present article we also take for the first time a closer look at the rate-limiting step, namely the hydrogen migration from C2 to C1. In a mechanism which resembles that of isomerases containing two metal atoms at the catalytic centre (e.g., xylose isomerase), the hydrogen migration from C2 to C1 has been referred to as a hydride transfer.^{9,18–22} Theoretically, for an overall hydride transfer there are four pathways that can lead to the same result, albeit with different energy requirements. They are: (i) the one-step, strict hydride-ion transfer, with two electrons, all along the reaction coordinate. (ii) A H-atom transfer followed by electron transfer ($H + e^-$). (iii) Electron transfer followed by a H-atom transfer ($e^- + H$, the reverse of (ii)). (iv) Sequential electron-proton-electron transfer ($e^- + H^+ + e^-$). A ubiquitous elementary step, playing an important role in many chemical and biochemical processes and often being rate-limiting, the hydride transfer has been studied over the years for various classes of reactions in order to identify which of the four possible 'modes' it follows and thus to appropriately model the kinetic constant and to interpret kinetic data (e.g., kinetic isotope effects).²³ Using the case of xylose, we investigate the particular mechanism for hydride transfer in Lewis acid-catalysed aldose-ketose isomerization.

2. Methods

2.1. Computational

The free energy profiles reported in this article are based on gas-phase electronic structure and frequency calculations of the singlet ground state at the B3LYP/6-31+G(d,p) and MP2/6-31+G(d,p) theory levels; for Sn we used the LANL2DZ effective core potential basis. Full geometry optimizations were performed for all the structures reported herein, at both the B3LYP and MP2 theory levels. We should note that we did not identify any significant differences between B3LYP-optimized and MP2-optimized structures. Transition states were obtained using the Berny algorithm and confirmed to be first-order saddle points by frequency calculations; initial guess geometries for the transition states were obtained from relaxed scans along appropriate internal degrees of freedom using low-level theories (e.g., RHF/4-31G* or B3LYP/4-31G* proved quite helpful in this respect). The transition state optimization calculations were followed by IRC (Intrinsic Reaction Coordinate) calculations. B3LYP optimization and frequency calculations required ca. 8 CPU hours. MP2 optimization and frequency calculations required ca. 300 CPU hours, when they were started with B3LYP-optimized structures. Benchmarking calculations for transition state energy barriers were also performed, at the CCSD(T)/6-31+G(d,p)//MP2/6-31+G(d,p) theory level. Each CCSD(T) single point energy calculation required ca. 3300 CPU hours. All calculations were performed with the Gaussian 09 software package.²⁴

Following Boronat et al., who have shown that the Sn-BEA active sites in the MPV reaction are partially hydrolysed Sn–O–Si bonds, we have modelled the catalyst active site with a $(H_3Si-O)_3Sn-OH$ cluster of tetrahedral geometry.^{13,18}

2.2. Experimental

The Sn-BEA zeolite was synthesized in fluoride medium, following the procedure reported in the literature.²⁵ The kinetic experiments were carried out using 10 ml glass vials, which were heated in a temperature-controlled oil bath, placed on a digital stirring hotplate. Reaction samples were analysed using high performance liquid chromatography (HPLC), using a Waters Alliance system (e2695) equipped with refractive index detector. Sugars were detected with a Biorad HPX87C (300 × 7.8) column. Further details on experimental procedure and the synthesis of Sn-BEA have also been reported in an earlier publication.⁶

3. Results and discussion

3.1. Mechanism and energetics

The isomerization reaction starts with the opening of the sugar ring. Formally, this involves H transfer from the OH group of the anomeric carbon to the ring oxygen. In the presence of the $(H_3Si-O)_3Sn-OH$ cluster, the H transfer is in fact a proton transfer that is mediated by the OH group on Sn—in essence, the Sn–OH moiety behaves as a base catalyst. We have calculated the opening of the β -furanosic and β -pyranosic forms of xylose; pyranose is the predominant form, by being present at ca. 65% at equilibrium at 20°C in aqueous solution.^{26,27} According to our calculations, in neither case is the opening of the ring the rate-limiting step of the isomerization reaction. In the case of the furanose, the proton abstraction from the anomeric OH has an MP2 free energy barrier of 7.7 kcal/mol; the proton back-donation (to the ring oxygen) is slower, requiring 16.7 kcal/mol of activation. In the case of the pyranose, however, the initial proton abstraction is slower than the subsequent proton back-donation, with MP2 free energy barriers of 16.9 and 10.4 kcal/mol, respectively. We attribute these differences to the different degrees of hydrogen bonding of these molecules, either intra-molecularly or inter-molecularly with the active site cluster. We should note that the free energies above are with respect to the reactants interaction complex (and not the infinitely separated reactants). Transition state structures for the ring-opening are shown in Figure 1.

Given that the isomerization reaction proceeds through the acyclic form of the sugar molecule, in the following we use the acyclic xylose–catalyst cluster bound state as an energy reference. Our conclusions on the relative kinetics between the isomerization and epimerization reactions are not dependent on the energy reference.

For the isomerization and epimerization, following the ring opening, B3LYP predicted an increase in the free energy ($\Delta G > 0$) whereas MP2 predicted $\Delta G < 0$. The mechanism is shown in Scheme 1. The relevant free energy profiles, at 298 K, are given in Figures 2 and 3. The structures of intermediates and transition states are shown in Figures 4 and 5.

The interaction complex between the acyclic xylose and the active site is through a hydrogen bond between the OH group at the C2 carbon and the OH group on Sn (Fig. 4, **grnd**). The carbonyl group of the acyclic sugar interacts with Sn and according to our calculations, upon binding, the carbonyl stretching vibration red-shifts from 1780 to 1754 cm^{-1} (unscaled, frequencies).

Formally, the isomerization entails the transfer of two H atoms: one from O2 to O1 and another from C2 to C1. The catalysed reaction requires activation by a proton transfer from O2 to the Sn–OH and water formation; a formal Sn–O2 bond ensues while the carbonyl stretching vibration red-shifts further to 1714 cm^{-1} . This proton transfer activates the subsequent, and slower, hydride transfer from C2 to C1 by way of a transition state **ts2** in which

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