Journal of Catalysis 295 (2012) 122–132

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Mechanism of Brønsted acid-catalyzed conversion of carbohydrates

Gang Yang, Evgeny A. Pidko *, Emiel J.M. Hensen

Inorganic Materials Chemistry Group, Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands

ARTICLE INFO

Article history:
Received 24 April 2012
Revised 16 July 2012
Accepted 3 August 2012
Available online 3 September 2012

Keywords:
Biomass
Reaction mechanism
Acid catalysis
DFT calculations
Hexose
5-Hydroxymethylfurfural
Levulinic acid

ABSTRACT

A comprehensive DFT study of acid-catalyzed glucose and fructose reactions in water covering more than 100 potential reaction paths is performed with the aim to identify the main reaction channels for obtaining such desirable biorefinery platform products as 5-hydroxymethylfurfural (HMF) and levulinic acid (LA). Characteristic for fructose dehydration by Brønsted acids is the preferred protonation of the O2H group at the anomeric carbon atom, which initiates a sequence of facile reactions toward HMF. Further rehydration to LA is more difficult and competes with condensation reactions leading to humins. A very different result is obtained when glucose is the reactant. The preferred protonation site is the O1H hydroxyl group. The associated reaction paths do not lead to the formation of HMF or LA but result in humin precursors and reversion products. Protonation of other sites occurs at a much lower rate. Nevertheless, when glucose is activated at these less reactive sites, it can lead to LA via a reaction mechanism that does not involve the intermediate formation of fructose and HMF. This direct mechanism is argued to be preferred over the conventional sequential conversion scheme. It is concluded that the differences in the reactivity of glucose and fructose in acidic aqueous solutions are dominated by the regioselectivity of the initial protonation step.

1. Introduction

The depletion of fossil fuel reserves and growing concerns about negative climate effects as a result of their combustion are the main drivers to explore alternative renewable feedstocks for the large-scale production of fuels and chemicals [1,2]. Lignocellulosic biomass made up of cellulose, hemicellulose, and lignin is the most abundant renewable source of carbon for this purpose. Hemicellulose and cellulose are biopolymers that can be decomposed in their constituent carbohydrates by conventional acid hydrolysis [3] or by alternative methods such as dissolution and depolymerization in ionic liquid solvents [4]. One of the most attractive routes toward carbohydrate valorization in future biorefineries is their conversion to platform molecules such as 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) (Scheme 1), which can serve as versatile building blocks for the production of various value-added chemicals ranging from pharmaceuticals to fuels [1,2,5,6]. The selective conversion of sugars and oligosaccharides to these value-added products represents currently one of the key challenges in biorefining processes.

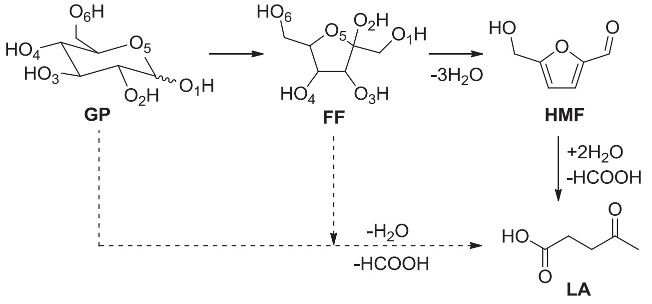
HMF is the product obtained by removal of three water molecules from hexose sugars. It is easily obtained in good yields from fructose using a wide variety of homogeneous and heterogeneous catalysts [7–10]. In acidic aqueous solutions, HMF will undergo further transformation into LA and formic acid (FA) via rehydration (Scheme 1). The acid-catalyzed route from sugars to LA has recently been proposed as one of the key steps in future biorefineries [11,12]. Compared to fructose, the selective conversion of glucose, the most abundant monosaccharide in biomass is much more difficult. Typically, the use of Brønsted and Lewis acid catalysts results in sluggish reaction and low selectivity. In this case, sugar dehydration is usually accompanied by undesired cross-polymerization reactions leading to the formation of insoluble humins.

Brønsted acid-catalyzed conversion of carbohydrates in aqueous solutions proceeds through a complex network of elementary steps such as protonation, deprotonation, isomerization, dehydration, hydration, and intramolecular hydrogen transfer. These reactions involve a large number of intermediates, which are prone to side-reactions. The mechanism, kinetics, and thermodynamics of sugar conversion have been the subject of many experimental and theoretical studies with the main focus on fructose dehydration to HMF [13–26]. The two main pathways, which have been studied, involve the closed and open forms of fructose. Shaw et al. proposed that fructose dehydration proceeds with the preservation of the 5-membered ring structure [13]. An alternative acyclic mechanism involves the formation of the 1,2-enediol intermediate [27]. As this 1,2-enediol is the key intermediate in the isomerization of glucose to fructose, such a mechanism has also been argued to be relevant for the conversion of glucose in acidic aqueous solutions [14].

---

* Corresponding author.
E-mail address: e.a.pidko@tue.nl (E.A. Pidko).

0021-9517/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcat.2012.08.002



Scheme 1. Glucose conversion to levulinic acid.

It is extremely difficult to derive a complete and consistent mechanistic picture of catalytic sugar transformations based on experimental data because of the many reaction routes involving intermediates with relatively short life-time. Instead, quantum chemical calculations can provide detailed information about the energetics of sugar conversion chemistry [28]. The cyclic mechanism of Brønsted acid-catalyzed fructose dehydration to HMF has recently been confirmed by quantum chemical calculations [17–19]. The activation of fructose was assumed to proceed by protonation of the O2H hydroxyl group at the anomeric C2 site followed by dehydration to HMF.

Glucose dehydration initiated by protonation of the C2—O2H site has been investigated by means of ab initio MD simulations [25]. A direct reaction path to HMF has been identified that does not involve the initial isomerization to fructose. The protonation of the C2—O2H site of glucose followed by water removal results in the rearrangement of the pyranose ring involving the formation of a C2—O5 bond within a 5-membered ring structure. A competing condensation to reversion products was proposed to originate from a more favorable activation of the C1—O1H group. An alternative proposal was made in a combined experimental and computational study by Jadhav et al. [29]. It was argued that glucose dehydration to HMF predominantly proceeds via the intermediate formation of 3-deoxyglucosane with only a fraction of the product formed via the pathway through fructose. Nevertheless, only low HMF yields are obtained from glucose in acidic aqueous solution [21]. In contrast to fructose conversion, convincing evidence for the pivotal role of HMF as the reaction intermediate to LA is lacking for glucose.

A limitation of the computational studies about sugar conversion mechanism reported so far is that no systematic comparison of the possible reaction routes starting from glucose has been made. Therefore, the aim of the present work is to provide an as complete as possible overview of the conversion routes of α-D-glucopyranose catalyzed by hydrated protons as a model for mineral acids toward HMF and LA and precursors of humins. We start our analysis by comparing the protonation of the oxygen-containing groups in glucose and fructose. Fructose is included because it is a potential reaction intermediate in glucose conversion. Our main goals are (i) to construct potential energy diagrams for the conversion of hexose sugars to HMF, LA and humin precursors, (ii) on their basis to identify the most favorable reaction routes, and (iii) to explore possible alternative routes, which may guide further experimental research. The results will be discussed against experimental results for acid-catalyzed conversion of glucose and fructose.

2. Computational details

Quantum chemical calculations were performed with Density Functional Theory (DFT) using the B3LYP [30] hybrid exchange-correlation functional in combination with the full-electron 6-311+G(d,p) basis set. Full geometry optimizations and saddle-point searches were performed using the Gaussian 09 program [31]. No symmetry restrictions were used in the calculations. To justify the selected computational methodology, reaction energies for selected paths were also calculated by the G4MP2 composite method [32]. The results of this higher-level ab initio method deviated by not more than 15 kJ mol^{-1} from those obtained from DFT calculations (see Section S1 of Supporting information).

The nature of the stationary points was evaluated from the harmonic modes. No imaginary frequencies were found for the optimized structures corresponding to local minima on the potential energy surfaces. Transition states corresponding to intramolecular rearrangements of different reaction intermediates showed a single imaginary frequency corresponding to the eigenvector along the reaction path. The assignment of the transition state to a particular reaction path was tested by perturbing the structure along the reaction path eigenvector in both directions of products and reagents with subsequent geometry optimization. Zero point, finite temperature, and entropic energy contributions were computed using the results of the normal-mode analysis within the ideal gas approximation at a pressure of 1 atm and a temperature of 298 K. The reaction (ΔG) and activation free energies ($\Delta G^{\#}$) were calculated for these reaction conditions.

The selection of conformers of α-D-glucopyranose (α-GP), β-D-fructofuranose (β-FF), and levulinic acid was based on results of previous studies [18,19,33–40] and was additionally validated by analysis of their stability by the methods employed in this study. A thorough thermodynamic analysis of different conversion paths was performed only for these anomers of glucose and fructose. To investigate the effect of the orientation of O1H group (Scheme 1) at the anomeric carbon of glucose on the stereospecificity of the initial protonation and dehydration steps, the respective elementary reactions were also considered for β-D-glucopyranose (β-GP). For HMF, a complete conformational analysis was carried out to determine the global energy minimum configuration. Reaction paths were constructed by directing the conversion of glucose toward the formation of levulinic acid via different routes. The initial structures of reaction intermediates were generated by introducing or removing H^+ or H_2O species in or from the desired site of the previous intermediate structure. Because intramolecular hydrogen transfer reactions do not generally show correlation between the reaction and activation energies, such elementary steps were treated explicitly by calculating the associated transition states. The Brønsted acid was modeled as Zundel complex $H_5O_2^+$ as an approximation for a proton in water. Accordingly, the protonation (ΔG^{prot}) and deprotonation energies (ΔG^{deprot}) are defined as

$$\Delta G^{prot} = G^o(A^+) + G^o(H_4O_2) - G^o(A) - G^o(H_5O_2^+) \quad (1)$$

$$\Delta G^{prot} = G^o(A) + G^o(H_5O_2^+) - G^o(A^+) - G^o(H_4O_2) \quad (2)$$

where A^+ is the protonated form of species A and G^o stands for the DFT-computed formation free energy.

To account for solvent effects, test calculations on selected elementary sugar conversion steps have been performed using three different methods. The polarizable continuum model was used to evaluate the bulk solvent effect employing the reaction field with the integral equation formalism model (PCM) [41] and that within the conductor reaction field (COSMO) approach [42]. Standard parameters for water solvent as implemented in Gaussian 09 were used. To evaluate the effect of hydrogen bonding with the solvent H_2O molecules on the computed reaction paths, the two-layer ONIOM(B3LYP/6-311+G(d,p):UFF) methodology was employed [43]. In this case, the structures corresponding to the gas-phase reaction intermediates were selected as the high-level region and the envi-