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Direct cleavage of sorbitol from oligosaccharides via a sequential hydrogenation-hydrolysis pathway

Leila Negahdar[a], Peter J.C. Hausoul[a], Stefan Palkovits[b], Regina Palkovits[a,*]

[a] Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Aachen, Germany
[b] Center for Molecular Transformations, RWTH Aachen University, Aachen, Germany

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ABSTRACT

The production of sorbitol from polysaccharides is widely believed to proceed via hydrolysis to glucose and subsequent hydrogenation. Nevertheless, our previous study on the hydrolytic hydrogenation of cellobiose confirmed simultaneous hydrolysis and hydrogenation with a higher kinetic selectivity of hydrogenation over hydrolysis. Herein, kinetics of hydrogenolysis of trisaccharides with α-1,4 and β-1,4 glycosidic linkages were studied using Ru/C in combination with a molecular acid as catalyst system. Kinetic analysis emphasises a fast hydrogenation of the reducing end of trisaccharides followed by a facilitated cleavage of the terminal sorbitol unit. Considering the obtained reaction rate constants, hydrogenation compared to hydrolysis proceeds up to 24 and 15 times faster for maltotriose and cellotriose, respectively. Additionally, superior reaction rate constants and decreased activation energies for hydrolytic cleavage of sorbitol can be observed. Hence, a sequential hydrogenation-hydrolysis pathway clearly contributes to sorbitol formation based on oligosaccharides.

1. Introduction

Increasing concerns about future energy supply and the environmental impact of fossil fuels have enforced the society to find renewable resource alternatives. Biomass, both renewable and environmentally friendly, is considered to be one of the best alternatives [1,2]. Lignocellulose and starch-based materials are the most abundant source of biomass. Recently, the production of biofuels and value-added chemicals from cellulose and starch has gained much attraction [3–5]. Special attention has been devoted to the conversion of polysaccharides into sorbitol which has been proposed as potential platform chemical for the production of fuels, monomers for polymer industries and as feedstock for renewable hydrogen production [4,6,7]. Additionally, sorbitol and its secondary products are already used today, e.g. as sweetening agent, for the production of surfactants and in pharmaceutical industry [8].

Sorbitol can be produced selectively, e.g. via hydrogenation of a hydrolysed starch solution in the presence of catalysts such as Raney nickel or Ru/C [9]. Also a direct transformation of cellulose into sorbitol has been demonstrated, e.g. cellulose can be converted into sorbitol in the presence of molecular acids such as H_2SO_4, HCl or heteropoly acids together with supported metal catalysts (Pt, Pd and Ru) [10–15]. Combined with a mechanocatalytic prehydrolysis of cellulose to cellooligomers, Schüth and co-workers [16] achieved up to 94% yield of sorbitol based on cellulose.

Despite numerous studies on production methods, a fundamental understanding of the reaction and kinetics of a conversion of polysaccharides to sorbitol is hardly available, mostly because of the complex molecular structure of polysaccharides. It is generally believed that the conversion of polysaccharide to sorbitol passes through hydrolysis to monosaccharides consecutively followed by hydrogenation to sorbitol [17–19].

In contrast, our pervious investigation and studies by the groups of Wang et al. and Makkee et al. on the hydrolytic hydrogenation of cellobiose as model molecule of cellulose confirmed a direct hydrogenation to cellobitol (3-β-D-glucopyranosyl-D-glucitol) followed by hydrolysis as alternative reaction pathway [20,21]. Our kinetic analysis revealed that this reaction pathway can contribute significantly to sorbitol formation [22]. Consequently, the question arises whether a selective formation of sorbitol via hydrogenation followed by hydrolysis should also be considered for oligo- and polysaccharides, respectively. Therefore, the study is extended to include trisaccharides which sufficiently resemble polysaccharides and still have a relatively simple structure. The trisaccharides, cellotriose (β-linked D-glucose) based on cellulose and maltotriose (α-linked D-glucose) based on starch were chosen for this study (Fig. 1).

* Corresponding author. Tel.: +49 241 8026497.
E-mail address: palkovits@itmc.rwth-aachen.de (R. Palkovits).

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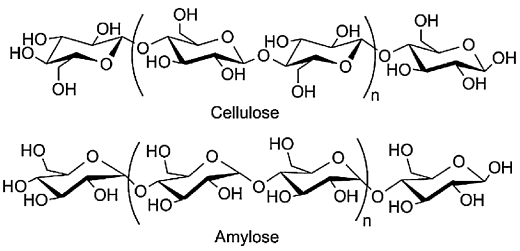

Fig. 1. Structure of cellulose and amylose.

The aim is to understand the role of hydrogenation-hydrolysis sequences within the overall reaction network. In the present study, a heteropoly acid (silicotungstic acid, $H_4[W_{12}SiO_{40}]$) combined with a supported ruthenium catalyst (5 wt% Ru/C) have been used as catalytic system due to high selectivity for sorbitol production [10,13,14,22]. A systematic kinetic analysis has been carried out providing a quantitative interpretation of the reaction pathways paving the way for a novel view on the transformation of oligosaccharides and potentially polysaccharides into sorbitol.

2. Materials and methods

Maltotriose, maltotriitol, maltose, maltitol, glucose, sorbitol, the heteropoly acid (HPA, silicotungstic acid) and 5 wt% Ru/C were purchased from Aldrich. Cellotriose and cellotriitol were supplied by Megazyme, and cellobiose was purchased from Alfa Aesar. All the above-mentioned chemicals were of analytical grade and used without further purification. Cellobitol was self-synthesized with a purity of 99% and characterized by ^{13}C NMR spectroscopy. All experiments were performed three times in a batch-type high-pressure autoclave reactor. Typically, trisaccharides (2 mmol), Ru/C (0.1 g) and heteropoly acid (0.2 g) were added into a Teflon-lined stainless steel reactor precharged with H_2O (20 cm^3). The reactor was flushed several times with N_2 and H_2 at room temperature. The reactor was pressurized with H_2 and then preheated to the defined temperature. The reaction was operated at a pressure of 4 MPa, a temperature range of 393–433 K and a stirring speed of 800 rpm. Time zero was set at the beginning of the isothermal reaction stage. The reactor was equipped with a sampling valve and the progress of the reaction was monitored by periodically taking sample from the autoclave. Samples were filtered through a 25 μm nylon filter prior to analysis. Analyses of products were performed using an HPLC system consisting of a ligand exchange column (Shodex sugar SZ5532, 6 mm × 150 mm) and an RI detector. The eluent was an aqueous solution of acetonitrile and water at a flow rate of 1 mL min^{-1}. The column was operated at 323 K and sample analysis was completed within 50 min. The samples were dissolved in acetonitrile (1:1) prior to injection into the HPLC system. The concentration of each compound in the product mixture was determined using calibration curves of pure compounds in standard solutions.

3. Results and discussion

3.1. Reaction network analysis

Our analysis suggests that in the presence of a supported metal catalyst (Ru/C) and a molecular acid (HPA, silicotungstic acid), the catalytic conversion of trisaccharides proceeds via a network of parallel and consecutive reactions (Scheme 1). The hydrolysis of trisaccharides (cellotriose or maltotriose) to the corresponding disaccharides (cellobiose or maltose) and glucose as well as the hydrogenation to the reduced trisaccharides (cellotriitol or maltotriitol) can be observed.

The hydrolysis of reduced trisaccharides yields either a disaccharide and sorbitol or a reduced disaccharide (cellobitol or maltitol) and glucose. In subsequent transformations, the disaccharide can be either hydrolysed to glucose or hydrogenated to the reduced form which can be further hydrolysed to glucose and sorbitol. It should be noted that trisaccharides have two different glycosidic bonds that can be hydrolysed [23,24]. Here, the cleavage of these two glycosidic bonds is not distinguished.

Fig. 2 shows the time evolution of product formation at different reaction temperatures for the conversion of cellotriose to sorbitol. The product distribution at different reaction temperatures illustrates a significant contribution of a prior hydrogenation of the substrate to the reduced form. This effect is favoured at lower reaction temperatures.

Cellotriitol, the hydrogenation product of cellotriose, is the major product with a maximum yield of 69% at 393 K (Fig. 2a). As the reaction temperature increases, the yield of cellotriitol decreases. At the same time, the yield of the target product sorbitol increases reaching a maximum of 74% at 443 K (Fig. 2c). Cellobiose presents a potential reaction intermediate and is simultaneously converted via two catalytic pathways: (1) hydrogenation to cellobitol and (2) hydrolysis to glucose. At lower reaction temperatures, a higher cellobitol yield can be observed which again points out the preferential hydrogenation of cellobiose over its hydrolysis. For all reactions, only small amounts of glucose were observed. We relate this to the direct formation of sorbitol through hydrolysis of cellotriitol together with a fast hydrogenation of glucose to sorbitol [25].

Under the applied reaction condition, no side reactions based on glucose, e.g. via dehydration to 5-hydroxymethylfurfural or levulinic acid, were observed and degradation products from sorbitol including sorbitan and isosorbide were negligible. In the described temperature range, carbon balances could be closed with mean carbon balances of above 95% based on threefold experiments and no humin formation was observed. Overall, these findings suggest that the hydrogenation of substrates and intermediates proceeds faster compared to hydrolysis. Unlike a simple hydrolysis to glucose, trisaccharides are mainly converted via hydrogenation-hydrolysis sequences.

3.2. Kinetic assessment of reaction sequences

A kinetic analysis of the reaction network has been carried out to quantify the relative contribution of the different reaction pathways. Both hydrolysis and hydrogenation reactions are assumed to follow pseudo-first-order kinetics [22,26]. The concentrations of each compound as a function of time as well as the curve fittings are summarized in the supplementary information (ESI). Additionally, reference experiments of the individual reactions have been carried out confirming the major role of the individual catalyst compounds in the overall reaction network (ESI, Fig. S2). Indeed, over Ru/C maltotriitol is the major product, while in the presence of silicotungstic acid maltose and glucose form. Kinetic rate constants are solved using the least-square optimization algorithm relative to the experimental data. Temperature dependency of the rate constants are taken into account using Arrhenius equation within the range of 373–433 K.

Cellotriose and maltotriose exhibit a comparable behaviour. In the following, cellotriose is discussed comprehensively. From Scheme 2 and for cellotriose, the hydrolysis reactions include hydrolysis of cellotriose (k_1), cellotriitol (k_3, k_4), cellobiose (k_6) and cellobitol (k_7). The hydrogenation reactions comprehend the hydrogenation of cellotriose (k_2), cellobiose (k_5) and glucose (k_8). As mentioned previously, for hydrolysis of cellotriose, the cleavage of bonds is not distinguished. Therefore, the rate constant is