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Mechanistic Studies of the Base-Catalyzed Isomerization of Aldoses to Ketoses

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PURPOSE OF THE ABSTRACT

Ketoses play a pivotal role in the food as well as the pharmaceutical industry, and their demand exceeds their natural abundance. Thus, ketoses are synthesized from abundant aldoses via isomerization in an atom-efficient method. On an industrial scale, the isomerization is facilitated in a biocatalytic process.[1-3] However, due to various drawbacks of biocatalysts, such as low stability and high price, suitable chemo-catalysts potentially present a feasible alternative. Moreover, transformation of aldoses into ketoses exhibits an important step in the valorization of abundant polysaccharide feedstocks to renewable platform chemicals, further highlighting the demand for a suitable chemo catalyst. Up to date, many known chemo-catalysts suffer from low yield, monosaccharide decomposition or the need of complexing agents.[1, 3] Detailed knowledge of the mechanism and the kinetics may facilitate design of a suitable catalyst. Yet, key parts of the mechanism are not fully understood despite being subjected to intensive research.[3-4] Thus, we aim to provide more insight into the reaction mechanism and the kinetics of the isomerization in the presence of bases. In our work we focus the isomerization of D-glucose into D-fructose in the presence of aq. NaOH as an exemplary system. We employ a combination of kinetic studies and operando UV/Vis and NMR spectroscopy.

In the kinetic studies D-mannose and D-allulose were verified as co-products of the isomerization. We investigated the isomerization staring from D-glucose, D-fructose and D-mannose. Under the applied reaction conditions (T = 50 ? 90 °C, c(Hexose) = 2 ? 10 wt.%, pH = 9.5 ? 11.5), we observed no significant influence of temperature, substrate concentration of pH value on selectivity of the reaction. The maximum yield of D-fructose from D-glucose was 28%. Most importantly, we uncovered a salt effect, i.e. acceleration of the reaction rate in the presence of neutral salts, such as sodium chloride or sodium sulfate,. The salt effect was observed in the presence of both soluble and solid basic catalysts. Most probably, the salt effect is caused by variation of activity coefficients in the presence of electrolytes. This results, for example, in a dependence of ionization constants of saccharides as well as water autoprotolysis constant Kw on the presence of salts.[5] These equilibrium constants were determined potentiometrically.

As previously described,[6] the isomerization occurs via enediol anion intermediates, showing an absorbance at 312 nm, which is in steady state after an induction time. We observed the rate of enediol formation to be in the following order: D-allulose > D-fructose > D-glucose > D-mannose. In order to verify enediol species as an intermediate and observe their formation, we synthesized partially deuterated D-glucose and D-fructose to perform operando 1H NMR-experiments.

FIGURES

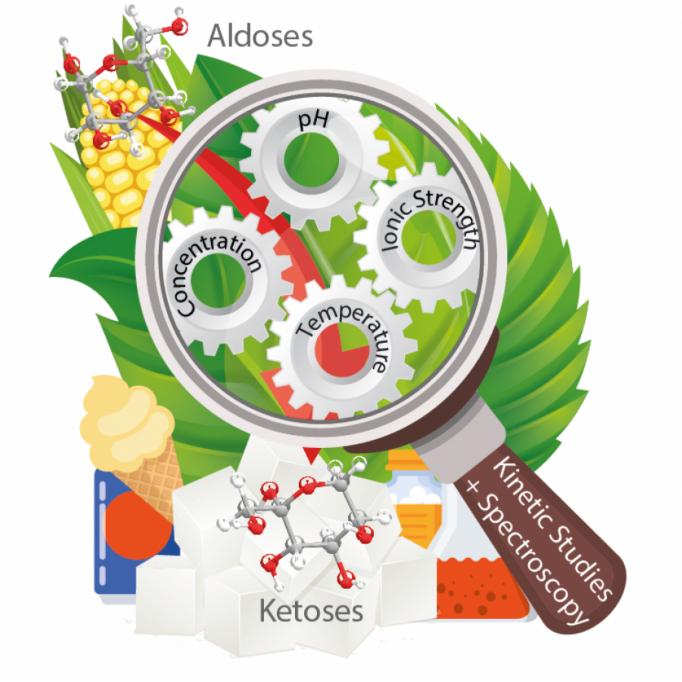

FIGURE 1

Graphical Abstract

Mechanistic investigation of the isomerization of glucose to fructose.

FIGURE 2

KEYWORDS

Glucose | Fructose | Isomerization | Catalysis by bases

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