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# Kinetic variations in Acid-Catalyzed Monosaccharide Conversion

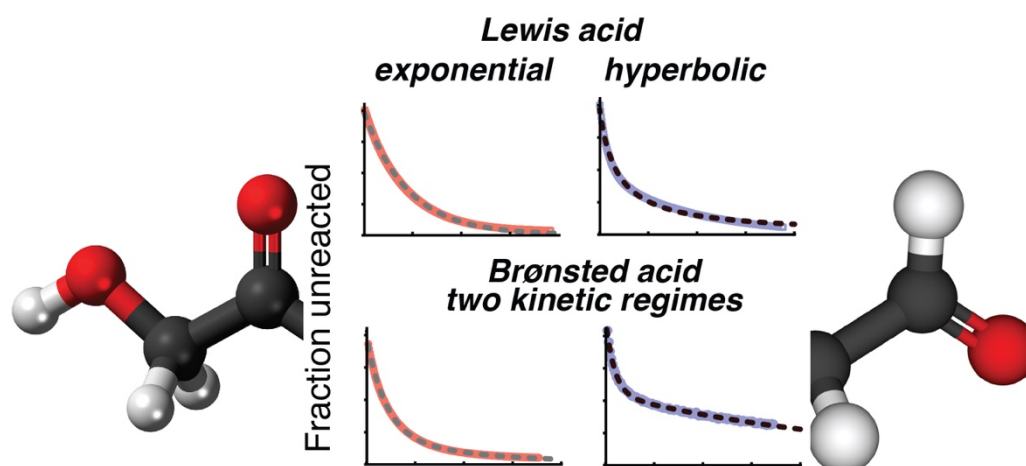
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Abstract:

Kinetic models for the conversion of abundant carbohydrates have often remained controversial. Direct spectroscopic observations show that conversion of ketoses by Lewis acidic salts follows an exponential time course, while the corresponding conversion of aldoses follows a second order kinetics in various solvents and using various metal chloride catalysts. Brønsted acid catalyzed conversion of glucose and fructose displays two kinetic regimes due to the competition between the kinetically favoured formation of anhydrosugars and the thermodynamically favored formation of furanics. Thus, slow kinetic phases occur towards the end of glucose conversion by Lewis and Brønsted acidic catalysis, albeit for different reasons.

Keywords: Brønsted acid, Glucose, in situ NMR, Kinetics, Lewis acid, Reaction order

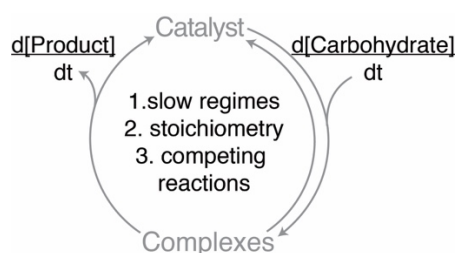


## 1. Introduction

Sustainable production of chemicals and energy has been a top priority in recent chemocatalytic research. Dehydration of sugars in acidic media is arguably among the most important pathways that have been explored in order to generate precursors with reduced oxygen content [1-5]. For the conversion of hexoses, these pathways lead to hydroxymethylfurfural (HMF), which is widely investigated as a prospective chemical precursor for fuels and materials [6-9]. The urgency of discovering alternatives to petrochemical processes has led to a strong focus on the discovery of catalyst systems for the formation of known products at high yields. In contrast, experimental mechanistic and kinetic studies have remained sparser [4, 10-15]. As a consequence, comparably high-yielding byproducts in chemocatalytic carbohydrate conversion have been discovered only recently [16, 17], active site structures have remained difficult to fully comprehend [18, 19], kinetic models and reaction order have remained controversial [5, 20-22], as has the usage of competing acyclic and cyclic pathways to HMF [23-25].

Conflicting previous interpretations of kinetic profiles in carbohydrate valorization indicate the necessity for direct and quantitative high-resolution methods to characterize reaction kinetics. Acid catalyzed carbohydrate conversion reactions are often characterized by rate-limiting initial steps and a concomitant dearth of accumulating intermediates. In such instances, time-resolved *in situ* spectroscopy can stipulate reaction progress kinetic analysis to obtain insight into elusive details of the catalytic cycle. Different kinetic regimes, reaction mechanisms and stoichiometry may thus be inferable from substrate conversion kinetics (Scheme 1).

High-resolution NMR spectroscopy was employed herein to track carbohydrate reaction conversions due to the suitable prowess of NMR in providing quantitative signals that are baseline-separated from isomeric species and from dehydration or cleavage products. *In situ* NMR was used in the kinetic study of carbohydrate conversion to provide kinetics of a rarely studied elementary step



**Scheme 1.** Topics addressed using *in situ* NMR kinetic analysis of carbohydrate conversion.

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(initial conversion) in a multistep pathway. Kinetic comparisons between different substrates under identical reaction conditions were obtained in this way. Various solvent systems, Lewis acidic salts and Brønsted acid catalysis were probed. Reaction progress was consistent with a mixed reaction order for various Lewis acidic salts, and with a bi-exponential trend in Brønsted acidic hexose conversion to HMF. Both the Lewis acid and the Brønsted acid catalyzed reactions of glucose thus showed inherently slow conversion at high substrate conversion.

## 2. Experimental

### Chemicals

All chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA) or Carbosynth (Compton, UK). Catalyst salts were weighed into a 1.5 ml Eppendorf safelock tube at concentrations of 2.5-10 mol% relative to hexoses or pentoses and pre-dissolved in the solvent of choice. The pre-dissolved catalyst solution was added to the substrate weighed into a 1.5 ml Eppendorf safelock tube and reaction solutions were mixed immediately prior to transfer to a 5 mm NMR sample tube, which was rapidly transferred to an NMR spectrometer equilibrated to the desired temperature for *in situ* kinetic experiments. Substrate concentrations on the order 0.5 M were used for unlabeled substrates and 0.25 M were used for  $^{13}\text{C}$  enriched substrates.

### *In situ* NMR spectroscopy

All *in situ* NMR spectra were acquired on a Bruker (Fällanden, Switzerland) Avance III 600 MHz (14.1 T) magnet equipped with a BBO smart probe and shim gas cooling. The *in situ* spectra of individual carbohydrate substrates and of aldoses and ketoses of same length were acquired as pseudo-2D spectra. Series of  $^1\text{H}$  spectra were acquired by sampling the FID for 1.8 seconds with an inter-scan recycle delay of 2 seconds, employing composite pulses and presaturation. Series of  $^{13}\text{C}$  spectra were acquired by sampling 64k complex data points in the FID for 1.8 seconds with an inter-scan recycle delay of 4.2 seconds using inverse-gated decoupling. Integrals of solvent signals indicated a relative error on the order of 1 % for integrations between different time points (Fig. S1). The comparison of aldohexose conversion curves was conducted using a time series of  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra sampling 1024 and 256 complex data points in the  $^{13}\text{H}$  and  $^{13}\text{C}$  dimension, respectively, with spectral widths of 13.3 ( $^1\text{H}$ ) and 15 ( $^{13}\text{C}$ ) ppm, sampling the NMR signal for 127 ( $^1\text{H}$ ) and 113 ( $^{13}\text{C}$ ) milliseconds. All spectra were processed with extensive zero filling in all dimensions and with baseline correction in Bruker Topspin 3.5pl7 and were subsequently integrated in the same software, where pseudo-2D

spectra were integrated using the Dynamics center. Experimental details are provided in the Supporting information. Identical kinetic behavior for different tautomers indicated that the tautomers equilibrate rapidly in a pre-equilibrium that is faster than the subsequent isomerization and dehydration reactions at the relevant temperatures (see for instance Fig. S4B). Substrate signals with the least overlap with emerging intermediates or products were thus integrated to represent the time course of substrate conversion.

## Data analysis

Time-resolved measurements were fitted to rate laws for first order, second order, mixed order and bi-exponential first order reactions. The data fitting minimised mean square deviations (chi-squared) between data and fitfunctions in proFit 7 (Quansoft, Switzerland). The reaction rates  $v$  of substrate conversion were treated as  $v = k[S]$ ,  $v = k[S]^2$  and  $v = k_1[S] + k_2[S]^2$  for first, second and mixed reaction order rate laws, respectively, where  $[S]$  is the substrate concentration and  $k$  are the corresponding rate constants. Reactions in Brønsted acidic medium were fitted to a bi-exponential first order rate law as the suitable approximation for reactions rapidly forming kinetic side products in parallel to slower formation of the thermodynamic product [26].

## 3. Results and discussion

### 3.1 Aldoses and ketoses behave kinetically differently beyond different rates

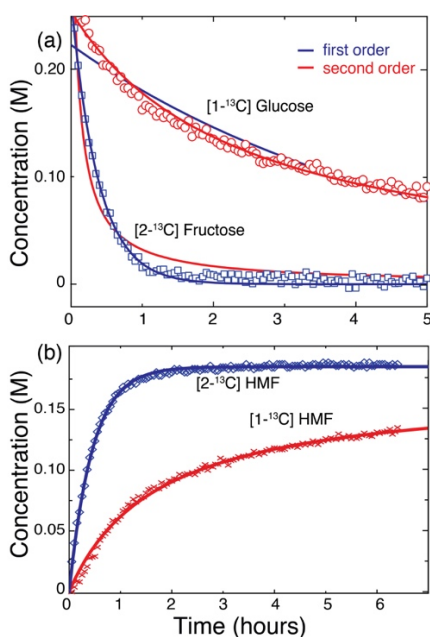
The emphasis of the current study lay on reaction progress kinetic analysis by time-resolved *in situ* NMR spectroscopy in polar aprotic solvents. These solvents have commonly been described as attractive reaction media for carbohydrate conversion due to low humin formation and the suppression of HMF rehydration and conversion to levulinic acid [24]. Polar aprotic media also often have a high ability to solubilize carbohydrates and favor acid catalysis towards high product yields.

In the presence of  $\text{CrCl}_3$ , glucose is converted to HMF via fructose as an intermediate and the comparison of glucose and fructose conversion to HMF thus requires special measures. Such a comparison was motivated by the fact that some disagreement has persisted as to whether glucose conversion by Lewis acidic catalysts resembles a first-order or a second-order reaction kinetics [20, 22].

Substrate conversion was probed for a 1:1 mixture of  $[1\text{-}^{13}\text{C}]$  glucose and  $[2\text{-}^{13}\text{C}]$  fructose. This mixture takes advantage of the ability of NMR to track the provenance of molecular species through isotope labelling under identical reaction conditions:  $[1\text{-}^{13}\text{C}]$  glucose and  $[2\text{-}^{13}\text{C}]$  fructose were

predominantly converted to the respective  $[1-^{13}\text{C}]$  and  $[2-^{13}\text{C}]$  HMF products and these reactions to the same chemical could be distinguished by producing isotopic isomers with the  $^{13}\text{C}$  isotope in different positions. Besides functioning as a catalyst, the chromium salt also acted as a relaxation agent, which rapidly restored nuclear magnetization to its equilibrium and thus permitted the rapid accumulation of high-quality NMR spectra [27].

Resultant time courses for the conversion of glucose and fructose and for the formation of  $[1-^{13}\text{C}]$  HMF (from glucose) and of  $[2-^{13}\text{C}]$  HMF (from fructose) are shown in Fig. 1. Fructose was converted to HMF with initial rates more than an order of magnitude above corresponding initial rates for glucose conversion under identical conditions. In addition, the curves for conversion of glucose and fructose to HMF exhibited different functional forms (Fig. 1). The reaction progress curves for glucose conversion to HMF followed a hyperbolic function, consistent with reaction that is of second order in the substrate concentration, while reaction progress curves for fructose conversion to HMF follow an exponential trend consistent with a first order reaction. As a consequence, HMF yields from glucose continue to increase slowly, similar to curves of HMF increase shown in the literature for *ex situ* experiments [5]. This slow increase in HMF deriving from glucose may partly contribute to some of the lower yields described for glucose conversion as compared to yields for fructose conversion for acceptable experiment durations. *In situ* NMR spectra for the parallel formation of furanics from xylose and glucose validated that product formation from neither aldose followed an exponential increase (Fig. S2).

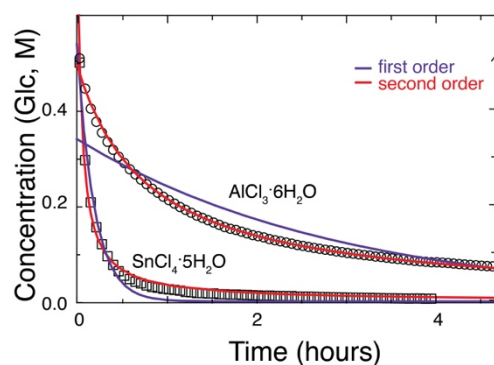


**Fig. 1** Reaction kinetics in the Cr(III)-catalyzed conversion of (a) glucose and fructose to (b) HMF in DMSO as tracked by integration of *in situ*  $^{13}\text{C}$  NMR data. Reaction conditions: 25 mg  $[1-^{13}\text{C}]$  glucose, 25 mg  $[2-^{13}\text{C}]$  fructose,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (2.5 mol% relative to the hexoses), 0.6 ml  $\text{DMSO-d}_6$ , 130 °C.

For Brønsted acid catalyzed dehydration of xylose in aqueous solutions, second-order kinetics have been ascribed to the reaction between xylose and furfural [28, 29]. In the conversion of aldoses by Lewis acidic metal salts in solvents that suppress humin formation, second order kinetics have been ascribed to the formation of 2:1 complexes between the aldose and the metal salt [5, 20], while other studies maintained a first-order treatment of aldose conversion in metal salt catalyzed reactions [21, 22]. Kinetic *in situ* NMR experiments conducted herein showed that xylose conversion was hardly affected by addition of stoichiometric amounts of furfural or glucose to the reaction mixture (Fig. S3). Intermolecular aggregation with reactive intermediates thus does not appear to be the main reason for the second-order substrate kinetics. Second order kinetics may thus reflect recent observations of glucose predominantly in 2:1 complexes with Lewis acidic salts [30]. The kinetic trend of furanics formation itself (Fig. 1b) also indicated that second order kinetics arises in the metal-catalyzed reaction step converting substrate to furanics. Byproducts in these reactions include levulinic acid, disaccharides, isomeric sugars and anhydrosugars [27, 31].

### 3.2 Full conversion is slow with different Lewis acidic catalysts, substrates and solvents

In order to test whether similar functional forms in reaction progress kinetic behavior is observed for different catalysts, Cr(III) was replaced with various other Lewis acidic salts to probe the reaction kinetics in glucose conversion. Among the salts described to show high activity in glucose conversion





**Fig. 2** Al(III) and Sn(IV)-catalyzed conversion of glucose in DMSO as followed by integration of a time series of *in situ*  $^{13}\text{C}$  NMR spectra and fitted to first order and second order models. Reaction conditions: 50 mg glucose, 6 mg  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 130 °C and 0.55 ml  $\text{DMSO-d}_6$ .

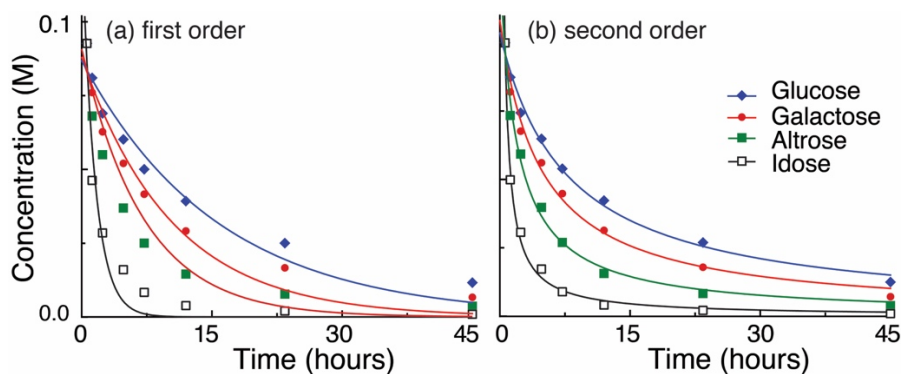
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in DMSO were Al(III), Sn(IV) and In(III) salts [20, 32-34]. When using these catalysts, both the conversion of glucose and the formation of HMF were found to follow second order reaction kinetics (Fig. 2 and Fig. S4, S5).

A comparative study of substrates was then pursued to probe the Lewis acid catalyzed conversion of all eight aldohexoses by  $\text{SnCl}_4$ . Sn(IV) was chosen as a particularly active metal salt in the conversion of glucose (Fig. 2) [34]. As the eight substrates are regioisomers, reaction progress was difficult to track as a series of one-dimensional spectra due to the resultant signal overlap especially in  $^1\text{H}$  NMR spectra. In contrast, suitably optimized  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra have adequate prowess in distinguishing carbohydrates in mixtures. Hence, a time series of  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra was acquired to track the conversion of all eight linear aldohexoses.

Reaction progress curve analysis validated that conversion of all linear aldohexoses followed hyperbolic kinetics (Fig. 3, Fig. S6). The mean square deviations (chi-squared values) between observed and predicted values showed that each single of the substrate curves was better described by a second order kinetics than by a first order kinetics. Fits to hyperbolic trends in a second order kinetic model were on average approximately five times better than fits to a first order model (Fig. S7). The analysis also showed that deviation of experimental data from first order kinetic trends in Fig. 3 occurred at different time points for different substrates, indicating that catalyst deactivation does not cause the slowdown of the reactions at low fractions of unreacted substrate.

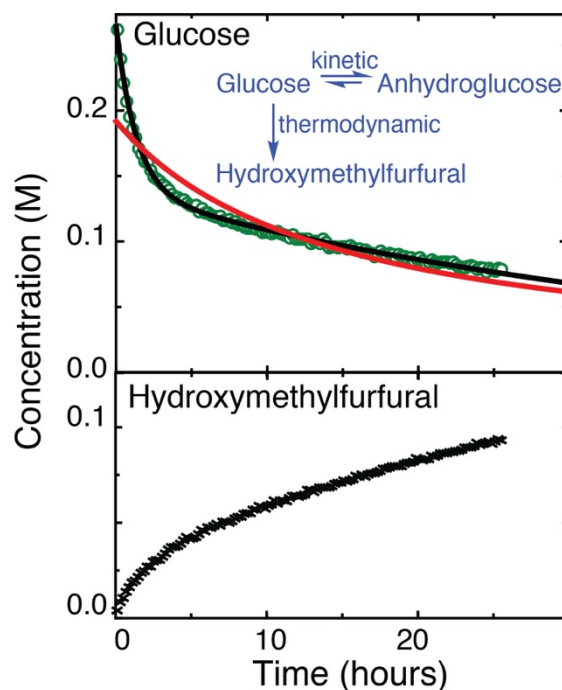
Various solvents other than DMSO have attracted interest in the conversion of carbohydrates to furanics due to preferable product yields, purification, or for being biomass-derived solvents. Glucose conversion in propylene carbonate (Fig. S8, S9),  $\gamma$ -valerolactone (Fig. S10) and [EMIM]Cl (Fig. S11, S12) showed agreement between reaction progress and a second order model. Conversion proceeded noticeably faster than predicted for low substrate concentration, possibly through contribution from first order kinetics, as could be expected in the presence of predominant 2:1 and minor 1:1 substrate:metal complexation [30]. Overall, real-time NMR spectroscopic observations detected that aldose conversion follows second order kinetics for a broad range of solvents, substrates, and Lewis acidic salts.



**Fig. 3** Sn(IV)-catalyzed conversion of four selected aldohexoses in DMSO, as followed with *in situ*  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR in a single mixture of all linear aldohexoses. Data were fitted to (a) a first order or (b) a second order reaction model. Reaction conditions: 10 mg of each aldohexose, 15 mg  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 100 °C and 0.6 ml  $\text{DMSO-d}_6$ .

### 3.3 Hexose conversion with HCl is bi-exponential

Mechanistic differences between Lewis acid and Brønsted acid catalyzed carbohydrate conversions are expectable and should be reflected by dissimilar conversion kinetics. For comparison with the reactions catalyzed by Lewis acidic salts, the reaction progress of glucose conversion to HMF was followed for the Brønsted acid catalyzed conversion (40 mM HCl in DMSO at 130 °C). Neither glucose conversion nor the formation of HMF were indicative of second order kinetics (Fig. 4). In the Brønsted acid catalyzed conversion of glucose to HMF,  $\beta$ -anhydroglucose (first in its furanose and subsequently in its pyranose form) [27] accumulated in competition to slower glucose conversion to HMF (Fig. S13). The rate constants of the two kinetic regimes of glucose conversion differ by more than twentyfold. The efficient conversion of glucose to HMF in Brønsted acidic aprotic media thus depends on the extent of competing anhydroglucose formation and the possibility of its avoidance. This finding is consistent with previous observations that addition of water can be beneficial for HMF formation from glucose in aprotic solvent [31]. Analogously, intramolecular ketalization occurs when fructose is the substrate. Also for fructose, conversion in aprotic Brønsted acidic medium thus shows bi-exponential rather than exponential kinetics (Fig. S14). This behavior is somewhat reminiscent of the ketalization of fructose to methyl fructosides in competition with the conversion to the thermodynamic product methyl lactate for the Sn-Beta catalyzed carbohydrate conversion in methanol [26].



**Figure 4.** Brønsted acid catalyzed conversion of glucose in DMSO to anhydroglucose and HMF as tracked by a series of  $1\text{D }^{13}\text{C}$  NMR spectra. Concentrations can be described by bi-exponential kinetics due to competing formation of kinetic and thermodynamic product (see inset). Reaction conditions: 25 mg  $[1\text{-}^{13}\text{C}]$  glucose, 40 mM HCl,  $130\text{ }^{\circ}\text{C}$ , 0.6 ml  $\text{DMSO-}d_6$ .

#### 4. Conclusions

Real time *in situ* NMR spectroscopy was used to track monosaccharide conversion by Lewis and Brønsted acidic catalysts in polar aprotic solvents. Slow conversion regimes posed a notable challenge to the full conversion especially of aldoses. Aldoses displayed second order reaction kinetics that were very little affected by compounds implicated in intermolecular aggregation. Ketoses exhibited reaction kinetics that were consistent with first order reactions along the entire reaction path. Limitations in reaching high conversion of glucose as a consequence of the reaction mechanism were equally inherent to Brønsted acid catalyzed conversion of Glucose to HMF. Here, competing reactions to masked anhydrosugars resulted in bi-exponential kinetics, where the rate constants of the two kinetic regimes differed by more than twentyfold for glucose conversion and by approximately tenfold for fructose conversion.

#### Acknowledgements

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