



## Conversion of glucose and cellobiose into 5-hydroxymethylfurfural (HMF) by rare earth metal salts in *N,N'*-dimethylacetamide (DMA)

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### ABSTRACT

D-Glucose and cellobiose were converted into 5-hydroxymethylfurfural (HMF) by rare earth metal chlorides  $\text{LnCl}_3$  ( $\text{Ln} = \text{Sc}, \text{Y}, \text{La}$ ) in *N,N'*-dimethylacetamide (DMA). Both conversion and selectivity strongly depend on the ionic radii of the rare earth metal center. Conversion of fructose into HMF proceeds significantly faster and with higher selectivity than of glucose, suggesting a mechanism that involves the transformation of glucose into fructose as a crucial, rate determining step.

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### 1. Introduction

For the production of chemical energy carriers for transportation from biomass, two basic routes can be considered: one is breaking up biomass to synthesis gas and building up fuel molecules using Fischer–Tropsch process; the other would be breaking down biomass molecules to directly give combustible molecules. The latter is confined to the utilization of biomass celluloses, hemicelluloses, and lignin to avoid conflict with the food chain that starch as feedstock would inevitably bring [1]. As one of the promising candidates as fuel components or platform chemicals, 5-hydroxymethylfurfural (HMF) plays a pivotal role as it is directly accessible from hexoses and can be transformed into a variety of furan-based compounds [2].

In the ongoing search for simple, cheap and environmentally benign processes for HMF production, chromium(II) and chromium(III) chlorides have drawn considerable attention as effective catalysts [2c,3]. They have been studied in ionic liquids as well as in DMA/LiCl (DMA = *N,N'*-dimethylacetamide) and afforded up to 53% HMF after 3 h (6 mol% chromium; 120 °C) in the latter system and up to 70% in IL. Available data suggest that the isomerization of glucose into fructose is a crucial step in the formation of HMF. On the other hand, Brønsted acids have shown

their ability to catalyze the dehydration of saccharides at elevated temperatures [4]. Since initial studies showed little efficiency for rare earth metal salts in comparison to chromium catalysts [3a], not much attention has been paid to the use of rare earth metal catalysts. Lewis acidic rare earth metal salts were reported to generate HMF in water under hydrothermal conditions [5] and in ionic liquids [6].

Potential solvents for saccharides and glucose oligomers are ionic liquids (IL) and DMA/LiCl. Of these, ionic liquids have been studied for the formation of HMF from glucose in combination with rare earth metals. While the reaction occurs, the stability of the product depends strongly on the nature of the IL. In general HMF yields as well as selectivity, are low for all the rare earth metal based catalysts examined [3a,6], with a maximum yield of 25–30% HMF depending on reaction conditions. In DMSO on the other hand, rare earth metal salts were reported to yield HMF from fructose and fructose-containing oligomeric saccharides, but from glucose only moderate amounts (around 10% in case of  $\text{LaCl}_3$ ) were obtained [7].

Since it is desirable to reduce the number of separation steps for the valorization of cellulosic materials, efficient routes for the direct conversion of cellulose or cellulose oligomers such as cellobiose are needed. Rare earth metal salts can be expected to act as multifunctional catalysts for several steps on the route from cellulose to HMF including hydrolysis, isomerization of glucose to fructose, and dehydration. They are strongly Lewis acidic and allow for high coordination numbers, but have not been investigated in the reaction with glucose oligomers in organic solvents under conditions reported for HMF formation by chromium catalysts.

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## 2. Experimental

### 2.1. General

DMA (98%), DMF p. A., D-glucose (96%) and cellobiose (98%) were purchased from Aldrich, fructose (99.5%) was purchased from Südzucker,  $\text{YCl}_3 \cdot 6 \text{H}_2\text{O}$  was purchased from Nanosolutions,  $\text{ScCl}_3$  and  $\text{LaCl}_3$  were purchased from Strem chemicals and  $\text{LiCl}$  extra pure from Riedel-de Haën; all chemicals were used without further purification.

Experiments at temperatures up to  $145^\circ\text{C}$  were performed on a Chemspeed ASW 1000 synthesizer with up to 36 wells with a reaction volume of 13 mL connected to argon supply. The hood containing the reactor blocks with the wells was permanently flushed with nitrogen. Temperature was controlled by a Huber Tango Nuevo cryostat. Reactions were vortexed at 600 rpm.

4 mL of a stock solution of the substrate (and  $\text{LiCl}$  where appropriate; see below) in DMA containing DMF as internal standard were transferred to the reactor wells. Where necessary, 0.5 mL of DMA were added to adjust the overall volume to 5 mL and the atmosphere in the reactor wells was exchanged against argon by repeated cycles of decreasing pressure and flushing with argon. The reaction zone was heated to the desired temperature. A 0.1 mL sample of the mixture was injected into 0.5 mL of  $\text{D}_2\text{O}$  as a reference for NMR spectroscopic analysis prior to the transfer of 0.5 mL of stock solution of the appropriate metal chloride in DMA (1 mL for  $\text{ScCl}_3$  stock solution), giving reaction mixtures that contained 2.24 mmol of glucose or fructose (1.12 mmol of cellobiose) and 0.22 mmol of metal chloride. The sampling procedure was repeated at the respective times.

Experiments at temperatures above  $150^\circ\text{C}$  were performed in a thick-walled Büchi glass reactor and stirred with a magnetic stirring bar. Stock solutions were transferred manually with a plastic syringe and the mixture was flushed with argon for 1 min before the reactor was closed.

The results with scandium were reproduced manually as scandium(III) chloride had to be applied as a suspension in DMA due to its low solubility.

Experiments with fructose were conducted manually as deviation of reaction times were to high due to the sampling speed of the Chemspeed ASW 1000.

The following stock solutions were used:

Yttrium(III) chloride: 673 mg (2.22 mmol) of  $\text{YCl}_3 \cdot 6 \text{H}_2\text{O}$  in 5 mL of DMA, giving a 0.444 M solution.

Lanthanum(III) chloride: 544 mg (2.22 mmol) of  $\text{LaCl}_3$  in 5 mL of DMA, giving a 0.444 M solution.

Scandium(III)chloride: 168 mg (1.11 mmol) of  $\text{ScCl}_3$  in 5 mL of DMA, giving a 0.222 M solution.

Glucose: 10 g (0.056 mol) D-Glucose (and 4.71 g  $\text{LiCl}$  where appropriate) were transferred to a 100 mL volumetric flask. 5 mL of *N,N'*-dimethylformamide (DMF) were added as internal standard for NMR measurement. Overall volume was adjusted to 100 mL with DMA.

Cellobiose: 9.5 g of cellobiose and  $\text{LiCl}$  (4.71 g) were transferred to a 100 mL volumetric flask. 5 mL of *N,N'*-dimethylformamide (DMF) were added as internal standard for NMR measurement. Overall volume was adjusted to 100 mL with DMA.

### 2.2. Analytical

NMR measurements were performed on a Bruker Avance 400 MHz spectrometer. For determination of glucose conversion the integrals of the hydrogen on the anomeric carbon at 4.52 and 5.11 ppm were used and correlated with the proton of the formic acid moiety of DMF at 7.83 ppm. As separation from the tailing of

the water peak can cause problems, considerable deviations can occur for single points in the conversion curves. Determination of cellobiose conversion refers to the doublet of the proton on the glycosidic bond at 4.40 ppm. HMF content was determined based on the average of the doublets of the ring protons at 6.58 and 7.44 ppm. As there is no well separated signal for any single proton in fructose, the overall integral of all the protons was used to estimate fructose conversion.

In order to confirm the formation of HMF, several samples were further analyzed by GCMS. For GCMS analysis, 2 mL samples were diluted with water to 10 mL and extracted 3 times with  $\text{CH}_2\text{Cl}_2$ . The organic phase was separated and filtered over a glass fibre filter to remove any humins. The volume of the collected organic extracts was reduced to 5 mL and the analysis of the solution was performed on a Shimadzu GCMS-QP 2010 plus with helium as carrier gas. Oven temperature was raised from  $60^\circ\text{C}$  to  $250^\circ\text{C}$  at a heating rate of 10 K/min. A Supreme-5-MS column (30 m length, 0.25 mm diameter, 0.25  $\mu\text{m}$  pores) at a column flow of 2 mL/min. No soluble products other than HMF could be detected.

## 3. Results and discussion

The conversion of fructose into HMF appears to be a fairly simple process as the five-membered ring is already formed and dehydration leads to the stable furan ring. The reaction with glucose or cellulose as starting materials becomes more complicated as additional equilibria and side reactions occur. Specifically, hydrolysis of glucose oligomers has to be addressed when HMF yield needs to be optimized (Scheme 1). Another crucial step in the transformation into HMF is the rearrangement of glucose to fructose [8]. If the equilibrium between these two hexoses is shifted towards fructose, or if equilibration proceeds quickly, the problem of HMF production from D-glucose is reduced to the optimization of fructose conversion.

Experiments in DMA revealed that substantial amounts of HMF are formed from D-glucose at elevated temperatures in the presence of rare earth metal chlorides but high yields are hampered by humin generation. At  $145^\circ\text{C}$  and with 10 mol% of yttrium trichloride, glucose is fully converted after 3 h, while only 20% of HMF are formed (Fig. 1), with the HMF yield decreasing further at prolonged reaction times.

Analysis of the  $^1\text{H}$  NMR spectra of samples suggests that there is no substantial build-up of intermediates such as open-chained saccharides, fructose, or coordination compounds. They should be visible in the double bond region of the spectra in the case of dehydration and in the region around  $\delta 9\text{--}10$  ppm for aldehydes that are present in many of the intermediates discussed in the literature [9]. Since there are no by-products that could be converted into HMF

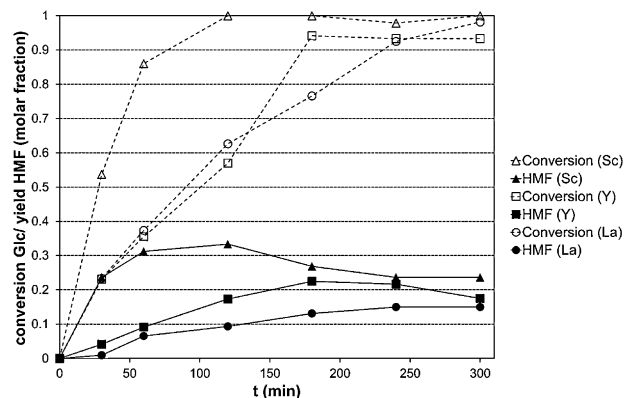


Fig. 1. Conversion of D-glucose into HMF in DMA at  $145^\circ\text{C}$  with 10%  $\text{LnCl}_3$ .

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