Highly Efficient Catalytic Activity of Lanthanide(III) Ions for Conversion of Saccharides to 5-Hydroxymethyl-2-furfural in Organic Solvents

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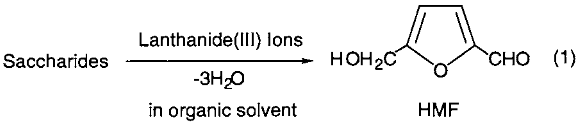
All lanthanide(III) ions were found to catalyze dehydration of saccharides to 5-hydroxymethyl-2-furfural (HMF) in DMSO at 100 - 120 °C. Particularly, D-fructose was almost quantitatively converted to HMF without generating any byproducts. The results of the reaction with di- and trisaccharides indicated that the D-fructose moiety in the substrates was selectively converted to HMF.

Utilization of saccharides, the most abundant biomass, as a carbon resource has been strenuously explored. In particular, the conversion of hexose into HMF (eq. 1) has been investigated as an industrial utilization of saccharides.[1-4] This reaction has been catalyzed by Brønsted acids such as hydrogen chloride and sulfuric acid in aqueous solutions. Under such conditions, however, the product HMF tends to decompose to levulinic acid by the acid catalysts and the yield remains moderate; e.g., the reported HMF yield was 26% in an aqueous solution of D-fructose (0.5 M) and HCl (0.5 M) at 95 °C.[3] We have found that lanthanide(III) ions can catalyze the dehydration of D-glucose into HMF, however, the yield was quite low; the maximum yield was 8% with $ErCl_3$ catalyst in water at 140 °C in an autoclave.[5] Moreover, the catalytic activity toward the other saccharides has never been reported. We report herein that the conversion of saccharides to HMF efficiently proceeds in the presence of lanthanide(III) ion catalysts. We will also describe that fructose was almost quantitatively converted to HMF in DMSO and only the fructose moiety was selectively dehydrated in di- or trisaccharides substrates.



(1)

The reaction was carried out by heating an organic solution (50 cm^3) containing a saccharide (0.20 M) and a lanthanide(III) ion (5.0 - 10.0 mM) under an N_2 atmosphere at 100 - 120 °C. Quantitative analysis of HMF was performed by gas chromatography on a polyethylene glycol 20M column (Shimadzu GC-9A (FID)).

In representative experiments, dehydration of D-fructose catalyzed by $LaCl_3$ was examined in six solvent systems at 100 °C (Figure 1). The reaction efficiently proceeded in DMSO, DMF, and DMA. The yields of HMF attained to more than 90% after 4 h. Neither byproducts nor levulinic acid, which would be generated as a decomposition product of HMF, was observed. Among these solvents, DMSO gave the best yields up to 95.2%. The turnover number for the reaction was 38, evidently indicating that the reaction proceeded catalytically. In sulfolane, the reaction did not further proceed after the HMF yield attained to *ca.* 50%. In 1,4-dioxane and 1-butanol, HMF was generated much more slowly than in the other solvents, and the ultimate HMF yields were ca. 25%.

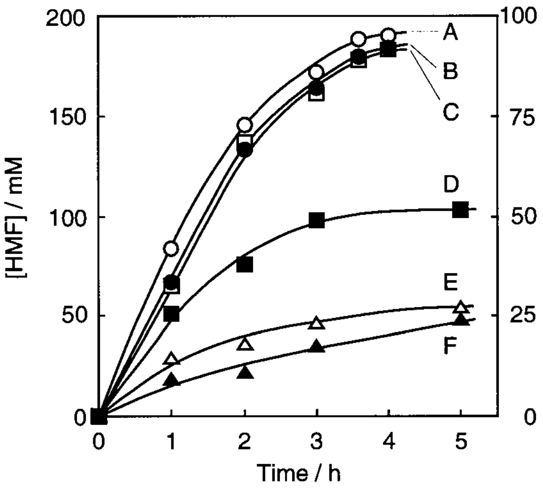


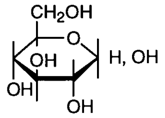
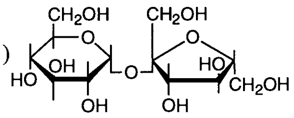
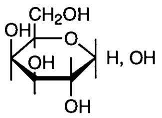
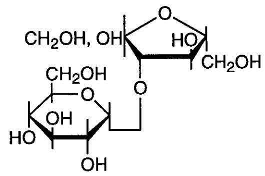
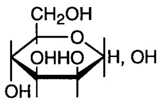
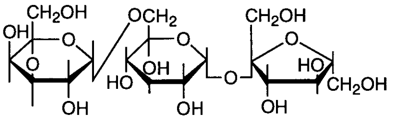
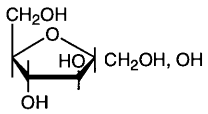
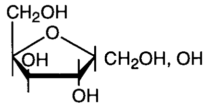
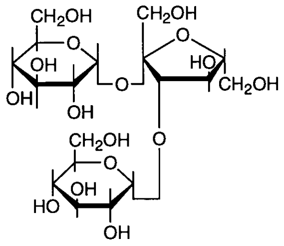
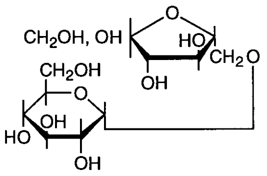
Figure 1. Time courses of HMF production from D-fructose (0.20 M) catalyzed by $LaCl_3$ (5.0 mM) at 100 °C in organic solvents: (A) DMSO, (B) DMF, (C) DMA, (D) sulfolane, (E) 1,4-dioxane, and (F) 1-butanol.

Next, the catalytic activities of the other lanthanide ions than $LaCl_3$ were examined. The yields of HMF from D-fructose in DMSO at 100 °C for 12 h were 90.5, 91.8, 93.0, 94.8% for $NdCl_3$, $EuCl_3$, $DyCl_3$, and $LuCl_3$ catalysts, respectively. Thus, all of the lanthanide ions examined were satisfactorily good catalysts for the reaction, and the yields were almost independent of the lanthanide(III) ion employed.

Lanthanide(III) ions have been used as Lewis acid catalyst.[6] It is also reported that lanthanide(III) ions are strongly hydrated and therefore the reaction could be inhibited or influenced by the existence of water,[7] which is generated during the reaction. Hence we examined the effects of water on the conversion of saccharides to HMF. The reaction of D-fructose by $LaCl_3$ in 10%-water/DMSO at 100 °C proceeded slower than in DMSO, but the yield of HMF, 90.4% after 24 h in 10%-water/DMSO, is virtually the same as that in DMSO, 95.2% after 4 h. The results clearly indicate that the presence of water up to 10% do not affect the HMF yields.

The reactions of various saccharides catalyzed by $LaCl_3$ in DMSO were examined (Table 1). Although aldoses such as D-glucose, D-galactose, D-mannose in mono-saccharides scarcely produced HMF (yields < 10%), the yields of HMF for ketoses

Table 1. HMF concentration and yields obtained upon dehydration of saccharides (0.20 M) catalyzed by $LaCl_3$ (10.0 mM) in DMSO at 120 °C for 2 h

Saccharides		[HMF] / mM (Yield / %)		Saccharides		[HMF] / mM (Yield / %)	
D-Glucose		19.6	(9.8)	Sucrose (Glc*p*α1 ↔2βFru*f*)		185.8	(93.0)
D-Galactose		13.4	(6.7)	Turanose (Glc*p*α1 →3Fru*f*)		49.4	(24.8)
D-Mannose		9.6	(4.8)	Raffinose (Gal*p*α1→6Glc*p*α1↔2βFru*f*)		129.6	(64.8)
D-Fructose		185.2	(92.6)				
L-Sorbose		122.8	(61.4)	Melezitose (Glc*p*α1→3Fru*f*β2↔1αGlc*p*)		47.5	(23.8)
Palatinose (Fru*f*1 →6Glcα)		71.5	(35.8)				

(e.g. D-fructose and L-sorbose) were considerably high. In particular, D-fructose almost quantitatively produced HMF. More interestingly, the yield (61.4%) of HMF from L-sorbose, which possesses different C3 and C4 hydroxyl configuration, was smaller than that for D-fructose. A similar tendency is observed in the results for disaccharides. Although the disaccharides consisting of only aldoses scarcely yielded HMF (data not shown), the HMF yields from the disaccharides containing D-fructose were relatively high. Specifically, sucrose, in which D-fructose connects with D-glucose (aldose) at 2 position, did produce HMF in 93.0% yield.[8] By considering the results that aldose scarcely yielded HMF and an equimolar HMF was generated from sucrose, we conclude that the D-fructose moiety was selectively converted to HMF. In contrast, palatinose and turanose, in which D-fructose binds with D-glucose at 1 and 3 positions, gave relatively fewer amounts of HMF in 35.8 and 24.8% yields, respectively. The similar propensity was also observed in the results for trisaccharides: raffinose (D-fructose connects at 2 position) gave the higher HMF yield (64.8%) than melezitose (D-fructose connects at 2 and 3 positions; 23.8% yield).

In summary, it was found that lanthanide(III) ions efficiently catalyze dehydration of saccharides, particularly D-fructose, in organic solvents such as DMSO. D-Fructose in di- and trisaccharides was found to be selectively converted to HMF. Also, the hydroxyl groups at 1 and 3 positions of D-fructose was suggested to be involved in the dehydration reaction. The interaction between a lanthanide(III) ion and a saccharide on a molecular level is currently under investigation.

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References and Notes

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8 D-Glucose (170.3 mM, 85.2% yield) was also detected from the same solution by an HPLC analysis.