

## Conversion of Glucose to 5-Hydroxymethylfurfural Catalyzed by Metal Halide in *N,N*-Dimethylacetamide

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A simple strategy is reported for catalytic conversion of glucose to 5-hydroxymethylfurfural (HMF) over  $\text{AlI}_3$  in *N,N*-dimethylacetamide (DMAC). When the reaction was conducted in DMAC at 120°C for 15 min over  $\text{AlI}_3$  catalyst, HMF was obtained with a yield of 52%. The reaction course was monitored by  $^{13}\text{C}$  NMR spectroscopy and HPLC analysis. The results suggest that  $\text{AlI}_3$  catalyzes the three consecutive reactions consisting of mutarotation of  $\alpha$ -glucopyranose to  $\beta$ -glucopyranose, isomerization of glucose to fructose, and dehydration of fructose to HMF.

*Keywords:* Glucose; Dehydration; Metal halide; 5-Hydroxymethylfurfural

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### INTRODUCTION

In view of the costs and challenges inherent in safely and continuously providing fossil energy resources, increasing attention has been paid to the conversion of biomass to biofuels and chemicals (Gallezot 2012; Zhou *et al.* 2011; Bozell 2010; Alonso *et al.* 2010). 5-Hydroxymethylfurfural (HMF), an important biomass-derived platform chemical, can be converted to biofuels and a broad range of chemicals (Rosatella *et al.* 2011; Román-Leshkov *et al.* 2007; Zhao *et al.* 2007; Huber *et al.* 2005), which are currently produced from petroleum. Recently, our group has developed methods for converting HMF to maleic anhydride (Du *et al.* 2011), which is now mainly produced via selective oxidation of benzene, *o*-xylene, or *n*-butane in industry. In addition, we have developed methods for converting HMF to furan-based polyester and copolyester materials, fluorescent material, porous organic frameworks, and liquid fuel products, respectively (Ma *et al.* 2011; Ma *et al.* 2012a,b,c; Che *et al.* 2012). However, a simple and reliable way of acquiring HMF remains as a bottleneck for extending biomass chains.

HMF could be formed through acid-catalyzed dehydration of fructose (Román-Leshkov *et al.* 2006; Tong *et al.* 2010; James *et al.* 2010). However, glucose, the isomer of fructose, is a better feedstock for HMF production because it is cheaper. It is the most abundant monosaccharide in nature, and it can be obtained from starch and cellulose. However, in comparison with fructose, it is more difficult to convert glucose to HMF. Zhang and co-workers reported the conversion of glucose to HMF using a  $\text{CrCl}_2$ /ionic liquid system (Zhao *et al.* 2007). Some other Cr-containing catalytic systems have also been developed (Yong *et al.* 2008; Binder and Raines 2009; Yu *et al.* 2009; Li *et al.* 2009; Qi *et al.* 2010; Zhao *et al.* 2011; Zhang and Zhao 2011; Yuan *et al.* 2011; Hu *et al.* 2012). More efforts have been taken to develop low-toxic catalytic systems. In ionic liquids,  $\text{Yb}(\text{OTf})_3$ ,  $\text{H}_3\text{BO}_3$ , H-ZSM-5,  $\text{GeCl}_4$ ,  $\text{ZrO}_2$ , and  $\text{SnCl}_4$  have been used to catalyze this process. HMF was obtained with yields of 24 to 61% (Stahlberg *et al.* 2010; Stahlberg *et al.* 2011; Jadhav *et al.* 2012; Zhang *et al.* 2011; Qi *et al.* 2012; Hu *et al.* 2009). Under

microwave irradiation, the reactions over  $\text{TiO}_2$  and  $\text{AlCl}_3$  catalysts gave 37 to 61% yields of HMF (Dutta *et al.* 2011; De *et al.* 2011; Yang *et al.* 2012). In addition,  $\text{ScCl}_3$ ,  $\text{ZnCl}_2$  combined with HCl,  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-Al}_2\text{O}_3$ , hydrotalcite combined with Amberlyst-15, Sn-Mont, Sn-Beta zeolite combined with HCl, and  $\text{AlCl}_3$  combined with HCl have also been used to catalyze this process; HMF was obtained with yields of 30 to 62% (Beckerle and Okuda 2012; Deng *et al.* 2012; Yan *et al.* 2009; Ohara *et al.* 2010; Wang *et al.* 2012; Nikolla *et al.* 2011; Pagán-Torres *et al.* 2012). Unlike previous studies, we herein demonstrate a simple method for the catalytic conversion of glucose to HMF over metal halide. It was found that aluminum halides in *N,N*-dimethylacetamide (DMAC) were efficient for this important reaction, and the catalytic performance of aluminum halides decreases in the order of  $\text{AlI}_3 > \text{AlBr}_3 > \text{AlCl}_3$ . A tentative reaction route, including mutarotation, isomerization, and dehydration, is proposed based on NMR and HPLC analysis.

## EXPERIMENTAL

### Materials

All reagents were of analytical grade and were used as purchased without further purification unless otherwise stated.  $\text{AlI}_3$  and methyl benzoate were purchased from Alfa Aesar. HMF,  $\text{GaCl}_3$ , and  $\text{InCl}_3$  were purchased from Sigma-Aldrich. *D*-glucose and *D*-fructose were purchased from Tianjin Kermel.  $\text{AlCl}_3$ , DMAC, and other reagents were purchased from Shanghai Chemical Reagent Company. DMAC was distilled under reduced pressure before being used.

### Typical Procedure for Glucose Conversion

All the reaction experiments were conducted in a 50 mL two-necked flask equipped with a condenser and a magnetic stirrer. Typically, 0.5 mmol glucose and 0.1 mmol  $\text{AlI}_3$  were mixed in 2 mL DMAC under  $\text{N}_2$ . The mixture was stirred in a preheated oil bath at the desired temperature for a certain period of time. After reaction, the mixture was immediately cooled in an ice bath to terminate the reaction, followed by filtering off solid particles. The filtrate was added to a certain amount of methyl benzoate as internal standard and was diluted with ethyl acetate to 10 mL. The sample was filtrated with a 0.2  $\mu\text{m}$  micropore membrane before its analysis by GC and HPLC.

### HMF Quantification Procedure

HMF was analyzed with an Agilent 4890D GC device equipped with a flame ionization detector and FFAP capillary column (30 m  $\times$  0.32 mm  $\times$  0.4  $\mu\text{m}$ ). HMF was confirmed by  $^1\text{H}$  NMR measured with a Bruker DRX-400 spectrometer, as well as an Agilent 6890N GC device equipped with an Agilent 5973 mass selective detector and HP-5 capillary column (30 m  $\times$  0.25 mm  $\times$  0.3  $\mu\text{m}$ ). HMF yield was determined by the internal standard curve method with methyl benzoate as internal standard.

### Glucose and Fructose Quantification Procedure

Glucose and fructose are analyzed with a Waters 2695 HPLC equipped with 2414 refractive index detector at 30°C and high performance carbohydrate column (4.6 mm  $\times$  250 mm) at 30°C controlled with the column oven. Acetonitrile/water solution (75:25) with a flow rate of 1.4 mL/min was used as the mobile phase. The injection amount was

10  $\mu$ L. Both glucose conversion and fructose yield were calculated by using an external standard curve method.

## RESULTS AND DISCUSSION

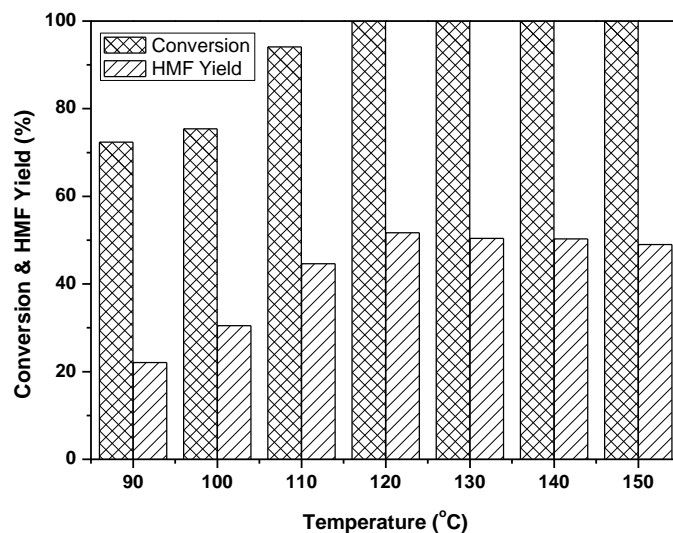
In the initial experiment,  $\text{AlCl}_3$  (10 mol% based on glucose) was used as the catalyst to convert glucose in DMAC at  $100^\circ\text{C}$  for 15 min. Very low yield (6%) of HMF was obtained. The yield of HMF was increased to 36% when the reaction temperature was  $130^\circ\text{C}$ . Prolonging the reaction to 240 min had little effect on the yield of HMF (Table 1, entries 1 to 3). When  $\text{GaCl}_3$  and  $\text{InCl}_3$  were used, lower yields of HMF were obtained (Table 1, entries 4 and 5). Several other metal chlorides such as  $\text{FeCl}_3$ ,  $\text{LaCl}_3$ ,  $\text{CuCl}_2$ , and  $\text{NiCl}_2$  were tested. Much lower yields of HMF were obtained (Table 1, entries 6-9). However, when  $\text{AlBr}_3$  and  $\text{AlI}_3$  were used, high yields of HMF were achieved (Table 1, entries 10 and 11). In particular, when 20 mol%  $\text{AlI}_3$  was used, HMF was obtained with a yield of 50% (Table 1, entry 12). Therefore,  $\text{AlI}_3$  was selected as the catalyst for the following study. Furthermore, a blank experiment was conducted without adding any metal chloride and only little HMF was obtained (Table 1, entry 13).

**Table 1.** Conversion of Glucose to HMF Catalyzed by Metal Halides <sup>a</sup>

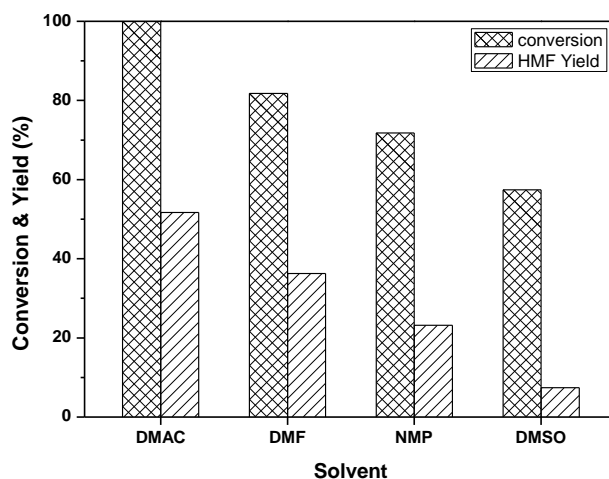
Entry	Metal chloride	T ( $^\circ\text{C}$ )	t (min)	Yield (%) <sup>b</sup>
1	$\text{AlCl}_3$	100	15	6
2	$\text{AlCl}_3$	130	15	36
3	$\text{AlCl}_3$	130	240	39
4	$\text{GaCl}_3$	130	15	29
5	$\text{InCl}_3$	130	15	22
6	$\text{FeCl}_3$	130	15	10
7	$\text{LaCl}_3$	130	15	9
8	$\text{CuCl}_2$	130	15	9
9	$\text{NiCl}_2$	130	15	6
10	$\text{AlBr}_3$	130	15	44
11	$\text{AlI}_3$	130	15	46
12 <sup>c</sup>	$\text{AlI}_3$	130	15	50
13	-	130	15	5

<sup>a</sup> Reaction conditions: 0.5 mmol glucose, 0.05 mmol metal chloride, 2 mL DMAC.  
<sup>b</sup> GC yields.  
<sup>c</sup> 0.1 mmol  $\text{AlI}_3$  was used.

The effect of reaction temperature on the conversion of glucose to HMF was optimized. As shown in Fig. 1, from  $90^\circ\text{C}$  to  $120^\circ\text{C}$ , higher reaction temperatures gave higher conversion and HMF yields. When the reaction was performed at  $120^\circ\text{C}$ , glucose conversion reached over 99%, and HMF was obtained with a yield of 52%. An increase in the temperature to  $130$ - $150^\circ\text{C}$  gave slightly decreased yields of HMF. Moreover, the increase of temperature generated more dark-brown insoluble solid polymers, commonly known as humin (Binder and Raines 2009), originating from the side-reaction of the decomposition of glucose. Thus, to avoid the formation of humin, the optimized temperature was set at  $120^\circ\text{C}$ .



**Fig. 1.** Effect of temperature on the conversion of glucose to HMF catalyzed by  $\text{AlI}_3$ . Reaction conditions: 0.5 mmol glucose, 0.1 mmol  $\text{AlI}_3$ , 2 mL DMAC, 15 min

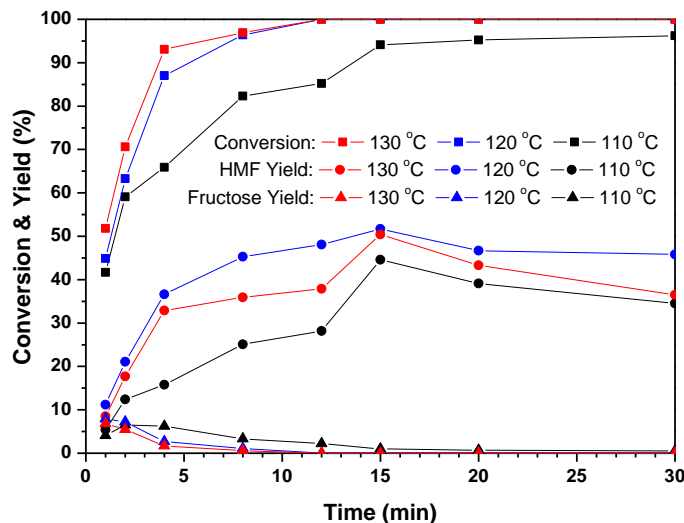


**Fig. 2.** Effect of solvent on the conversion of glucose to HMF catalyzed by  $\text{AlI}_3$ ; Reaction conditions: 0.5 mmol glucose, 0.1 mmol  $\text{AlI}_3$ , 2 mL Solvent, 120°C, 15 min

Conversions of glucose to HMF over  $\text{AlI}_3$  in different solvents were conducted. The polar aprotic solvents that have good solubility for glucose, such as DMAC, *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), and dimethyl sulfoxide (DMSO), were investigated. As shown in Fig. 2, solvents remarkably influenced the catalytic efficiency. The effect of solvents on glucose conversion and HMF yield were in the order DMAC > DMF > NMP > DMSO. Neither levulinic acid nor formic acid (the rehydration products of HMF) was detected in the reaction mixtures, which indicated that the rehydration side reaction of HMF was prevented.

The effect of reaction time on the conversion of glucose to HMF at 120°C was investigated, and the results are shown in Fig. 3. Glucose conversion increased in the course of the reaction and reached over 99% in 30 min. The maximal HMF yield of 52%

was obtained in 15 min. Fructose was detected. Initially, fructose yield reached 8% in 1 min, and then decreased slowly until no fructose could be detected in 30 min. The variation of glucose conversion and HMF yield with reaction time was also investigated at 110°C and 130°C, and the results were similar to those obtained at 120°C.



**Fig. 3.** Variation of glucose conversion, HMF yield, and fructose yield with reaction temperature and time; Reaction conditions: 0.5 mmol glucose, 0.1 mmol  $\text{AlI}_3$ , 2 mL DMAC

In the reaction of converting glucose to HMF, water was produced.  $\text{AlI}_3$  was probably hydrolyzed to aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ) and hydroiodic acid (HI), which might also catalyze the conversion of glucose to HMF. In order to clarify whether  $\text{Al}(\text{OH})_3$  or HI catalyzed this reaction, some comparison experiments were conducted. The results are listed in Table 2. Both  $\text{Al}(\text{OH})_3$  and HI were found to be inactive, no matter whether they were used alone or together, suggesting that  $\text{AlI}_3$  itself, not its hydrolyzed products, catalyze the conversion of glucose to HMF.

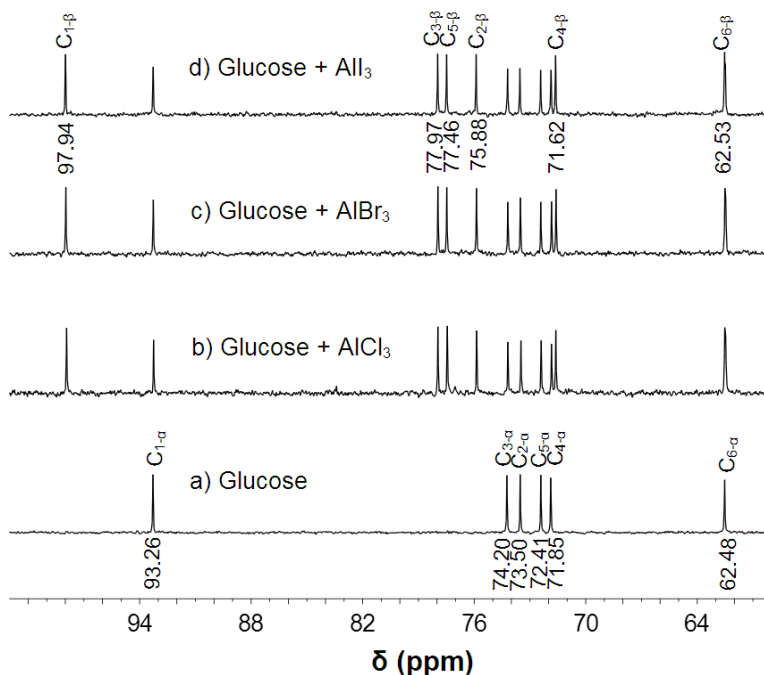
**Table 2.** Effects of  $\text{AlI}_3$  and its Hydrolyzed Products on Converting Glucose to HMF<sup>a</sup>

Entry	Catalyst	Yield (%) <sup>b</sup>
1	0.1 mmol $\text{AlI}_3$	52
2	0.1 mmol $\text{Al}(\text{OH})_3$	3
3	0.3 mmol HI	3
4	0.1 mmol $\text{Al}(\text{OH})_3$ + 0.3 mmol HI	3

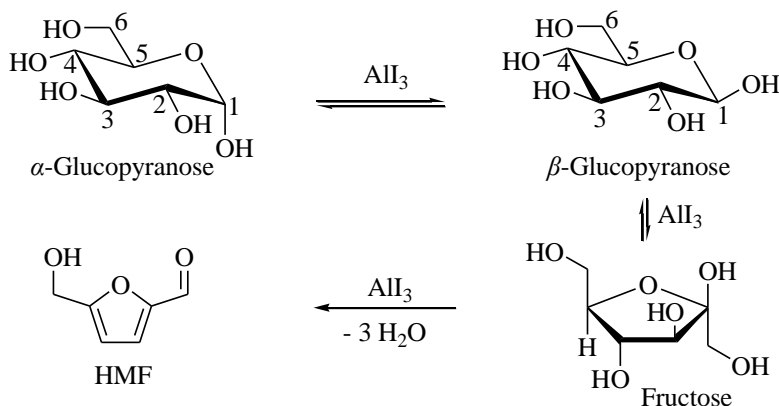
<sup>a</sup> Reaction conditions: 0.5 mmol glucose, 2 mL DMAC, 120°C, 15 min.  
<sup>b</sup> GC yields.

To gain more insight into the process for glucose conversion to HMF catalyzed by  $\text{AlI}_3$ , we collected a series of  $^{13}\text{C}$  NMR spectra of glucose in DMAC under different conditions (Fig. 4). It can be seen from Fig. 4a that in DMAC at 120°C for 1 min, glucose was in the  $\alpha$ -glucopyranose form. The six peaks appearing in Fig. 4a belong to the six carbons of  $\alpha$ -glucopyranose. When  $\text{AlI}_3$  was added, a mixture of  $\alpha$ -glucopyranose and  $\beta$ -glucopyranose was obtained. The twelve peaks in Fig. 4d belong to six carbons of  $\alpha$ -glucopyranose and six carbons of  $\beta$ -glucopyranose (Duquesnoy *et al.* 2008; Roslund *et al.*

2008). This indicated that  $\text{AlI}_3$  promoted the mutarotation of  $\alpha$ -glucopyranose to  $\beta$ -glucopyranose. Similarly, it can be seen from Figs. 4b and 4c that  $\text{AlBr}_3$  and  $\text{AlCl}_3$  also promoted the mutarotation of  $\alpha$ -glucopyranose to  $\beta$ -glucopyranose.



**Fig. 4.**  $^{13}\text{C}$  NMR spectra of 0.5 mmol glucose in 2 mL DMAC (with  $\text{d}_6$ -DMSO as external standard) at  $120^\circ\text{C}$  for 1 min under different conditions: a) without  $\text{AlX}_3$ ; b) in the presence of 0.1 mmol  $\text{AlCl}_3$ ; c) in the presence of 0.1 mmol  $\text{AlBr}_3$ ; d) in the presence of 0.1 mmol  $\text{AlI}_3$



**Scheme 1.** Speculated reaction route of conversion of glucose to HMF catalyzed by  $\text{AlI}_3$

It should be noted that fructose was obtained during the reaction process. However, no fructose was obtained in the absence of  $\text{AlX}_3$  under the same conditions, which indicated that  $\text{AlI}_3$  could promote the isomerization of glucose to fructose. To clarify whether  $\text{AlI}_3$  can catalyze the dehydration of fructose to HMF, an experiment with fructose as feedstock was conducted, and HMF was obtained with a yield of 54%, while only little HMF was obtained in the absence of  $\text{AlI}_3$ . These results clearly indicated that  $\text{AlI}_3$  could catalyze the dehydration of fructose to HMF. On the basis of the NMR study and the experiments described above, a speculated reaction route is proposed in Scheme 1.

Potentially catalytic applications in conversion of various carbohydrates and reaction mechanism investigation are currently under study.

## CONCLUSIONS

1. Aluminum halides in DMAC can provide a simple and efficient system for converting glucose to HMF. The catalytic performance of aluminum halides decreases in the order of  $AlI_3 > AlBr_3 > AlCl_3$ . When  $AlI_3$  in DMAC was used, HMF was obtained with a yield of 52% at 120°C in 15 min.
2.  $^{13}C$  NMR spectra indicated that aluminum halides could promote the mutarotation of  $\alpha$ -glucopyranose to  $\beta$ -glucopyranose.
3. HPLC and comparison experiments indicated that  $AlI_3$  could promote the isomerization of glucose to fructose and catalyze the dehydration of fructose to HMF.

## ACKNOWLEDGMENTS

The authors are grateful for support from Main Direction Program of Knowledge Innovation of Chinese Academy of Science, Grant. No. KSCX2-EW-G-5; and the National Natural Science Foundation of China, Grant. No. 21233008, 1273231 and 21073184.

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Article submitted: October 12, 2012; Peer review completed: December 21, 2012;  
Revised version received: January 30, 2013; February 1, 2013; Published: February 4, 2013.