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Dehydration of Carbohydrates to 5-Hydroxymethylfurfural in Ionic Liquids Catalyzed by Hexachlorotriphosphazene†

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Development of efficient catalysts for the dehydration of carbohydrates to produce 5-hydroxymethylfurfural (HMF) is a very attractive topic. In this work, dehydration of fructose catalyzed by three organic molecules, including hexachlorotriphosphazene ($N_3P_3Cl_6$), trichloromelamine ($C_3N_6H_3Cl_3$) and *N*-bromosuccinimide (NBS), was studied in ionic liquids. It was discovered that the three organic molecules had high activity in accelerating the dehydration of fructose and $N_3P_3Cl_6$ was the most efficient catalyst among them. The effects of amount of catalysts, temperature, solvents, reaction time, and substrate/solvent weight ratio on the reaction were investigated using $N_3P_3Cl_6$ as the catalyst and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) as the solvent. It was demonstrated that the $N_3P_3Cl_6$/[Bmim]Cl catalytic system was very effective for catalyzing the reaction. The yield of HMF could reach 92.8% in 20 min at the optimized conditions and the $N_3P_3Cl_6$/[Bmim]Cl system could be reused. Further study indicated that the $N_3P_3Cl_6$/[Bmim]Cl system was also effective for the dehydration of sucrose and inulin and satisfactory yield could be obtained at suitable conditions.

Keywords carbohydrates, 5-hydroxymethylfurfural, dehydration, hexachlorotriphosphazene, ionic liquids

Introduction

With growing concerns about global climate change and energy security, the research for sustainable, alternative energy has attracted more and more attentions.[1] Renewable and abundant biomass resources are promising alternatives for the sustainable supply of liquid fuels and valuable intermediates,[2] and the biomass-derived carbohydrates are potential chemical feedstocks.[3] However, efficient methods to transform carbohydrates into useful organic compounds need to be developed. Dehydration of carbohydrates to produce 5-hydroxymethylfurfural (HMF) is one of the most successful routes for biomass transformation because HMF is considered to have the potential to be a sustainable substitute for petroleum-based building blocks.[4]

Catalysis is crucial for effective dehydration of carbohydrates to produce HMF. Up to now, many catalysts have been developed, such as mineral acids,[5] lanthanide chlorides,[6] stannous chloride,[7] chromium chlorides,[8] tungsten salts,[9] germanium chloride,[10] aluminium chloride,[11] boric acid,[12] heteropoly acids,[13] strong acid cation exchange resins,[14] Tin-Beta Zeolite,[15] acid-functionalized SBA-15,[16] sulfated zirconia,[17] ionic liquid (IL) supported on silica nanoparticles,[18] imidazolium salts,[19] and so on. In addition, different reaction media, including water,[20] organic solvents,[21] ILs,[22] and water/organic biphasic systems,[23] have been used in the dehydration reactions. ILs are among promising media because they have some unique properties, such as negligible vapor pressure, nonflammability, high thermal and chemical stability, and adjustable solvent power for organic and inorganic substances.[24]

1,3,5-Triazo-2,4,6-triphosphorine-2,2,4,4,6,6-tetrachloride, commonly called as hexachlorotriphosphazene ($N_3P_3Cl_6$), has been widely used as the catalyst in organic reactions,[25] such as Beckmann rearrangement of ketoximes to lactams,[26] oxidation of sulfides and deoxygenation of sulfoxides,[27] and N-alkylation of amines with alcohols.[28]

Exploration of highly efficient catalysts for the synthesis of HMF from dehydration of carbohydrates under mild reaction conditions is still highly desirable, although many catalytic systems have been developed. In this work, we conducted the dehydration reaction using $N_3P_3Cl_6$ as the catalyst in ILs under mild reaction conditions. It was demonstrated that $N_3P_3Cl_6$ could catalyze the dehydration of carbohydrates very effectively. To the best of our knowledge, this is the first application of

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$N_3P_3Cl_6$ to catalyze the dehydration of carbohydrates to produce HMF.

Experimental

Materials

Fructose, sucrose, inulin, glucose, hexachlorotriphosphazene ($N_3P_3Cl_6$), trichloromelamine ($C_3N_6H_3Cl_3$), and *N*-bromosuccinimide (NBS) were all A. R. grade and were purchased from Alfa Aesar. Dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were A. R. grade and were obtained from Beijing Chemical Reagent Company. The ILs 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim]BF_4$), and 1-butyl-3-methylimidazolium hexafluorophosphoate ($[Bmim]PF_6$) were provided by Lanzhou Greenchem ILS, LICP, CAS, China, and their purity was ＞99%. All chemicals were used as received.

Analysis methods

The amount of HMF was analyzed by HPLC with Supelcosil LC-18 5ìm column at 30 ℃, Shimadzu LC-20AT pump, Sama UV-Vis LC-830 detector at 282.0 nm. Before analysis, the reaction mixture was diluted to 1000 mL. Methanol/water solution (50/50 *V*/*V*) was used as the mobile phase at 0.8 mL/min.

Catalytic reaction

Conversion of fructose into HMF In a typical experiment, known amounts of fructose and $N_3P_3Cl_6$ were dissolved in the solvent in a flask of 10 mL sealed with a glass stopper. The mixture was stirred at a fixed temperature for desired time. Then the mixture was cooled to room temperature immediately. The samples were analyzed by HPLC to obtain the yields. Each reaction was repeated at least two times. In the experiments to test the reusability, 1 mL of water was added into the reaction system after the reaction. Then the mixture was extracted 5 times with 50 mL of ether. After extraction, the water in the $N_3P_3Cl_6$/IL mixture was removed under reduced pressure at 80 ℃. It was then used directly for the next run by adding new fructose.

Conversion of sucrose, inulin and glucose in [Bmim]Cl In an experiment, suitable amounts of reactant and $N_3P_3Cl_6$ were dissolved in the IL (2 g) in a flask of 10 mL sealed with a glass stopper. The mixture was stirred at 80 ℃ for a desired time. Then the mixture was cooled to room temperature immediately. The sample was analyzed by HPLC to obtain the yields. Each reaction was repeated at least two times.

Calculation of 5-HMF yield The yield of 5-HMF was calculated by the following equation:

$$\text{5-HMF yield (mol\%)} = \frac{\text{Moles of 5-HMF formed}}{\text{Moles of fructose used}} \times 100\%$$

Results and Discussion

Reaction with various catalysts

The activity of various catalysts for the dehydration of fructose (Scheme 1) was tested at 80 ℃ in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), and the results are summarized in Table 1. It can be seen from Table 1 that nearly no product was produced without catalyst (entry 1). It was shown that three types of organic molecules (Scheme 2), $N_3P_3Cl_6$, trichloromelamine ($C_3N_6H_3Cl_3$), and *N*-bromosuccinimide (NBS), could catalyze the dehydration of fructose to produce HMF effectively, and $N_3P_3Cl_6$ had the best activity among them. Therefore, $N_3P_3Cl_6$ was used to study the effects of various conditions on the reaction, and the results are discussed in the following.

Scheme 1 Dehydration of fructose to produce HMF

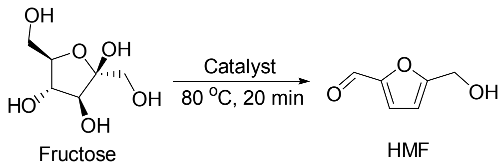
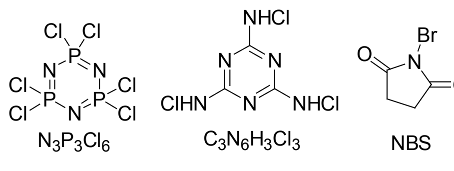


Table 1 Dehydration of fructose catalyzed by various catalysts in IL [Bmim]Cl [a]

Entry	Catalyst	Yield[b]/%
1	None	0.1
2	$N_3P_3Cl_6$	92.8
3	$C_3N_6H_3Cl_3$	90.1
4	NBS	82.3
5[c]	$N_3P_3Cl_6$	90.3
6[d]	$N_3P_3Cl_6$	89.5
7[e]	$N_3P_3Cl_6$	88.8
8[f]	$N_3P_3Cl_6$	87.5

[a] Reaction conditions: 0.1 g fructose, 5 mg catalyst, 2 g [Bmim]Cl, reaction time 20 min, reaction temperature 80 ℃. [b] Yields were determined by HPLC. [c] Recycled $N_3P_3Cl_6$/IL from Entry 2. [d] Recycled $N_3P_3Cl_6$/IL from Entry 5. [e] Recycled $N_3P_3Cl_6$/IL from Entry 6. [f] Recycled $N_3P_3Cl_6$/IL from Entry 7.

Scheme 2 The structures of the three catalysts



Effect of solvents

We studied the effect of different solvents on the reaction and the results are shown in Figure 1. The reaction did not occur when water was used as the solvent due to the poor solubility of $N_3P_3Cl_6$ in water. High yields of HMF were obtained in dimethylformamide

(DMF) and dimethylsulfoxide (DMSO), and the yields were 65.5% and 80.7%, respectively. We also studied the reaction catalyzed by $N_3P_3Cl_6$ in other two ILs, ([Bmim]BF_4) and ([Bmim]PF_6). All the results are presented in Figure 1. It can be known from the figure that an HMF yield of 92.8% was achieved in [Bmim]Cl. The HMF yield in [BMim]PF_6 was very low because of the insoluble nature of fructose in the IL.

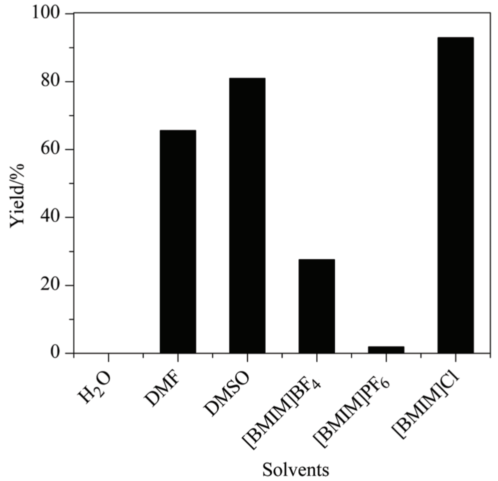


Figure 1 Effect of different solvents on the yield of HMF. Reaction conditions: 0.1 g fructose, 5 mg $N_3P_3Cl_6$, 2 g solvents, reaction temperature 80 ℃, reaction time 20 min.

Effect of catalyst amount

The results above indicate that $N_3P_3Cl_6$/[Bmim]Cl was the most efficient catalytic system studied in this work. The influence of the amount of $N_3P_3Cl_6$ in the system on the dehydration of fructose to HMF was investigated at 80 ℃ with a reaction time of 20 min (Figure 2). As shown in Figure 2, the yield of HMF increased to a maximum of 92.8% with an increase in the amount of $N_3P_3Cl_6$ from 0 to 5 mg and then slowly decreased to 84.5% with further increase of the amount of $N_3P_3Cl_6$ from 5 to 20 mg. The results suggest that smaller amount of the catalyst resulted in slower reaction rate and excess catalyst could cause the side reactions such as polymerization and rehydration of products. Therefore, 5 mg of the catalyst would be an appropriate amount at the reaction conditions.

Influence of reaction temperature

Figure 3 shows the effect of reaction temperature on the dehydration of fructose to produce HMF in [Bmim]Cl catalyzed by $N_3P_3Cl_6$ in the temperature range of 70 to 120 ℃, and the reaction time was 20 min. The maximum yield occurred at 80 ℃. Increase of reaction temperature affected the reaction in two opposite ways. First, the dehydration reaction was accelerated by increasing temperature, which was favorable to achieving high yield. At the same time, the side reactions were also enhanced by rising temperatures. The competition of the two opposite factors led to the largest yield at 80 ℃.

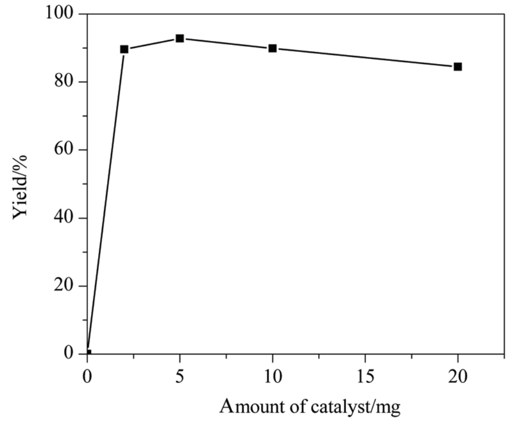


Figure 2 Effect of catalyst amount on the yield of HMF. Reaction conditions: 0.1 g fructose, 2 g [Bmim]Cl, reaction temperature 80 ℃, reaction time 20 min.

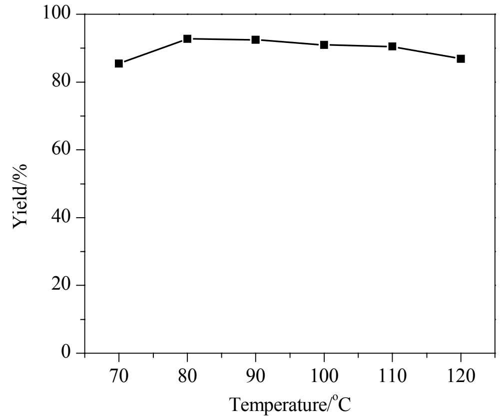


Figure 3 Influence of reaction temperature on the reaction. Reaction conditions: 0.1 g fructose, 2 g [Bmim]Cl, 5 mg $N_3P_3Cl_6$, reaction time 20 min.

Effect of reaction time

The dependence of the yield of HMF on reaction time is presented in Figure 4. The reaction was performed in the presence of 5 mg $N_3P_3Cl_6$ at 80 ℃ in [Bmim]Cl. The yield increased dramatically at the beginning, and reached the maximum at 20 min. Then the yield decreased slightly with reaction time. The main reason was that the conversion of fructose increased at the beginning, and prolonged reaction time resulted in rehydration of the HMF produced. Therefore, the maximum yield occurred at 20 min.

Influence of substrate/solvent weight ratio

The dependence of HMF yield on the fructose/[Bmim]Cl weight ratio was also investigated and the results are demonstrated in Figure 5. The yield of HMF decreased continuously with the increasing substrate/solvent weight ratio. This is easy to understand because the amount of the catalyst was fixed in all the experiments. However, the yield of HMF was still as high as 80.1% at the fructose/[Bmim]Cl weight ratio of

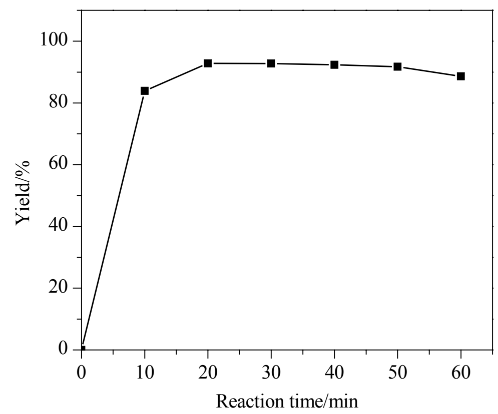


Figure 4 Effect of reaction time on the reaction. Reaction conditions: 0.1 g fructose, 2 g [Bmim]Cl, 5 mg $N_3P_3Cl_6$, reaction temperature 80 ℃.

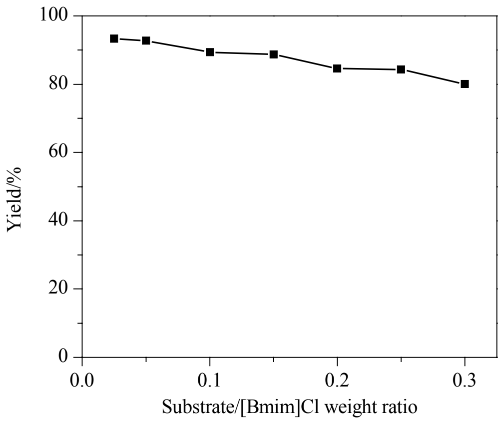


Figure 5 Influence of substrate/solvent weight ratio on the reaction. Reaction conditions: reaction temperature 80 ℃, reaction time 20 min.

0.3∶1.

The reusability of catalyst system

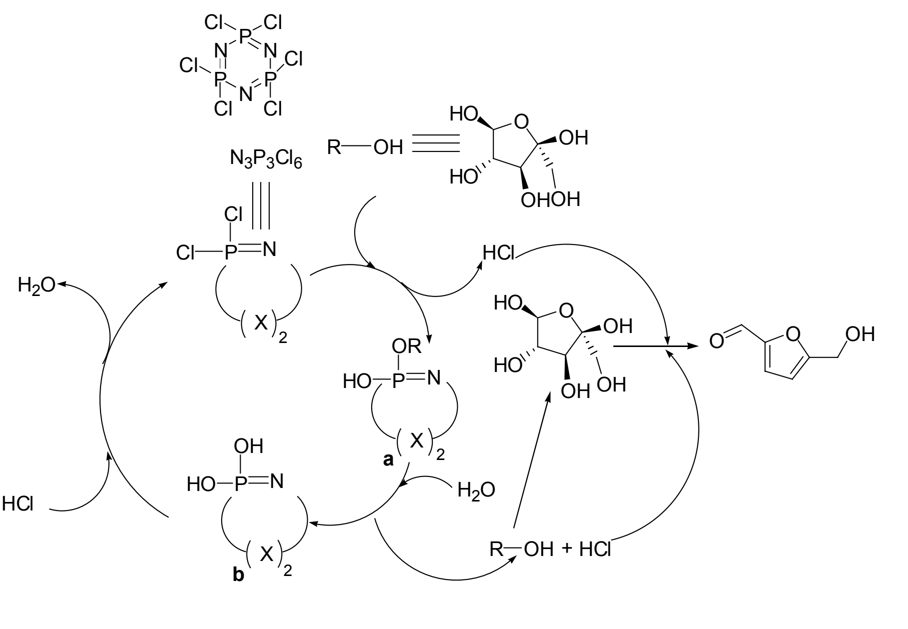
The reusability of the $N_3P_3Cl_6$/[Bmim]Cl catalytic system was studied in this work. After the reaction, the product was extracted by ether, and the catalytic system was used directly for the next run after drying, as described in the Experimental section. The results are also listed in Table 1 (Entries 1, 5—8). It can be seen that the decrease of the activity of the catalyst system was not considerable after reused five times.

Reaction mechanism

As shown in Figure 1, solvents had important impact on dehydration of fructose to HMF. Therefore, we thought that the imidazolium ILs played an important role in the catalyitc cycle. Imidazolium molecules may take the role of activating the reactants and stabilizing the products of each step through hydrogen-bonding interactions, which had been reported previously.[22c,29]

$N_3P_3Cl_6$ was easily nucleophilically attacked by O or N in functional group to generate HCl.[25-28] Based on the experimental results and discussions above, a plausible reaction mechanism for the dehydration of fructose catalyzed by $N_3P_3Cl_6$ was proposed, which is shown in Scheme 3. Firstly, the nucleophilic attack of fructose and water on $N_3P_3Cl_6$ leads to HCl, which is the catalyst for the dehydration of fructose. Then, the HCl catalyzed the dehydration reaction to produce HMF. In the catalytic cycle, the IL may interact with fructose and the intermediates through hydrogen bonding and nucleophilic effect to activate fructose and stabilize intermediates, which leads to the production of HMF with high selectivity.[22c,29] Finally, HCl reacted with intermediates **a** and **b** to regenerate the catalyst.

Scheme 3 The plausible reaction mechanism for the dehydration of fructose catalyzed by $N_3P_3Cl_6$



Dehydration of other carbohydrates

The $N_3P_3Cl_6$/[Bmim]Cl catalytic system was also used to catalyze the dehydration of other carbohydrates, and the results are illustrated in Figure 6. As expected, the sucrose (Scheme 4a) and inulin (Scheme 4b) with fructose unit in the molecular structures gave moderate HMF yields of 47.9% and 52.4%, respectively. Reaction times for reaching the maximum HMF yield for sucrose and inulin were 30 min and 60 min, respectively. However, the catalyst system had poor activity for the dehydration of glucose (Scheme 4c) to produce HMF, and the yield was only 1.3% after a reaction time of 120 min.

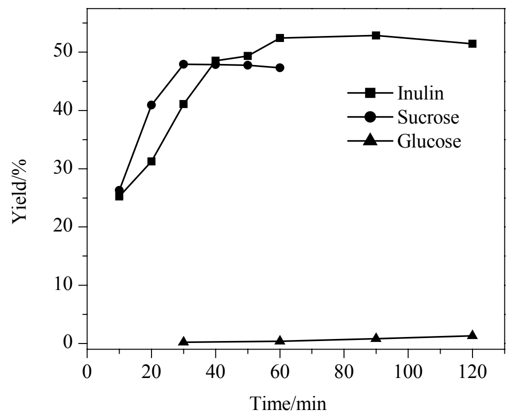
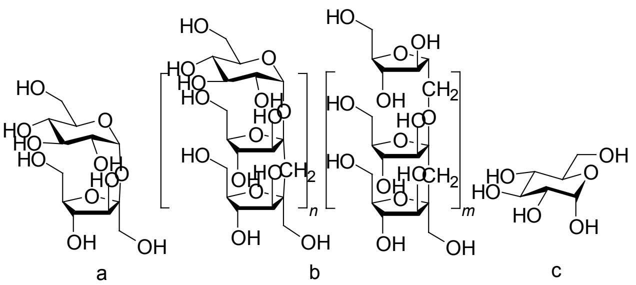


Figure 6 Dehydration of different carbohydrates. Reaction conditions: 0.1 g carbohydrates, 5 mg $N_3P_3Cl_6$, 2 g [Bmim]Cl, reaction temperature 80 ℃.

Scheme 4 The structures of sucrose (a), inulin (b) and glucose (c)



Conclusions

In summary, organic molecules $N_3P_3Cl_6$, $C_3N_6H_3Cl_3$, and NBS are very effective catalysts for the dehydration of fructose to produce HMF using [Bmim]Cl as the solvent, and the $N_3P_3Cl_6$ has the highest activity among them. Very high yield of 92.8% has been achieved at 80 ℃ with a reaction time of 20 min, and the $N_3P_3Cl_6$/[Bmim]Cl catalytic system can be reused at least five times without considerable reduction of the activity. In addition, the catalytic system can also promote the dehydration of sucrose and inulin to produce HMF efficiently. We believe that the simple, highly effective catalytic system has great potential of application in producing HMF by dehydration of the carbohydrates.

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