Carbohydrate Polymers 88 (2012) 891–895

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Conversion of fructose into 5-HMF catalyzed by $GeCl_4$ in DMSO and [Bmim]Cl system at room temperature

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ARTICLE INFO

Article history:
Received 22 November 2011
Received in revised form 4 January 2012
Accepted 11 January 2012
Available online 20 January 2012

Keywords:
Fructose
Germanium(IV) chloride
Ionic liquids
Dehydration
5-Hydroxymethylfurfural

ABSTRACT

Conversion of fructose into 5-hydroxymethylfurfural (HMF) catalyzed by Germanium(IV) chloride was studied in Dimethyl sulfoxide (DMSO) and [Bmim]Cl system at room temperature. The structure of ionic liquids and the ratio of ionic liquids to DMSO had a remarkable effect on this new catalytic system. The results indicated that 1-*n*-butyl-3-methylimidazolium chloride ([Bmim]Cl) was favorable for the dehydration of fructose to HMF. Under optimal conditions, a high HMF yield in 70% was obtained at 25 °C. In addition, it was also proved that there was a synergistic effect between the cation and anion of [Bmim]Cl on the dehydration of fructose to HMF by designed experiments. Finally, a possible mechanism for the dehydration of fructose to HMF was proposed.

1. Introduction

Concerns about global warming and energy crisis have led to the exploration of alternatives for fossil resources to supply chemicals and energy. Biomass with an estimated global production of around 1.0×10^{11} tons per year has attracted considerable attention as an alternative source for both fuels and chemicals (Mohamad Ibrahima, Zakariaa, Sipautb, Sulaimanc, & Hashimc, 2011). Carbohydrates represent the major portion of biomass and catalytic conversion of carbohydrates into high-value chemicals and fuels is important both in science and commerce (Huber, 2005).

Recently, extensive research and development programs have been initiated worldwide to convert carbohydrates into valuable products such as monosaccharides, furfural, 5-hydroxymethylfurfural (HMF) and levulinic acid (El-Zawawya, Ibrahima, Abdel-Fattahb, Solimanb, & Mahmoudc, 2011; Wu et al., 2010). Among the downstream products, HMF, currently derived from petrochemicals, has been recognized as a versatile and key precursor for the production of fine chemicals, polymeric materials and biofuels (Zakrzewska, Bogel-Łukasik, & Bogel-Łukasik, 2011). In the past few decades, the preparation of HMF through the dehydration of biomass-based sugars received much attention. In the case of fructose, acid catalysts were always used for the production of HMF either in water, organic phase, or biphasic phase (Kuster, 1990; Roman-Leshkov, Chheda, & Dumesic, 2006). The reaction temperature often reached near or above 100 °C, and the yields of HMF were low. It is acceptable that some side reactions such as HMF decomposition and oligomerization are always present under acidic conditions and high temperatures (Kuster, 1990).

Recently, ionic liquids (ILs) have attracted much attention due to their unusual properties, such as a wide liquid range, high ionic conductivity, a wide voltage window, non-volatility, and non-flammability (Abedin & Endres, 2007). Dehydration of fructose was studied in imidazolium based ILs with acid and metal salts as catalyst (Stahlberg, Fu, Woodley, & Riisager, 2011). It was reported that ILs may stabilize HMF in the reaction mixture and increase its selectivity. Zhao, Holladay, Brown, and Zhang (2007) carried out the dehydration of fructose to HMF in 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) with $CrCl_2$ as catalyst, and HMF was obtained in a yield of 83% for 3 h at 80 °C. Moreau and Lansalot-Matras (2003) also found that HMF was obtained in a yield up to 50% from the dehydration of fructose in $[Bmim]BF_4$ and $[Bmim]PF_6$ catalyzed by Amberlyst-15 for 3 h at 80 °C.

Moreover, acidic ionic liquids acting both as solvents and catalysts were also designed for the dehydration fructose to HMF (Hu et al., 2008; Moreau, Finiels, & Vanoye, 2006). Until now, most of these processes have been carried out above 80 °C, due to the high melting points of ILs and the viscous reaction mixture. Performing the reaction at a relatively high temperature would result in

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0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2012.01.032

high energy consumption and dangerous catalytic process. Fructose dehydration was recently demonstrated at 50 °C in 1-*n*-butyl-3-methylimidazole chloride ([Bmim]Cl)-tetrahydrofuran biphasic solvent system, using WCl_6 as catalyst with HMF yield in 63% for 6 h (Chan & Zhang, 2009). Later, Qi et al. developed a new method for fructose dehydration at room temperature by the addition of cosolvents such as acetone, DMSO, methanol, ethyl acetate into ILs using acidic resins (Qi, Watanabe, Aida, & Smith, 2009), and HMF yield was 80% with the mass ratio of fructose and catalyst at 1.

In our previous work (Zhang, Wang, Xie, Liu, & Zhao, 2011), it was found that $GeCl_4$ showed excellent catalytic activity for the dehydration of fructose in [Bmim]Cl, with HMF yield up to 92.1% for 5 min at 100 °C. To the best of our knowledge, it is the best result for the production of HMF from fructose in Lewis acids-ILs system. Although a good result was obtained, it is also desirable to carry out the dehydration of fructose at ambient temperature as one of the key goals among the twelve Principles of Green Chemistry. Herein, the dehydration of fructose to HMF was further carried out at room temperature in DMSO/ILs system. In addition, the effect of cations and anions of ILs was investigated, and it was found that both imidazolium cation and chloride anion have a synergistic and coordination interaction in promoting the dehydration of fructose.

2. Experiment

2.1. Materials

[Bmim]Cl and [Bmim]PF_6 were prepared according to the known procedures (Burrell, Del Sesto, Baker, McClesky, & Baker, 2007; Nara, Harjani, Salunkhe, Mane, & Wadgaonkar, 2003). [Bmim]OAc was purchased from Lanzhou Institute of Chemical Physics, CAS (Lanzhou, China). Fructose was purchased from Sanland-Chem International Inc. (Xiamen, China). Acetonitrile (HPLC grade) was purchased from Merck & Co. (Darmstadt, Germany). DMSO was purchased from J&K Co. Ltd. (Beijing, China). $GeCl_4$ was purchased from Sigma (St. Louis, USA). All other chemicals were supplied by local suppliers and used without further purification.

2.2. Typical procedure for the dehydration of fructose to HMF

A typical procedure for the dehydration of fructose is as follows: 100 mg fructose was initially added into 2.5 g DMSO/0.5 g [Bmim]Cl solvent, then 10 mol% $GeCl_4$ (based on fructose) was added, and the reaction was carried out at 25 °C for the desired time under atmospheric pressure with a magnetic stirrer. Samples were withdrawn, diluted with water, centrifuged at 10,000 rpm for 5 min and analyzed by a HPLC system.

2.3. Determination of HMF

HMF was determined by a HPLC method (Albalá-Hurtado, Veciana-Nogués, Izquierdo-Pulido, & Vidal-Carou, 1997). It was conducted on a Dionex system (Dionex Co., CA, USA) equipped with Dionex P680 four-unit pump and PDA-100 photodiode array detector. Samples were detected using a reversed-phase C18 column (200 mm × 4.6 mm) at 280 nm. The column temperature was maintained at 30 °C. The optimized mobile phase consisted of acetonitrile and 0.1 wt% acetic acid aqueous solution with the volume ratio at 15:85. The flow rate was set at 1.0 mL/min. The content of HMF in samples was obtained directly by interpolation from calibration curves, with the correlation coefficient of 0.999.

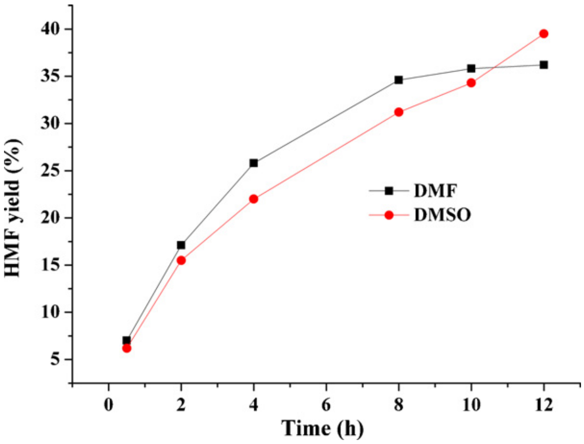

Fig. 1. The results of the dehydration of fructose to HMF catalyzed by $GeCl_4$ at 25 °C. Reaction conditions: fructose (100 mg) was added into DMSO or DMF (3.0 mL), then 10 mol% $GeCl_4$ was added.

3. Results and discussion

3.1. Conversion of fructose into HMF in DMSO and DMF catalyzed by $GeCl_4$ at 25 °C

It is known that the melting points of most ILs are higher than room temperature. For example, the most common ILs [Bmim]Cl has a melting point of 65 °C (Chen, Zhang, & Wang, 2011). Therefore, it is difficult to carry out chemical reactions at room temperature in [Bmim]Cl. It is known that some polar organic solvents have been extensively used for hexose dehydration for a long time (VanDam, Kieboom, & VanBekkum, 1986). In order to perform the dehydration of fructose catalyzed by $GeCl_4$ at room temperature, the dehydration process was firstly carried out in DMSO (Dimethyl sulfoxide) or DMA (Dimethylformamide). As fructose and $GeCl_4$ dissolved in DMSO and DMA, the reaction proceeded smoothly at 25 °C. Unfortunately, the efficiency of fructose dehydration was not satisfied in comparison with the previous results in [Bmim]Cl at 100 °C. The dehydration rate was slow in DMSO and DMF, and a maximum HMF yield was obtain approximately in 40% even with a prolonged reaction time of 12 h (Fig. 1). Nonetheless, to the best of our knowledge, dehydration of fructose has never been carried out in DMSO at 25 °C. Although the yield of HMF was not high, at least we have put forward the dehydration of fructose in DMSO at room temperature.

3.2. Conversion of fructose into HMF in DMSO with the addition of [Bmim]Cl catalyzed by $GeCl_4$ at 25 °C

It is reported that both the catalysts and the reaction environment had major effects on facilitating an efficient conversion of hexoses into HMF (Shanks, 2007). In recent years, the dehydration of hexoses in ILs catalyzed by metal chlorides was proved to be efficient. Therefore, it provides a possible chance that the efficiency of fructose dehydration in DMSO catalyzed by $GeCl_4$ at 25 °C will be improved by the addition of ILs. Herein, the influence of [Bmim]Cl on HMF yield was investigated, and the ratio of [Bmim]Cl to DMSO on the efficiency of fructose dehydration was systematically studied. In each experiment, the total mass of [Bmim]Cl and DMSO was kept at 3.0 g. As shown in Fig. 2, [Bmim]Cl has a profound effect. In comparison with the pure DMSO solution, adding 0.5 g [Bmim]Cl to 2.5 g DMSO made fructose dehydrate much more efficiently. In DMSO system, the yield of HMF was 15.5% at 2 h, whereas that was 37.5% at 2 h in 0.5 g [Bmim]Cl/2.5 g DMSO system. It indicated that [Bmim]Cl promoted the dehydration rate of fructose. Although HMF yield in DMSO system at the early stage was lower

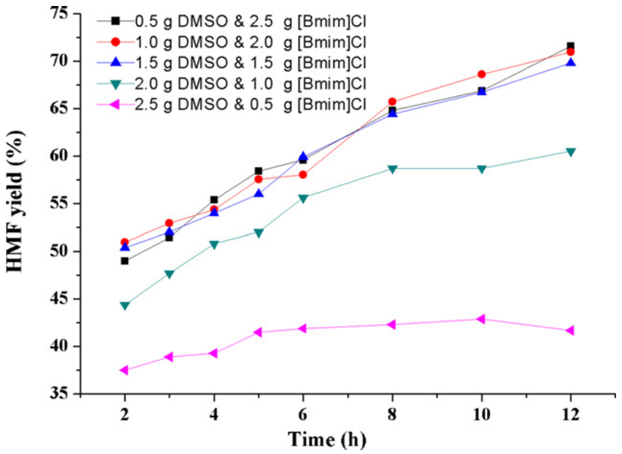

Fig. 2. The results of the dehydration of fructose to HMF catalyzed by $GeCl_4$ at 25 °C in different solvents. Reaction conditions: fructose (100 mg) was added into the mixture solvent of DMSO and [Bmim]Cl (3.0 g), then 10 mol% $GeCl_4$ was added.

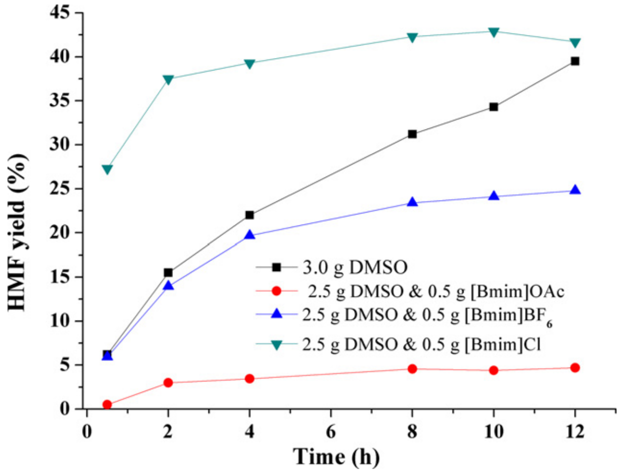

Fig. 3. The results of the dehydration of fructose to HMF catalyzed by $GeCl_4$ at 25 °C in DMSO with the addition of different ionic liquids. Reaction conditions: fructose (100 mg) was added into the solvent (3.0 g), then 10 mol% $GeCl_4$ was added at 25 °C.

than that in 0.5 g [Bmim]Cl/2.5 g DMSO, it slowly increased to 40% at 12 h. Whereas, the yield of HMF in 0.5 g [Bmim]Cl/2.5 g DMSO was almost kept stable with the extension of reaction time from 2 h to 12 h, and the maximum HMF yield was 42.9%. Some humins were precipitated out for the above two reaction systems, when the samples were diluted with water. The humins were formed through the polymerization and cross-polymerization of HMF and intermediates (Roman-Leshkov et al., 2006). The above results indicated that a little amount of [Bmim]Cl in DMSO could not improve the selectivity of HMF, only improving the dehydration rate. In order to improve HMF yield and get more insights into the effect of [Bmim]Cl, dehydration of fructose was carried out in several reaction mediums with different ratios of [Bmim]Cl to DMSO. With the increase mass ratio of [Bmim]Cl to DMSO, HMF yield increased sharply in the initial 2 h. When 2.0 g [Bmim]Cl/1.0 g DMSO was used, HMF yield reached 51.0% at 2 h. It should be noted that further increasing the mass ratio of [Bmim]Cl to DMSO at 2.5 g/0.5 g did not improve HMF yield in the initial 2 h, with HMF yield in 49.0%. This might be that a high concentration of [Bmim]Cl resulted in a high viscosity, which was not favorable for the mass transfer between the catalyst and the substrate. The maximum HMF yields for different solvent systems depend on the mass ratio of [Bmim]Cl to DMSO. The higher the mass ratio of [Bmim]Cl to DMSO, the higher the HMF yield. It was much more distinct when the mass of [Bmim]Cl was in a range of 0.5–1.5 g. Further increasing the mass of [Bmim]Cl from 1.5 g to 3 g, the maximum HMF yields were almost the same approximately in 70%. All of the results indicated that [Bmim]Cl indeed had a positive influence on fructose dehydration. Not only the dehydration rate of fructose was accelerated, but also HMF yield was improved in DMSO with the addition of [Bmim]Cl. It was clearly proved that [Bmim]Cl provided a superior reaction environment than organic solvents for the dehydration of hexoses. It was reported that imidazolium molecule may take the role of activating the reactants and stabilizing the products of each step through the hydrogen bonding interaction (Lai & Zhang, 2010). It is reported that the C-2 hydrogen of imidazolium ion exhibits acidic character, and it can catalyzed the dehydration of fructose at high temperature (Zhao et al., 2007). In order to exclude the effect of the acidic character of [Bmim]Cl, a control experiment was also carried out. The dehydration of fructose was carried out in 2.0 g [Bmim]Cl/1.0 g DMSO without $GeCl_4$ at 25 °C for 12 h, and a low yield of HMF only in 5.0% was obtain. The results clearly indicated that the $GeCl_4$ was the catalytic species.

3.3. Conversion of fructose into HMF in DMSO with the addition of different ionic liquids catalyzed by $GeCl_4$ at 25 °C

As [Bmim]Cl is composed of imidazolium cation and chloride anion, then which part plays the key role in the dehydration of fructose? In order to get a convincing answer to the proposed question, various ILs were used as cosolvents for fructose dehydration (Fig. 3). Firstly, imidazolium cation based ILs with two typical anions including 1-butyl-3-methylimidazolium acetate ([Bmim]OAc) and 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6) were found to be infertile. Both [Bmim]OAc and [Bmim]PF_6 did not improve HMF yield. Inversely, addition two of ILs in DMSO led to very low HMF yield especially in [Bmim]OAc/DMSO system. The yield of HMF was almost zero at 12 h, whereas the conversion of fructose reached 100% in [Bmim]OAc/DMSO system. It might be attributed to the possible side reactions between fructose and the imidazolium ring induced by the strong basic acetate group as described early for the reaction of glucose with imidazolium ring in [Bmim]OAc (Ebner, Schiehser, Potthast, & Rosenau, 2008). It was also found that [Bmim]PF_6 was not a good cosolvent for the dehydration of fructose. HMF yield in [Bmim]PF_6/DMSO was only 24.8% at 12 h, which was inferior to that in pure DMSO system (yield up to 39.5% at 12 h). It is challenge to recognize the difference between [Bmim]PF_6 and [Bmim]Cl in the process of fructose dehydration. As it is reported that [Bmim]PF_6 is not stable in the presence of water, it was assumed that water produced during the dehydration process would result in the decomposition of [Bmim]PF_6 to produce HF (Lenourry, Gardiner, & Stephens, 2005). Therefore, one possible reason for the lower HMF yield in [Bmim]PF_6/DMSO was that HF formed from [Bmim]PF_6 might lead to HMF further conversion into other by-products such as humins, levulinic acid (Kuster, 1990). In order to verify the possible reason of lower HMF yield in [Bmim]PF_6/DMSO, an extra experiment was carried out. 70 mg HMF was subjected in [Bmim]PF_6/DMSO with the addition of 30 mg H_2O (the amount was the theoretically value for 100 mg fructose dehydration) for 12 h at 25 °C, and HMF was recovered in 95.7% with 67 mg. The results clearly verified the lower HMF yield in [Bmim]PF_6/DMSO caused by HF was not true. As discussed in the mechanism part, chloride (Cl^-) acted as a nucleophilic reagent, which was beneficial for fructose dehydration (*vide infra*). It is known that the nucleophilicity of PF_6^- is weak. Therefore, it could not promote fructose dehydration in comparison with Cl^-, leading a relative lower HMF yield.

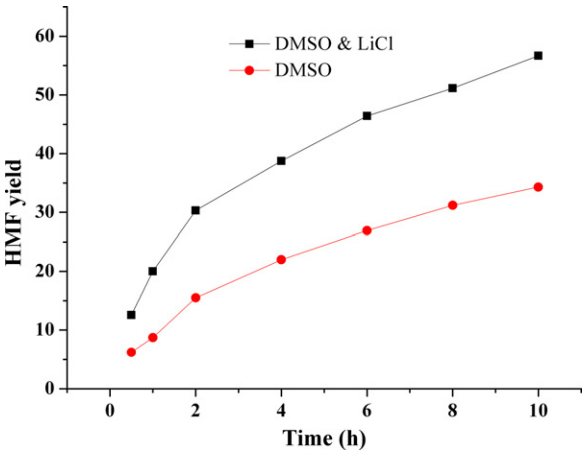

Fig. 4. The effect of chloride anion on the dehydration of fructose to HMF catalyzed by $GeCl_4$ at 25 °C. Reaction conditions: fructose (100 mg) was added into DMSO (3.0 mL) with or without addition of LiCl (23.6 mg), then 10 mol% $GeCl_4$ was added at 25 °C.

The results clearly indicated that anions of ILs had a remarkable effect on the dehydration of fructose. It is also reported that a moderate basicity and nucleophilicity of anions was required to obtain a high HMF yield (Binder & Raines, 2009). Therefore it is interesting to scrutinize the effect of chloride anion of [Bmim]Cl on the dehydration of fructose.

3.4. Conversion of fructose into HMF in DMSO with the addition of lithium chloride catalyzed by $GeCl_4$ at 25 °C

Finally, the effect of chloride anion was further investigated in order to get deep insights into the effect of [Bmim]Cl on the dehydration of fructose. Dehydration of fructose catalyzed by $GeCl_4$ should be carried out in DMSO only by the addition of chloride anion. As lithium chloride has a good solubility in DMSO, lithium chloride was selected as the source of chloride anion. As shown in Fig. 4, the chloride anion not only increased the dehydration rate, but also improved HMF yield. An equivalent amount of LiCl (based on fructose) in DMSO improved HMF yield from 39.5% to 56.8%. The results clearly indicated that chloride anion had a positive effect on HMF formation. Similar results were also found in recent work when treating corn stover with diluted inorganic salts and xylose in dilute aqueous solution (Liu, Sun, Cai, et al., 2009; Liu, Sun, Li, et al., 2009; Marcotullio & De Jong, 2010). Although chloride anion largely promoted the efficiency of fructose dehydration in DMSO, it should be noted that the yield of HMF was yet lower than that with the addition of [Bmim]Cl. Thus, it can be concluded that both the imidazolium cation and chloride anion have synergistic effect on the dehydration of fructose to HMF.

3.5. Possible mechanism of fructose conversion into HMF [Bmim]Cl/DMSO system

The above results encourage us to shed some light on the mechanism of the dehydration of fructose to HMF. It is reported that the cations of E14 elements can be stabilized thermodynamically by introduction of auxiliary NR_2 or OR groups (Kost et al., 2002). As the oxygen atoms in fructose have lone electron pairs, thus it is believed that the lone electron pairs of oxygen atoms in fructose are capable of bonding with Germanium center. As described in Fig. 5, the 2,3-dihydroxy group in α-D-fructose would be more steric favorable to bond with Germanium center to release the H^+. Then the 2-hydroxy group in the free fructose was activated by H^+, followed by the release of one H_2O with the aid of lone electron pair of oxygen in the furan ring. Therefore the intermediate of furanosyloxocarbenium ion was formed. As discussed in Section 3.4, we have already noted that the chloride anion had some positive effect on the dehydration of fructose. As discussed in the previous literature (Binder & Raines, 2009; Stahlberg, Sorensen, & Riisager, 2010), the chloride anion might have dual roles in the following dehydration step. One acts as a base, captures a proton connected with the C2 of fructose, and the other role acts as a nucleophile, attacks to the C2 of fructose. Then another intermediate enol was formed, which then converted into aldehyde through keto-enol tautomerism. Finally, two molecules of H_2O was released to produce HMF.

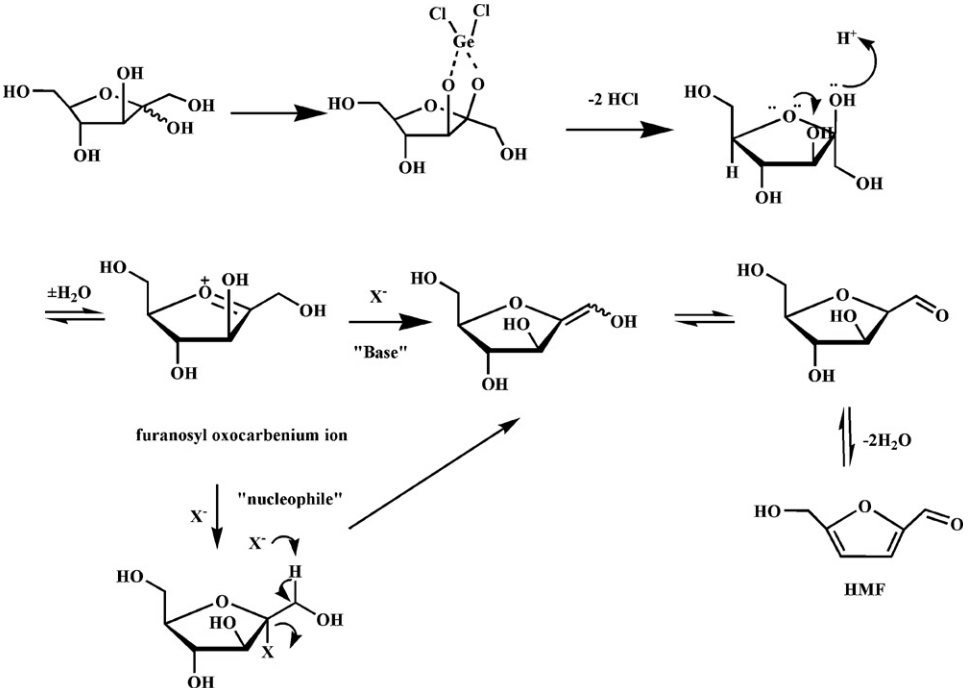

Fig. 5. Proposed mechanisms of the dehydration of fructose to HMF catalyzed by $GeCl_4$ in DMSO/[Bmim]Cl.

4. Conclusion

In this study, a new catalytic system based on Germanium(IV) chloride was developed for the dehydration of fructose to HMF at room temperature. Under optimal conditions, HMF was obtained in a high yield of 70% at 25 °C. It was proved that both the cations and anions of [Bmim]Cl played an important role in the dehydration of fructose to HMF, and a possible mechanism was proposed. Due to the low reaction temperature and low toxicity of Germanium species (VanDam et al., 1986), this new catalytic system would be valuable to facilitate energy efficient and cost-effective conversion of biomass into bio-based chemicals.

Acknowledgement

The project was supported by the Special Fund for Basic Scientific Research of Central Colleges, South-Central University for Nationalities (CQZ11024).

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