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Mechanism of 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed transformation of D-glucose to 5-hydroxymethylfurfural in DMSO: an NMR study

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ABSTRACT

The conversion of D-glucose to 5-hydroxymethylfurfural (HMF) in the presence of 5.48 mol % 1-(1-propylsulfonic)-3-methylimidazolium chloride acidic ionic liquid catalyst in DMSO at 150 °C was studied using ^{1}H, ^{13}C NMR, and visible spectroscopy. The HMF yield rapidly increases in the first 100 min of reaction, however yield drops beyond 100 min and levels off to a maximum yield of about 15.7% around 600 min. The visible spectroscopy study of the reaction mixture suggests that rate of HMF formation slows down after 100 min due to increase in the rate of humin formation after first 100 min. A mechanism has been proposed and key intermediates in the pathway could be identified by studying the ^{13}C NMR spectra of acidic ionic liquid catalyzed transformations of C-1 and C-2 ^{13}C labeled D-glucose under identical conditions. The proposed mechanism involves the isomerization of D-glucose to D-fructose via the complexation of the open chain sugar with the imidazolium cation of the acidic ionic liquid catalyst.

1. Introduction

The conversion of biomass derived hexoses to platform chemical 5-hydroxymethylfurfural (HMF) has become a current research topic since this furan has been identified as one of the primary renewable resources based feedstock chemicals. This six carbon bifunctional furan is considered as a precursor for several new generation platform chemicals including the potential terephthalic acid equivalent 2,5-furandicarboxylic acid for the production of a number of polymeric materials like polyesters, polyamides, and polyurethanes.[1–3] Dehydration of fructose could be used to produce HMF in high yield and this reaction is known with variety of catalysts or by heating in DMSO without an added catalyst; however one of the major drawbacks in the use of fructose as the starting material is its high cost.[3–5] In comparison, glucose is more abundant because it is the repeating unit of cellulose. Therefore, the conversion of glucose to HMF has attracted interest of many researchers in recent years. On the other hand, dehydration of glucose to HMF is difficult as it generally requires the isomerization to fructose before the dehydration. This isomerization can be carried out by Lewis acid catalysts and a number of research groups have published novel strategies focused on the isomerization of glucose to fructose with subsequent acid-catalyzed dehydration to HMF. Lewis acid catalysts in ionic liquids (ILs) have been shown to be the most promising systems for the conversion of glucose to HMF. Zhao et al. first reported HMF yields of 68−70% in a system using $CrCl_2$ catalyst in 1-ethyl-3-methyl-imidazolium chloride.[6] The high selectivity observed for the production of HMF in ionic liquids with chromium catalysts has been explained as a result of stabilization of the transition state for ring opening of glucose by the Lewis acidic Cr center during glucose isomerization. Later, Binder and Raines also demonstrated the use of $CrCl_2$ for the isomerization, where a mixture consisting of dimethylacetamide and LiCl was used as the solvent, and an 81% HMF yield was reported.[7] In addition to chromium, several other metal ions are also known in catalyzing glucose to fructose isomerization. Nikolla et al. reported a HMF yield of 57% at 79% conversion of glucose, using a Lewis acidic Sn-Beta zeolite and HCl in a water/NaCl/THF biphasic reaction system.[8] In another example, $AlCl_3{\cdot}6H_2O$ was used as the catalyst in a biphasic system where THF was the extracting solvent and Abu-Omar and co-workers reported an HMF yield of 62%.[9] Additionally, a number of Lewis acidic metal salts; 12-tungstophosphoric acid (12-TPA)/boric acid ($B(OH)_3$) in ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl),[10] $HfCl_4$-IL,[11] $Al(O^iPr)_3$-IL,[12] $CrCl_3{\cdot}6H_2O$–$B(OH)_3$–[BMIM]Cl,[13,14] Sn-Mont-THF/DMSO,[15] $Al(OTf)_3$,[16] TiO_2 nanoparticles,[17] $Ag_3PW_{12}O_{40}$,[18] $SnCl_4$–tetrabutyl ammonium bromide ($SnCl_4$–TBAB),[19] $IrCl_3/AuCl_3{\cdot}HCl$–[BMIM]Cl,[20] and $Zr(H_2PO_4)_2$[21] have been reported as catalysts for glucose–fructose isomerization followed by dehydration to HMF process. In a recent development Zhou et al. reported the use of a metallic ionic liquid, where they achieved a 53% yield of HMF from cellulose using chromium 1-(3-sulfonic acid) propane-3-methylimidazole hydrosulfate

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Table 1
The changes in α/β anomeric composition of D-glucose during the Brönsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed transformation of D-glucose to 5-hydroxymethylfurfural in DMSO

Time (min)	α/β
0.0	4.76
6.0	0.80
18.0	0.86
30.0	0.84
48.0	0.85

D-Glucose (45.0 mg) and 1-(1-propylsulfonic)-3-methylimidazolium chloride (3.3 mg) in 0.60 mL of DMSO-d_6 heated at 150 °C.

([PSMIM]HSO_4) in [BMIM]Cl.[22] Organo catalysis without a metal or Lewis acid catalyst is an attractive alternative due to toxicities of many of these metals and this is a relatively unexplored area. In one example, Ma and co-workers observed the production of HMF during the depolymerization of cellulose dissolved in BMIMCl, while using a sulfonic acid group functionalized acidic ionic liquid as the catalyst.[23]

The conversion of glucose to HMF can generally follow two reaction pathways as proposed by Dumesic and co-workers.[24] One pathway is through a Lewis acid catalyzed isomerization of glucose to fructose combined with the dehydration of fructose to HMF. The other pathway is through direct dehydration of glucose to HMF via a furan aldehyde intermediate.[24,25] Qian has studied Brönsted acid catalyzed dehydration of glucose to form HMF using CPMD-MTD simulation methods. According to his calculation, reactions are initiated by the protonation of C-2-OH to form a common 5-membered ring intermediate and dehydration occurs via the direct cyclic mechanism, rather than via the open chain mechanism converting glucose to fructose, then to HMF.[26]

Two recent NMR studies have shown the isomerization of glucose to fructose before the dehydration.[27,28] During these studies under hydrothermal reaction conditions in the 120–160 °C temperature range Matubayasi and co-workers found that D-glucose reversibly transformed first into D-fructose and subsequently to 5-HMF through a series of dehydration reactions.[27] In another study Davis and co-workers have reported the NMR evidence for mechanism involving Sn catalyzed glucose to fructose isomerization in water.[28] However, as far as we are aware there are no experimental mechanistic investigations on the Brönsted acidic ionic liquid catalyzed isomerization of glucose or dehydrations to HMF.

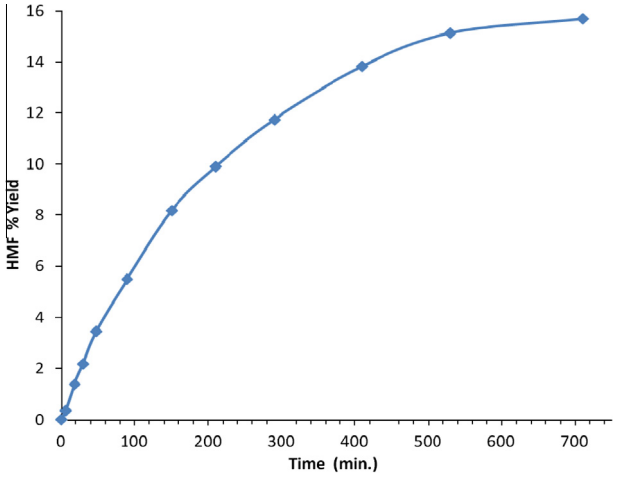

Figure 2. The changes of percent yields of 5-hydroxymethylfurfural (HMF) with time during the Brönsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed transformation of D-glucose to 5-hydroxymethylfurfural in DMSO. D-Glucose (45.0 mg) and 1-(1-propylsulfonic)-3-methylimidazolium chloride (3.3 mg) in 0.60 mL of DMSO-d_6 heated at 150 °C.

Our interest in the use of sulfonic acid group substituted Brönsted acidic ionic liquids as organo catalysts in the processing of carbohydrates and the mechanism of dehydration of C-6 sugars to HMF has led us to investigate the mechanism of dehydration of glucose to HMF using acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride as a catalyst in DMSO.[5,29–32] The acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride was chosen as the catalyst for the dehydration study because –SO_3H group functionalized imidazolium chloride type Brönsted acidic ionic liquids are known as the best non-metallic ionic liquid catalysts for dehydration of hexose sugars to HMF.[23]

2. Results and discussion

1-(1-Propylsulfonic)-3-methylimidazolium chloride catalyzed decomposition of D-glucose in DMSO-d_6 was studied by NMR

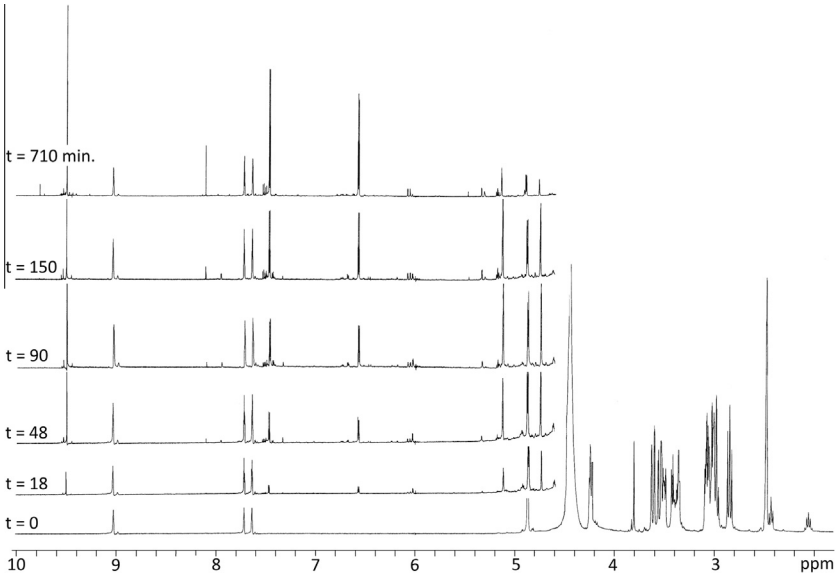

Figure 1. The changes in ^{1}H NMR spectra during Brönsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed transformation of D-glucose to 5-hydroxymethylfurfural in DMSO. D-Glucose (45.0 mg) and 1-(1-propylsulfonic)-3-methylimidazolium chloride (3.3 mg) in 0.60 mL of DMSO-d_6 heated at 150 °C.

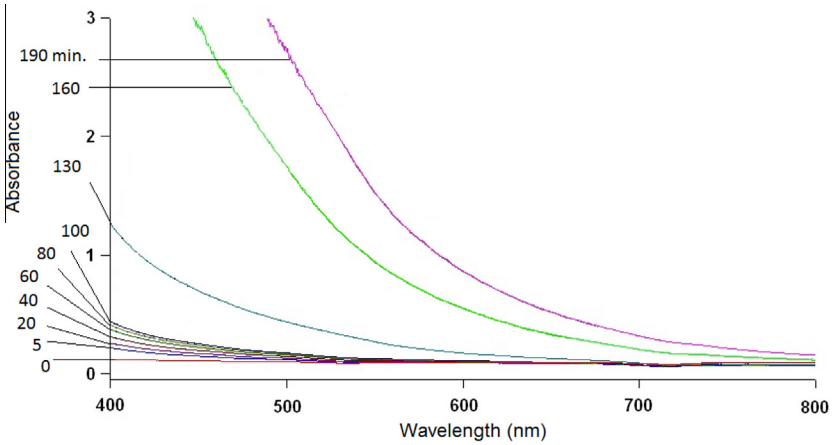

Figure 3. The changes in visible spectra of the DMSO solution during the Brönsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed transformations of D-glucose at 150 °C.

spectroscopy at 150 °C to explore the mechanism for the transformation to HMF. The acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium was selected as the catalyst for the study because $-SO_3H$ group functionalized imidazolium chloride type Brönsted acidic ionic liquids are known to promote dehydration of hexose sugars to HMF.[23] The anomeric composition of D-glucose during the reaction was estimated from the ^{1}H NMR peak area data from experiment 4.2. The area ratio of the anomeric proton signals at 4.23 ppm (α), and 4.86 ppm (β) was used in the estimation of anomeric composition of D-glucose during the reaction and the results are shown in Table 1. The room temperature sample showed α/β ratio of 4.76, whereas the ratio changed in favor of the β anomer after heating, and stabilized at an α/β ratio of approximately 0.85 after about 30 min heating at 150 °C.

The amount of HMF produced in the sample at different heating periods was calculated by integration of C-3,4 furan hydrogen peaks (6.57 and 7.47 ppm) and comparison of the areas with imidazole C-4,5 hydrogen peaks (7.64 and 7.72 ppm). A plot of HMF yields calculated at different stages of reaction against the time is used to monitor the progress of HMF formation, as shown in Figure 2. As revealed in this plot, HMF yield rapidly increases in the first 100 min, but levels off to a maximum yield of about 15.7% around 600 min. We have observed a rapid darkening of the reaction mixture from a light yellow solution to a dark brown solution while heating at 150 °C. This darkening can be attributed to the humin formation as acid catalyzed decomposition of D-glucose to humin type polymers is a well known reaction.[33,34] In an attempt to study this darkening reaction due to humin formation we have followed the changes of the visible light absorption in the 400–800 nm range in a separate experiment under identical conditions as described in Section 4.3. The changes in visible spectra of the DMSO solution during the Brönsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed transformations of D-glucose at 150 °C are shown in Figure 3. As shown in Figure 3, humin concentration and the rate of humin formation rapidly increase after 100 min of reaction, at the same time Figure 2 shows that rate of HMF formation slows down after 100 min, suggesting that humin formation may have caused the decline in HMF formation after this period.

The 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed decompositions of 1-^{13}C and 2-^{13}C D-glucose in DMSO-d_6 were studied by ^{13}C NMR spectroscopy as described in experiments 4.4 and 4.5. These NMR tube experiments were also carried out under conditions identical to the natural D-glucose experiment in Section 4.2. A representative ^{13}C NMR spectrum recorded at t = 48.0 min using 1-^{13}C D-glucose is shown in Figure 4, and the mechanism proposed is shown in Figure 6. The C-1 carbons in anomeric forms of D-glucose (**1** and **2**), D-glucofuranose (**4** and **5**) and

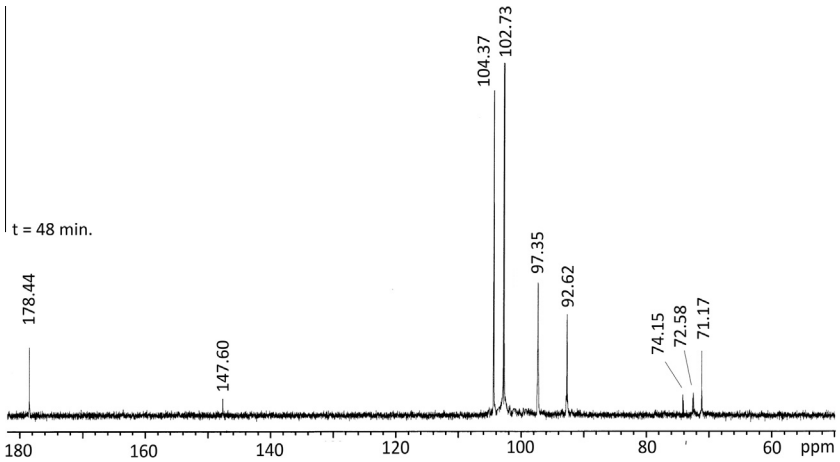

Figure 4. The representative ^{13}C NMR spectrum recorded at t = 48.0 min. during Brönsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed transformations of 1-^{13}C D-glucose in DMSO. 1-^{13}C D-glucose (45.0 mg) and 1-(1-propylsulfonic)-3-methylimidazolium chloride (3.3 mg) in 0.60 mL of DMSO-d_6 heated at 150 °C. 100 MHz, Relaxation delay = 2 s, number of scans = 128.

open chain D-fructose **8** can be identified by comparison with literature values reported by Kimura et al.[27] For instance, ^{13}C signals at 97.35 and 92.62 ppm can be assigned to C-1 carbons of α and β-D-glucose, respectively; whereas, signals at 104.37 and 102.73 ppm can be assigned to α and β-D-glucofuranose C-1 carbons, respectively (Figs. 4 and 6). The high field $-CH_2-OH$ carbon signal at 71.17 ppm was assigned to C-1 carbon of the open chain form of D-fructose **8**. The low field signals at 147.60 and 178.44 ppm are due to C-1 carbons of enol intermediate **10** and C-1 carbon of HMF (**12**) product, respectively. We have proposed a complexation of the imidazolium cation to open chain aldehyde **3** to form the complex **6** and keto form **7** during the aldose–ketose isomerization, similar to the metal ion-complexation proposed by Dumesic and co-workers[24] (Fig. 6). The ^{13}C NMR signals of imidazolium cation complexed aldose form **6** were not observed, probably due to rapid transformation to the ketose form **7**. The small ^{13}C peaks at 72.58 and 74.15 ppm in Figure 4 were assigned to the C-1 carbons of the two possible isomeric structures of **7** as shown in Figure 6. The key steps in the proposed mechanism in Figure 6 involve the isomerization via complexation to imidazolium cation and formation of the open chain D-fructose **8**, and D-fructofuranose **9**. There is no evidence for the formation of deuterium incorporated products or intermediates, suggesting that proton transfer from C-2 to C-1 during the isomerization must be occurring via an internal transfer mechanism. The acid catalyzed dehydration of D-fructofuranose (**9**) leads to the enol **10** and a second dehydration to the 4-hydroxy-5-hydroxymethyl-4,5-dihydrofuran-2-carbaldehyde **11**, which further dehydrate to 5-hydroxymethylfurfural (**12**). Interestingly no NMR signals were observed for the 4-hydroxy-5-hydroxymethyl-4,5-dihydrofuran-2-carbaldehyde **11**, as in our earlier NMR studies on the dehydration of D-fructose in DMSO without an added acid catalyst.[5] This may be due to a fast dehydration intermediate **11** to HMF.

The 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed decomposition of 2-^{13}C D-glucose in DMSO-d_6 at 150 °C was also studied to support the 1-^{13}C labeled D-glucose NMR study, and a representative ^{13}C NMR spectrum recorded at $t = 48.0$ min during this experiment is shown in Figure 5. This 2-^{13}C D-glucose

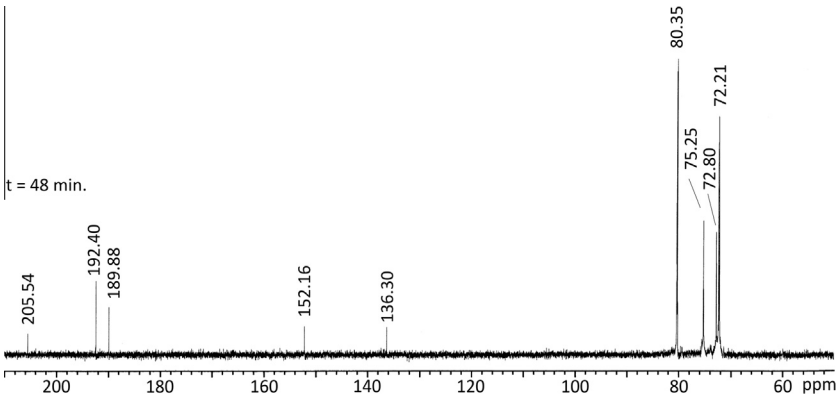

Figure 5. The representative ^{13}C NMR spectrum recorded at $t = 48.0$ min. during Brönsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed transformations of 2-^{13}C D-glucose in DMSO. 2-^{13}C D-glucose (45.0 mg) and 1-(1-propylsulfonic)-3-methylimidazolium chloride (3.3 mg) in 0.60 mL of DMSO-d_6 heated at 150 °C. 100 MHz, Relaxation delay = 2 s, number of scans = 128.

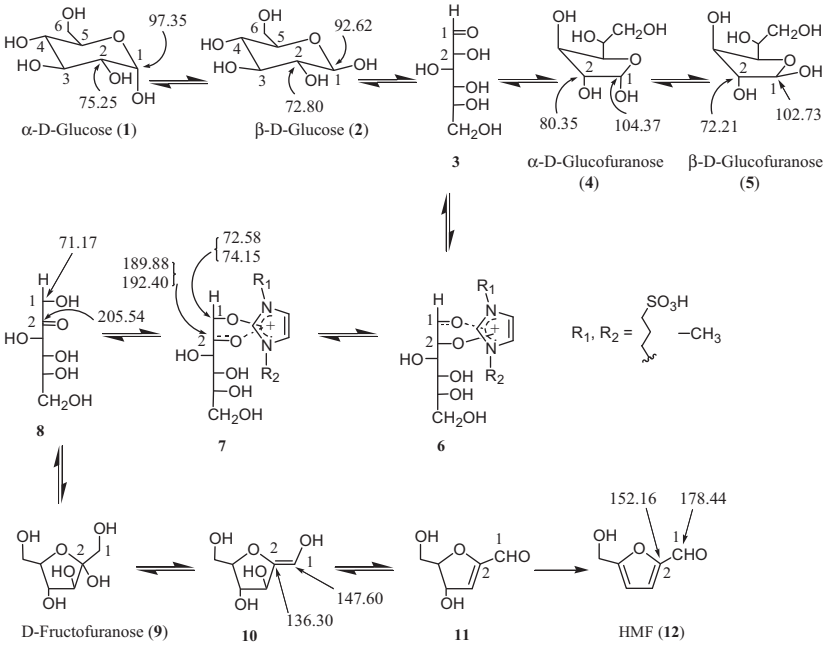

Figure 6. Proposed mechanism for Brönsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed transformation of D-glucose to 5-hydroxymethylfurfural (HMF) in DMSO. C-1,2 ^{13}C NMR chemical shifts are shown for D-glucose, HMF, and intermediates identified by ^{13}C isotope labeled D-glucose decomposition experiments.

study further confirmed the mechanism proposed in Figure 6. The C-2 carbons in the anomeric forms of D-glucose, D-glucofuranose and open chain D-fructose (**8**) can be identified in the spectrum shown in Figure 5 by comparison with literature values.[27] The ^{13}C peaks at 75.25 and 72.80 ppm can be assigned to α and β-D-glucose C-2 carbons, respectively; while peaks at 80.35 and 72.21 ppm can be assigned to α and β-D-glucofuranose C-2 carbons, respectively. The low field peak at 205.54 ppm was assigned to the C-2 carbon in the open chain D-fructose (**8**).[27] The remaining two low field peaks at 136.30 and 152.16 were assigned to the C-2 carbons of the intermediate **10** and the HMF (**12**) product. The 2-^{13}C D-glucose study also supports the possibility of two isomeric structures for imidazolium cation complexed open chain form **7**, where peaks at 189.88 and 192.40 are assigned to C-2 carbons of isomeric forms of **7**.

To further support the mechanism, we have studied the decomposition of D-fructose in 1-(1-propylsulfonic)-3-methylimidazolium chloride in DMSO-d_6 at 150 °C, under similar catalyst loading described in the experiment 4.2. In this experiment all D-fructose disappeared without a trace after 1.0 min at 150 °C, and could not observe the (4*R*,5*R*)-4-hydroxy-5-hydroxymethyl-4,5-dihydrofuran-2-carbaldehyde (**11**) intermediate seen in earlier experiments.[5] Additionally, HMF was the only identifiable product formed in 90% yield. Therefore, we believe that life-time of fructose and this intermediate is very short in strongly acidic medium at 150 °C used here, and could be the reason that a standing concentration of D-fructose is not observed in the present experiment.

3. Conclusion

We have proposed a mechanism for the Brönsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed transformation of D-glucose to 5-hydroxymethylfurfural in DMSO. The proposed mechanism involves the isomerization of D-glucose to D-fructose via the complexation of the open chain sugar with the imidazolium cation of the acid catalyst. Key intermediates in the proposed pathway could be identified by studying the changes in the ^{13}C NMR spectra of acidic ionic liquid catalyzed transformations of C-1 and C-2 ^{13}C labeled D-glucose under comparable conditions. HMF yield rapidly increases in the first 100 min of reaction at 150 °C, but then the rate of increase in the yield decreases beyond 100 min and levels off to a maximum yield of about 15.7% around 600 min. The visible spectroscopy study of the reaction mixture suggests that rate of HMF formation slows down after 100 min due to increase in the rate of humin formation after this period.

4. Experimental

4.1. Instrumentation and materials

D-Glucose (99.9%), 1-^{13}C-D-glucose (99% atom 1-^{13}C), 2-^{13}C-D-glucose (99% atom 2-^{13}C), anhydrous DMSO-d_6 (99.9% atom D) were purchased from Aldrich Chemical Co. Brönsted acidic ionic liquid catalyst 1-(1-propylsulfonic)-3-methylimidazolium chloride was prepared by condensation of 1-methylimidazole with 1,3-propanesultone and acidification of the resulting salt with concd HCl according to the literature procedure.[35,36] ^1H NMR spectra were recorded in DMSO-d_6 on a Varian Mercury Plus spectrometer operating at 400 MHz. Chemical shifts are given in ppm downfield from TMS ($\delta = 0.00$). ^{13}C NMR spectra in DMSO-d_6 were recorded on the same spectrometer operating at 100 MHz. Chemical shifts are reported relative to DMSO-d_6 and converted to δ (TMS) using δ (DMSO) = 39.51. Visible spectra of the reaction mixtures produced during the 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed decomposition of D-glucose were recorded using a Carey 50 UV–vis spectrophotometer and 1 cm quartz cells. Reaction tubes were heated in a mineral oil bath placed on a VWR VMS-C7 hot-plate attached to a VWR VT-5 temperature controller with ±0.1 °C accuracy.

4.2. 1-(1-Propylsulfonic)-3-methylimidazolium chloride catalyzed decomposition of D-glucose in DMSO-d_6—^1H NMR study

A solution of D-glucose (45.0 mg, 0.25 mmol) and 1-(1-propylsulfonic)-3-methylimidazolium chloride (3.3 mg, 0.0137 mmol, and 5.48 mol % catalyst) in 0.60 mL of anhydrous DMSO-d_6 was prepared in a 5-mm NMR tube. The sample was allowed to stabilize at room temperature for 4 h, then, ^1H NMR (rd = 1 s, NS = 8) spectrum was recorded as the initial baseline data. Afterward the NMR tube was heated in a thermostated oil bath at 150 ± 0.1 °C for 6.0 min, and then the reaction was quenched by immersing the NMR tube in an ice-water bath. The tube was immediately transferred to the NMR spectrometer, ^1H NMR spectrum was recorded using conditions identical to the first $t = 0$ spectrum. Further spectra were recorded after heating 18.0, 30.0, 48.0, 90.0, 150.0, 210.0, 290, 410, 530, and 710.0 min of total heating time at 150 ± 0.1 °C. D-Glucose α/β anomer compositions and the amount of HMF produced at different time intervals were measured by manual integration of the ^1H NMR peaks. The imidazole ring C4, C5 proton NMR peak areas of 1-(1-propylsulfonic)-3-methylimidazolium chloride were used as an internal standard for the calculation of HMF yields. The variations in the α/β D-glucose anomer ratios were monitored up to 48.0 min of the reaction and these data are shown in Table 1. The changes in the ^1H NMR spectra during the course of the reaction are shown as a selected sample of spectra in Figure 1. The calculated percent yields of HMF produced after different times of heating are shown in the plot in Figure 2.

4.3. 1-(1-Propylsulfonic)-3-methylimidazolium chloride catalyzed decomposition of D-glucose in DMSO—visible spectroscopy study

A solution of D-glucose (450.0 mg, 2.50 mmol) and 1-(1-propylsulfonic)-3-methylimidazolium chloride (33.0 mg, 0.137 mmol, 5.48 mol % catalyst) in 6.00 mL of anhydrous DMSO was prepared in a round bottom flask. The sample was allowed to stabilize at room temperature for 4 h, then, 100 μL of the solution was withdrawn and diluted with 3.00 mL of DMSO and visible spectrum was recorded in the 400–800 nm range against a pure DMSO blank. Afterward the reaction mixture was heated in a thermostated oil bath at 150 ± 0.1 °C for 5.0 min, and then 100 μL of the solution was withdrawn and diluted with 3.00 mL of DMSO and visible spectrum was recorded using conditions identical to the first $t = 0$ spectrum. Further visible spectra were recorded after heating 20.0, 40.0, 60.0, 80.0, 100.0, 130.0, 160, and 190.0 min of total heating time at 150 ± 0.1 °C. A stack plot of visible spectra showing the progress of the reaction is shown in Figure 3.

4.4. 1-(1-Propylsulfonic)-3-methylimidazolium chloride catalyzed decomposition of 1-^{13}C-D-glucose in DMSO-d_6—^{13}C NMR study

A solution of 1-^{13}C-D-glucose (45.0 mg, 0.25 mmol) and 1-(1-propylsulfonic)-3-methylimidazolium chloride (3.3 mg, 0.0137 mmol, 5.48 mol % catalyst) in 0.60 mL of anhydrous DMSO-d_6 was prepared in a 5-mm NMR tube. The sample was allowed to stabilize at room temperature for 4 h, then, ^{13}C NMR (rd = 2 s, NS = 128) spectrum was recorded as the initial baseline data.

Afterward the NMR tube was heated in a thermostated oil bath at 150 ± 0.1 °C for 6.0 min, and then the reaction was quenched by immersing the NMR tube in an ice-water bath. The tube was immediately transferred to the NMR spectrometer, ^{13}C NMR spectrum was recorded using conditions identical to the first t = 0 spectrum. Further spectra were recorded after heating 18.0, 30.0, 48.0, and 90.0 min of total heating time at 150 ± 0.1 °C. A representative ^{13}C NMR spectrum recorded at t = 48.0 min is shown in Figure 4, indicating C-1 signals from all identifiable intermediates.

4.5. 1-(1-Propylsulfonic)-3-methylimidazolium chloride catalyzed decomposition of 2-^{13}C-D-glucose in DMSO-d_6—^{13}C NMR study

A solution of 2-^{13}C-D-glucose (45.0 mg, 0.25 mmol) and 1-(1-propylsulfonic)-3-methylimidazolium chloride (3.3 mg, 0.0137 mmol, 5.48 mol % catalyst) in 0.60 mL of anhydrous DMSO-d_6 was prepared in a 5-mm NMR tube. The sample was allowed to stabilize at room temperature for 4 h, then, initial base line spectrum and a series of ^{13}C spectra were collected as in experiment 4.4. A representative ^{13}C NMR spectrum recorded at t = 48.0 min is shown in Figure 5, indicating C-2 signals from all identifiable intermediates.

Acknowledgments

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