

Research Article

Catalytic Transformation of Fructose and Sucrose to HMF with Proline-Derived Ionic Liquids under Mild Conditions

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L-Proline derived ionic liquids (ILs) used as both solvent and catalyst were efficient for transformation of fructose and sucrose to 5-hydroxymethylfurfural (HMF) in the presence of water. Response surface methodology (RSM) was employed to optimize fructose dehydration process, and a maximum HMF yield of 73.6% could be obtained at 90°C after 50 min. The recycling of the IL exhibited an almost constant activity during five successive trials, and a possible reaction mechanism for the dehydration of fructose to HMF was proposed.

1. Introduction

Biomass derivatives and related raw materials are the most abundant renewable resources available which have great potential as biofuels and chemical building blocks for a diverse range of applications [1–4]. Over the past decades, various acid and/or base catalysts have been employed to transform carbohydrates into different kinds of furans, providing a feasible way for supplying sustainable energy and chemicals [5–7]. Amongst them, 5-hydroxymethylfurfural (HMF), serving as an important precursor molecule in the production of fine chemicals, plastics, pharmaceuticals, and liquid fuels [8, 9], can be synthesized from biomass-derived carbohydrates such as fructose and sucrose. In this catalytic dehydration process, various acid catalysts including mineral acids [10, 11], metal ions [12–14], ion exchange resins [15–17], $-\text{SO}_3\text{H}$ functionalized catalysts [18, 19], and many other functional materials [20–24] have been used, which may find applications in HMF production.

During the past decade, ionic liquids (ILs) considered to be salts with a melting point below 100°C have been widely utilized as reaction media or catalysts for the dehydration of carbohydrates into HMF. Using 1-butyl-3-methylimidazol-3-ium hexafluorophosphate ([Bmim] PF_6) or 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim] BF_4) as

reaction medium, fructose could be selectively transformed into HMF with up to 50% yield in the presence of Amberlyst 15 at 80°C for 3 h [25]. Similarly, Li et al. [26] found that acidic ion-exchange resins in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) could effectively promote dehydration of fructose to HMF, and a 93.0% yield of HMF was obtained at 75°C for 20 min. Moreover, metal chlorides combined with ILs were also demonstrated to be highly efficient for carbohydrates. For instance, chromium(III)/(II) chloride mediated catalytic systems for dehydration of carbohydrates to HMF always showed excellent reactivity [27–29], giving up to 99% HMF yield from fructose at 100°C within 6 h [27]. Most recently, Zhou et al. [30] reported that synthesis of HMF from carbohydrates catalyzed by ScCl_3 in [Bmim]Cl under microwave irradiation at 400 W could be achieved with a high yield of 73.4% in 2 min. With the presence of HfCl_4 and NbCl_5 , HMF yield of up to 77.5% and 79% could be obtained from fructose after 30 min at 100°C and 80°C, respectively [31, 32].

Apart from acting as reaction media, acidic/basic ILs could be directly employed as catalysts for the production of HMF from carbohydrates. In an aqueous acetonitrile biphasic system, a HMF yield of up to 88.7% could be achieved in the presence of a Lewis acidic IL,

that is, 1-methyl-3-(butyl-4-chlorosulfonyl)-imidazolium chlorosulfate ([MBCIm] SO_3Cl), at 80°C after 4 h [33]. Likewise, 3-allyl-1-(4-sulfurylchloride butyl)-imidazolium trifluoromethanesulfonate ([ASCBI][Tf]) was capable of effectively catalyzing the dehydration of D-fructose to HMF with around 70% yield at 100% fructose conversion in DMSO (dimethyl sulfoxide) within 4 min under microwave irradiation of 200 W [34]. On the other hand, Brønsted acidic ILs [35–37] and even alkaline ILs [38] could promote the dehydration process, which indicated the high catalytic performance of ILs in the synthesis of HMF from carbohydrates.

Notably, Moreau et al. [39] found that 1-*H*-3-methylimidazolium chloride (HMIM^+Cl^-) could be used as both solvent and catalyst for the dehydration of fructose and sucrose to produce HMF in relatively high yield and selectivity. This catalytic system largely facilitated the separation of HMF from the reaction solution and showed great potential in industrial applications. Similarly, a dicationic room temperature IL [TetraEG(mim) $_2$][OMs] $_2$ (tetra ethylene glycol-bis (3-methylimidazolium) dimesylate) afforded 92.3% of HMF yield from fructose in 40 min at 120°C [40]. By using 3-(2-chloroethyl)-1-methylimidazolium chloride ([ClC $_2$ mim]Cl) as both catalyst and solvent in the presence of water, 76% HMF yield could be obtained from fructose at 100°C in 40 min [41]. However, imidazolium-based ILs are always expensive and have a certain toxicity [42]. With the increasing concern about economic development and environmental protection, ILs synthesized from biorenewable materials may offer a competitive route to the traditional imidazolium-based ionic liquids [37, 43].

Starting from amino acids, Tao et al. [44] prepared a series of amino acid-based ILs that are thermally stable up to 150–200°C via a simple protonation reaction carried out by mixing the correct molar ratio of amino acid with relevant strong acid in water. In particular, *L*-proline possessing nature endorsed chiral center was reported to exhibit excellent enantioselectivities in several types of asymmetric reactions [45, 46], and its ionic liquid counterparts could well promote organic synthesis [47, 48]. In the present study, proline chlorate (ProCl) and proline bisulfate (ProHSO $_4$) were synthesized and further employed for the dehydration of fructose and sucrose to HMF in the presence of water. Response surface methodology (RSM) was utilized to optimize fructose dehydration process, and a possible reaction mechanism for the dehydration of fructose to HMF was proposed.

2. Experimental

2.1. Materials. *L*-Proline, boric acid, glycerol, fructose, sucrose, and HMF of analytical grade were purchased from Shanghai Aladdin Industrial Inc.; 1-Methylimidazole (AR, 99%) and 1,3-propanesultone (>99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the other chemicals were of analytical grade and used as received, unless otherwise noted.

2.2. Preparation of Ionic Liquids. Proline chlorate (ProCl) and proline bisulfate (ProHSO $_4$) were synthesized according to the reported methods [49, 50] with slight modifications. Equal moles of hydrochloride or sulfuric acid (6 mol/L) were added dropwise to the solution of *L*-proline (2.88 g, 25 mmol) dissolved in 15 mL of water. The reaction mixture was then heated to 60°C and kept stirring for 24 h. Upon completion, the mixture was concentrated and evaporated under vacuum to give the target protic ionic liquid in high yield (around 95%).

ProCl ^1H NMR (DMSO, 500 MHz): δ (ppm) = 4.19 (m, 1H), 3.15 (m, 2H), 2.21 (m, 1H), 1.85 (m, 3H); ^{13}C NMR (DMSO, 125 MHz): δ (ppm) = 170.69, 59.05, 45.57, 28.49, 23.62; IR (KBr): ν (cm^{-1}) = 2940, 2700–2500, 1738, 1573, 1384, 1213, 821, 658.

ProHSO $_4$ ^1H NMR (DMSO, 500 MHz): δ (ppm) = 4.28 (m, 1H), 3.24 (m, 2H), 2.30 (m, 1H), 1.94 (m, 3H); ^{13}C NMR (DMSO, 125 MHz): δ (ppm) = 169.89, 58.84, 45.47, 28.19, 23.22; IR (KBr): ν (cm^{-1}) = 3168, 1741, 1587, 1423, 1341, 1138, 1062, 876, 658, 572.

For comparison, 1-methyl-3-(3-sulfopropyl)-imidazolium chloride ([C $_3$ SO $_3$ Hmim][Cl]), 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ([C $_3$ SO $_3$ Hmim][HSO $_4$]), and 1-propyl-3-methylimidazolium chloride ([C $_3$ mim][Cl]), as well as bis(glycerol)boric acid (H[Gly $_2$ B]), were synthesized according to the procedures depicted by Li et al. [19] and Safaei et al. [51].

2.3. Catalytic Transformation of Carbohydrates into HMF. As a general procedure, a 15 mL of sealed tube (Ace, pressure limit: 20 bar) was charged with 1.0 g of ionic liquid, 5 wt% water, and fructose or sucrose (100 mg, 0.56 mmol) by oil heating at a fixed temperature stirring for a specified time. Upon completion, the tube was removed from the oil bath and cooled to room temperature. Deionized water was then added to quantify the reaction mixture in a volumetric flask before the sample was taken for analysis by HPLC.

2.4. Product Analysis. High-performance liquid chromatography (HPLC; Agilent 1100, USA) fitted with a Lichrospher C18 column, an ultraviolet detector at 284 nm, a column oven temperature set at 25°C, and a mobile phase of methanol/water (35/65, v/v) at a flow rate of 0.8 mL/min were used to determine the yield of HMF. The concentration of HMF was calculated based on the standard curve obtained with the standard substances, and HMF yield was further calculated from the equation: HMF yield (%) = (moles of HMF)/(moles of hexose added) \times 100.

3. Results and Discussion

3.1. Catalytic Dehydration of Fructose into HMF with Different ILs. Ionic liquids (ILs) are often highly viscous and sensitive to moisture. In this study, a certain amount of water was added into the reaction system with the aim of reducing the viscosity of ILs and discussing the effect of water contents on catalytic performance. Initially, a water content of 5 wt% previously reported to promote HMF formation in carbohydrate

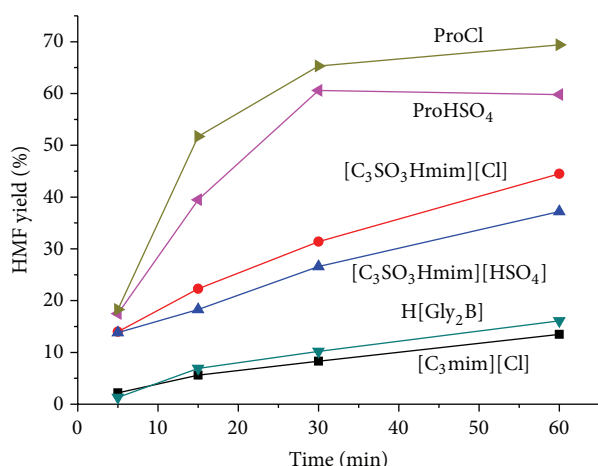


FIGURE 1: Catalytic dehydration of fructose to HMF over various ILs with 5 wt% water at 90°C for different reaction times.

dehydration [52] was employed to investigate the reactivity of various ILs. As shown in Figure 1, protic ionic liquids (ProCl and ProHSO₄) exhibited better catalytic activity (up to ~70% HMF yield) than others. However, boron core based protic ionic liquid (H[Gly₂B]) similar to [C₃mim][Cl] produced relatively low HMF yields despite boric acid could be used as a promoter for dehydration of carbohydrates in ionic liquids [53]. Although, -SO₃H functionalized imidazolium-based ILs ([C₃SO₃Hmim][Cl] and [C₃SO₃Hmim][HSO₄]) were reported to be efficient for fructose-to-HMF conversion in biphasic system at high temperature for a long reaction time [54]; they only displayed moderate HMF yields (30–40%) under mild reaction conditions (Figure 1). In both cases, the reactivity of chloride anion based ILs was superior to that of ILs containing hydrogen sulfate ion, which indicated the vital role of chloride anion in catalytic dehydration of fructose [55, 56]. On the other hand, the proline-derived ILs were much more efficient for fructose-to-HMF conversion than other cations based ILs, which implied the enhanced effect of carboxylic groups (-COOH) of proline-derived ILs on adsorption and transformation of the substrate.

3.2. Effect of Water Content on Catalytic Dehydration of Fructose to HMF. Due to the acceptable catalytic performance, ProCl and ProHSO₄ were further utilized to test the influence of water content on dehydration of fructose to HMF (Figure 2). Up to 10 wt% of water in the reaction mixture resulted in no detrimental effect on the formation of HMF from fructose, which to some extent showed the synergy of ProCl and water in the catalytic dehydration of fructose to HMF. However, the HMF yield significantly decreased as water content was above 10 wt%, which might be ascribed to the generation of hydrated chloride ions that are unable to participate in the reaction [57]. In contrast, very negative effect of water content on fructose-to-HMF conversion over ProHSO₄ was observed. Instead of HMF, large amounts of levulinic acid (up to 40% yield) and humins were obtained. It was speculated that free HSO₄⁻ with high acid strength as

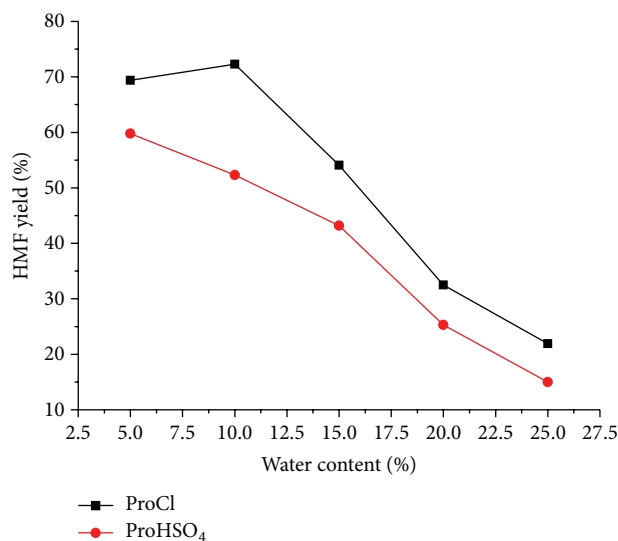


FIGURE 2: Effect of water content in ProCl and ProHSO₄ on dehydration of fructose to HMF at 90°C for 60 min.

well as water content in ProHSO₄ mediated reaction system was responsible for hydrolysis/degradation of HMF.

3.3. Influence of Reaction Time and Temperature on Fructose-to-HMF Conversion. Apart from water content, reaction temperature and time are another two important parameters to determine the yields of HMF. Optimized experiments were thus performed on fructose dehydration at reaction temperature ranging from 70 to 110°C for reaction duration in the range of 5–75 min in ProCl with 10 wt% of water (Figure 3). At a temperature of 70°C, HMF yields kept increasing with the increase of reaction time from 5 min to 75 min, giving only 36% yield of HMF even after 75 min. Seemingly, high temperature (110°C) was beneficial for fructose dehydration to HMF within short time. However, extension of the reaction duration to 75 min just afforded around 20% HMF yield. In turn, fructose dehydration at 90°C could produce a little higher yield of HMF (about 70.0%) after ~40 min though the reaction rate was somewhat slower.

3.4. Optimization of The Reaction Conditions Using Experimental Design. A three-factor two level design [58] was employed with the purpose of optimizing the reaction conditions for the dehydration of fructose to HMF with higher yields. Three factors as reaction temperature ($T/^{\circ}\text{C}$), reaction time (t/min), and ProCl amount (C/g) were tested for fructose-to-HMF transformation. Figures 4, 5, and 6 show the effects of reaction temperature, reaction time, and ProCl amount on HMF yield. With the experimental design, a model equation for predicting HMF yield in the fructose dehydration was generated: $\text{HMF yield (\%)} = -786.0522 + (2.3178t) + (17.4576T) + (32.9100C) - (0.0172tT) + (0.0600tC) + (0.1525TC) - (0.0085t^2) - (0.0936T^2) - (20.7300C^2)$. From the optimization, 90°C, 50 min, and 1.2 g ProCl were disclosed to be one of the optimum reaction conditions. Under the reaction condition, the actual HMF yield of 73.6%

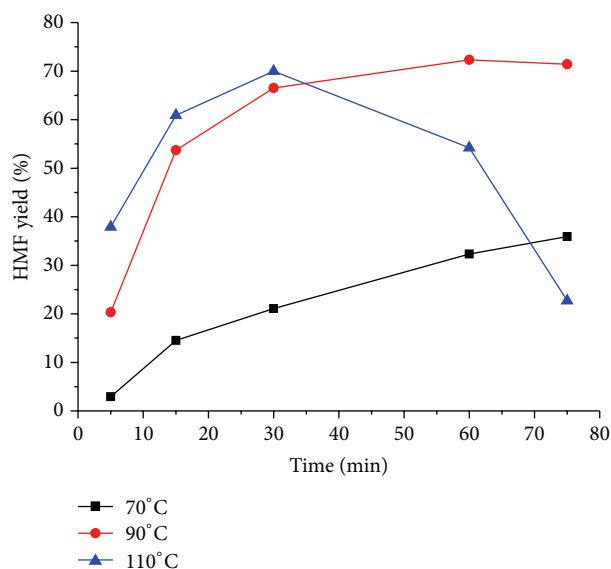


FIGURE 3: Effect of reaction time and temperature on catalytic dehydration of fructose to HMF in ProCl with 10 wt% of water.

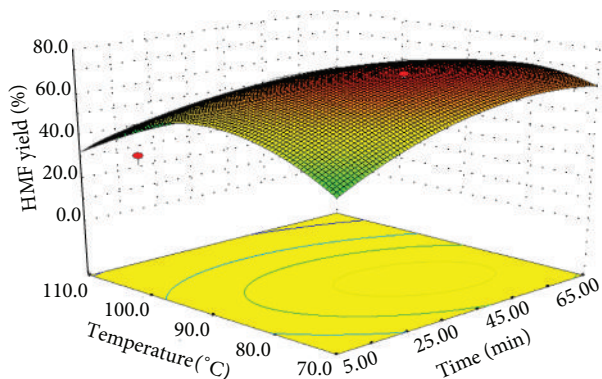


FIGURE 4: Response surface plot of HMF yield against reaction temperature and time.

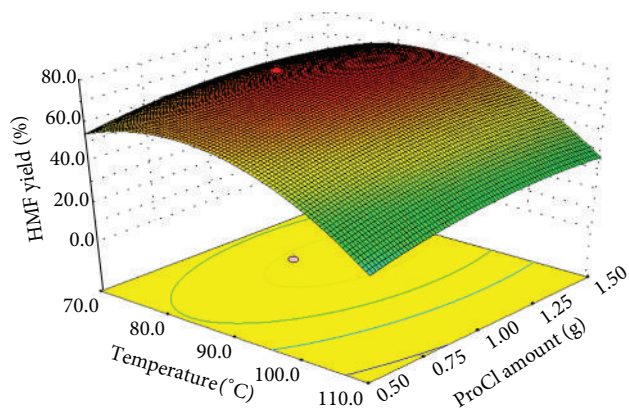


FIGURE 5: Response surface plot of HMF yield against reaction temperature and ProCl amount.

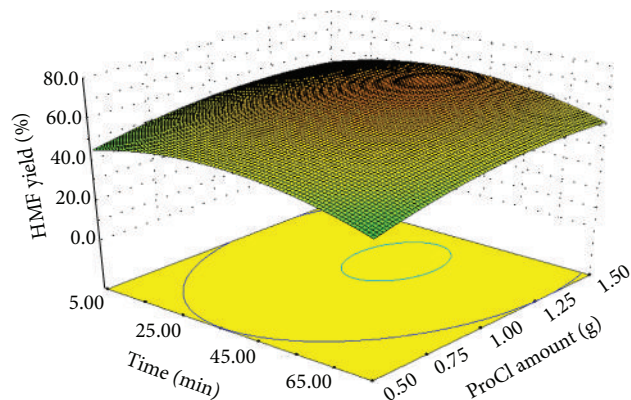


FIGURE 6: Response surface plot of HMF yield against reaction time and ProCl amount.

was achieved in accordance with the predicted yield of 74.1%, which well validated the model.

3.5. Catalytic Dehydration of Sucrose to HMF. Sucrose as a disaccharide consisting of glucose and fructose is widely distributed in the plant kingdom, showing promising prospect in the production of value-added chemicals [59]. However, only ~18% HMF yield was obtained from sucrose under the reaction condition optimized for fructose dehydration (i.e., 90°C, 50 min, 1.2 g ProCl, and 10 wt% of water), as shown in Figure 7. The HMF yield increased as the reaction proceeded for a long reaction time, and around 35% and 40% yield of HMF could be achieved within 150 min and 180 min, respectively, which clearly demonstrated the relatively higher stability of sucrose as compared with fructose. However, the catalytic performance in terms of HMF yield was decreased as the reaction time was further increased to 210 or 240 min, implying that glucose with equal amount of molar weight to fructose in sucrose could not be effectively dehydrated by the protic IL whereas the degradation of HMF seriously happened [39]. In this regard, further increasing water content as well as reaction temperature would only facilitate the side reactions to degrade HMF.

3.6. HMF Separation and IL Recycling. The separation of HMF and the recycling of ProCl were studied in fructose dehydration, and all the experiments (five cycles) were carried out in 1.2 g ProCl with 10 wt% of water at 90°C for 50 min. After the reaction, HMF was extracted with diethyl ether in a stepwise manner [39], and the IL recovered by removal of residual water was directly used for the next cycle after adding a certain amount of water. It was found that the amount of the recovered IL was slightly decreased from 1.20 g to 1.14 g after the first run. As illustrated in Figure 8, the recycling of ProCl exhibited almost constant reactivity with respect to the percent yield of HMF (around 70%) within five runs.

3.7. Proposed Mechanism for Catalytic Dehydration of Fructose to HMF with ProCl. Compared with the above discussed ILs, the relatively better activity of L-proline based protic ILs

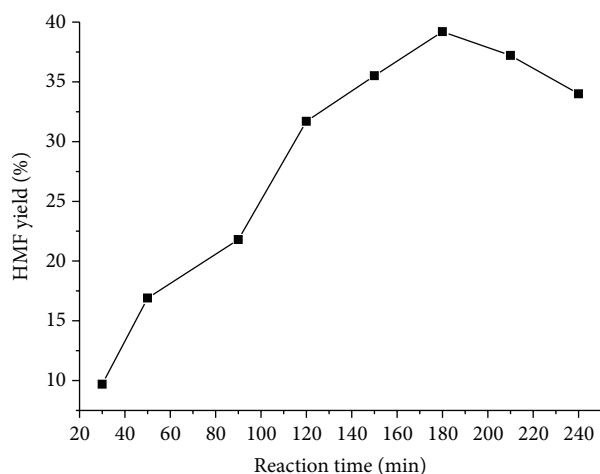


FIGURE 7: Catalytic dehydration of sucrose to HMF in ProCl with 10 wt% water at 90°C.

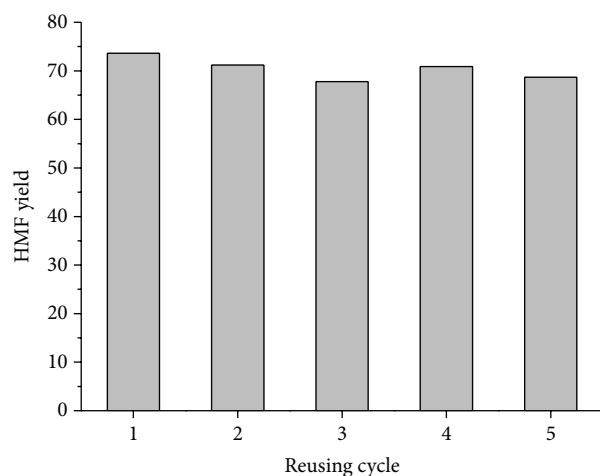


FIGURE 8: The recycling of ProCl for dehydration of fructose to HMF. Reaction conditions: ProCl (1.2 g), water (10 wt%) and fructose (100 mg) at 90°C for 50 min.

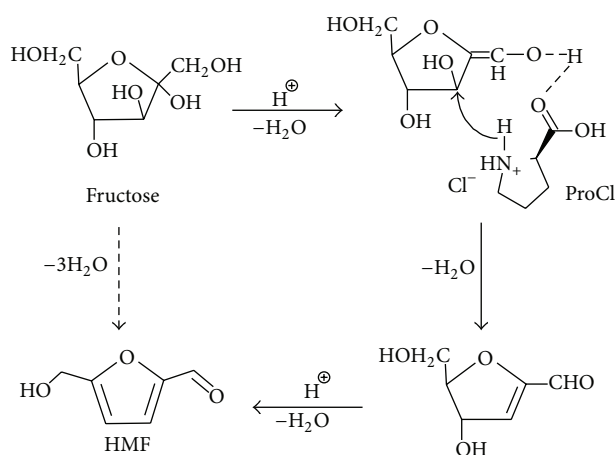


FIGURE 9: Proposed mechanism for catalytic dehydration of fructose to HMF with ProCl.

in fructose dehydration might be ascribed to the presence of proton and $-\text{COOH}$ that can promote the interaction of fructose and the IL via $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonding in the rate-determining step (Figure 9). In the whole catalytic process, three water molecules were successively lost with the assistance of H^+ to give the final product HMF [60].

4. Conclusion

ProCl synthesized from a simple protonation reaction by mixing *L*-proline with hydrogen chloride in water was demonstrated to be efficient for the dehydration of fructose as well as sucrose to HMF. A maximum HMF yield of 73.6% could be obtained from fructose under the response surface methodology (RSM) optimized reaction conditions. $-\text{COOH}$ in ProCl was proposed to promote the interaction of fructose with the IL via $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonding in the rate-determining step, which might facilitate the catalytic dehydration process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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