

Alcoholysis of Furfuryl Alcohol to Ethyl Levulinate Catalyzed by a Deep Eutectic Solvent

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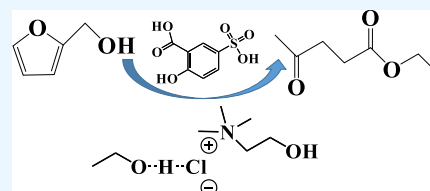


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Supporting Information

ABSTRACT: In this study, the alcoholysis of furfuryl alcohol (FA) into ethyl levulinate (EL) using a deep eutectic solvent (DES) composed of choline chloride (ChCl) and ethanol was investigated by experiments and calculations. Experimental results reveal that the addition of 5-sulfonic acid salicylic acid (5-SSA) can catalyze the alcoholysis of FA to produce EL. The combined presence of ChCl and 5-SSA significantly improved the selectivity for EL. The mechanism of the alcoholysis of FA to EL in acidic DES was investigated by density functional theory (DFT) calculations in Gaussian 03. It was found that hydrogen-bond acceptor ChCl is coupled with hydrogen-bond donor ethanol to form a structure similar to HCl and ethoxy, which facilitates the alcoholysis of FA into EL.



1. INTRODUCTION

Ethyl levulinate (EL) is widely known for its industrial applications as diesel additives, adhesives, and plasticizers used in transportation fuels, coatings, and pharmaceutical industries.¹ EL can be obtained by the esterification of levulinic acid (LA), with the advantages of a high yield, mild conditions, and a simple production process.² The esterification of LA to LA ester at room temperature has been reported to be catalyzed by an acidic mesoporous molecular sieve.³ As a fine chemical, high purity is a greater requirement for EL than high yield. Moreover, the price of LA is much higher than that of furfuryl alcohol (FA) directly converted from furfural (FF). Therefore, another current approach to produce EL is by alcoholysis of FA under the catalytic action of Brønsted acid.⁴ It is known that hemicellulose can be converted to pentose and hexose, which are good feedstocks for the preparation of high added-value chemicals and biofuels. Pentose loses three water molecules and is converted to FF, which in turn is converted to FA by transfer hydrogenation (TH) over a metal catalyst.⁵ Previously, homogeneous protic acids such as sulfuric acid and hydrochloric acid have been used in this process.⁶ Such protic acids are highly corrosive and often pollute the environment.⁷ To solve this problem, researchers have reported the use of a solid acid instead of a homogeneous protic acid. Among the solid acids, solid-acid catalysts such as molecular sieves, sulfonic acid resins, sulfonic acid solid catalysts, heteropoly acids, and metal salts have been typically used.⁸ The application of supported heteropoly acid catalyst is limited due to its small specific surface area, poor adsorption capacity, and easy loss of active sites in the catalytic process.⁹ Alcoholysis can be catalyzed using a heteropoly ionic liquid (IL) containing a heteropoly acid and an IL using imidazole sulfonate and phosphotungstic acid as the cation and anion, respectively.¹⁰ This catalyst exhibits a good self-separation effect. That is, the catalyst is in a homogeneous form during

the reaction process, after which it is automatically precipitated from the system, allowing it to be conveniently recovered after the reaction.¹¹

The melting point, viscosity, and other physical and chemical properties of deep eutectic solvent (DES) are common to ILs.¹² DES is a low eutectic mixture comprising a hydrogen-bond acceptor and a hydrogen-bond donor connected through a hydrogen bond, and its melting point is less than that of any single component.¹³ Compared to ILs, DES is cost-effective, simple to prepare, biodegradable, safe, and nontoxic. In addition, its atomic utilization rate is 100%, making it a suitable agent for green chemistry.¹⁴ The earliest application of DES was reported in metal electrodeposition and electropolishing.¹⁵ Recently, domestic and international research reveals that DES is a good solvent for degrading carbohydrates.¹⁶ In the initial stage of DES research method development, it has been investigated as a reaction system.¹⁷ With the development of biodegradable acidic ILs, DES formed by choline chloride (ChCl) and citric acid has been used as the reaction solvent to catalyze the conversion of fructose to 5-hydroxymethylfurfural, with ethyl acetate as the extraction solvent.¹⁸ The reaction at 80 °C for 1 h yields 5-HMF, with a yield of >90%. The results reveal that weak acidic sites can catalyze the dehydration of fructose to form 5-HMF in a DES reaction system.¹⁹

In this study, a new environmental protection DES system was used to convert FA into EL under the catalysis of 5-SSA.

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The coupling of Cl^- in ChCl with hydrogen in ethanol to form an HCl structure can not only facilitate the hydrogen transfer in the reaction process but can also promote the generation of ethoxyl group, which is conducive to the alcoholysis of FA. Although few studies have been reported on this topic, it provides ideas and possibilities for the development of new catalytic systems. Therefore, DES may become a highly efficient reaction system for energy conversion, and it is crucial to conduct in-depth studies on its structure design, reaction mechanism, and reaction method. The reaction mechanism of alcoholysis of FA to EL in acidic DES was elucidated in essence. Moreover, the transition states and energy barriers of each step of the reaction were clarified, which was beneficial to optimize the reaction.

2. MATERIAL AND METHODS

2.1. Materials. Choline chloride (ChCl), 5-sulfonic acid salicylic acid (5-SSA, 97%), FA, and ethanol were purchased from China Pharmaceutical Replacement Part Co., Ltd.

2.2. Reaction Process. Ethanol (10 mL) was added into four 25 mL reactors. Then, 0.018, 0.035, 0.07, and 0.15 g ChCl were added to each reactor, respectively. The reactors were sealed and stirred in four oil baths at 80 °C for 2 h before cooling. After opening the reactor, FA (1 mmol) and 5-SSA (0.25 mmol) were added to all reactors and stirred in four oil baths at a certain temperature. At the end of the reaction, quenching was conducted by rapidly cooling under cold water. Then, the reactor was opened, the reaction liquid was poured out, and a certain amount of ethyl acetate was added to extract the organic matter. The upper liquid was analyzed by gas chromatography (GC) using the GC9790II instrument. The testing conditions were as follows: the temperature of the injector and detector was 100 °C, and the column temperature was 180 °C. In addition, the effects of ChCl dosage and reaction temperature on the product were investigated. FA conversion and EL yield were calculated using eqs 1 and 2, respectively.

$$\begin{aligned} &\text{conversion of FA}(\text{mol } \%, C_{\text{FA}}) \\ &= \left(1 - \frac{\text{moles of FA}}{\text{initial moles of FA}} \right) \times 100\% \end{aligned} \quad (1)$$

$$\text{yield of EL}(\text{mol } \%, Y_{\text{EL}}) = \left(\frac{\text{moles of EL}}{\text{initial moles of FA}} \right) \times 100\% \quad (2)$$

All geometries for the reactants, intermediates, transition states, and products were fully optimized using hybrid density functional methods with the M062X/def2tzvp level of theory implemented in Gaussian 03 using an acidic catalyst at 373.15 K. Therefore, in this study, only the relative Gibbs free energies (in kcal/mol) obtained from PCM calculations are reported.

All vibrational frequencies were calculated using the same level of theory and basis set to verify whether the optimized structure (zero virtual frequency) corresponded to the minimum or first-order saddle point (a virtual frequency of the transition-state structure). TS was employed to scan the transition state between the optimized reactants and products. In addition, intrinsic reaction coordinates (IRC) of the transition state of the entire reaction process were tracked to determine that each phase of the reaction was linked to the reactants and desired products. The lowest Gibbs free-energy configuration was selected for further analysis. Vibrational

frequency calculations were also conducted to verify the optimized structures as minima (zero imaginary frequencies) or first-order saddle points (one imaginary frequency) and provide free energies at 373.15 K, including entropic contributions by considering vibrations, rotations, and translations of the structures.

3. RESULTS AND DISCUSSION

3.1. Investigation of Catalytic Performance. **3.1.1. Effect of Catalyst Type.** According to the characteristics of the catalysts reported in the literature,²⁰ activities of different catalysts were systematically investigated. In the entire alcoholysis reaction system, DES formed by ChCl and ethanol was used as solvent and 5-SSA as catalyst. In the absence of the acid catalyst, the conversion rate of FA was extremely low. Therefore, the conversion rate of FA did not increase significantly with the addition of only the ChCl catalyst. Adding 5-SSA (0.064 g, 0.25 mmol) into the reaction system of ethanol as solvent obviously improved the conversion rate of FA and the yield of EL at 100 °C for 2 h, which reached 91.98 and 80.24%, respectively. Notably, after the same amount of 5-SSA was added to the reaction system with DES as the solvent, the conversion of FA reached 94.91% and the yield of EL reached 88.82% at 100 °C for 2 h. The selectivity was considerably greater than that obtained using either ChCl or 5-SSA. These results suggest that Brønsted acid is a key component in the conversion of FA to EL. Moreover, after ChCl is added, it combines with hydrogen of ethanol hydroxyl group to form acidic DES and produces ethoxyl group easily, which can promote the FA alcoholysis process (Table 1).

Table 1. Performance of Different Catalysts^a

entry	catalysts	C_{FA} (%)	Y_{EL} (%)	S_{EL} (%)
1	none	0	0	0
2	ChCl	1.31	0	0
3	5-SSA	91.98	80.24	87.24
4	ChCl -5-SSA	94.91	88.82	93.58

^aReaction conditions: FA (0.098 g, 1 mmol), 5-SSA (0.064 g, 0.25 mmol), ChCl (0.035 g, 0.25 mmol), and ethanol (10 mL).

3.1.2. Effect of ChCl Dosage. With the increase in the ChCl dosage, the EL yield increased gradually (Figure 1). To evaluate the effect of ChCl dosage on the reaction at high temperatures, the FA conversion rate, EL yield, and EL selectivity were compared at 100 °C for a 1.5 h reaction. The conversion rate of FA and the yield of EL were investigated by adding different dosages of ChCl (0.018, 0.035, 0.070, and 0.15 g). The corresponding FA conversion rates were 75.90, 84.66, 85.64, and 86.34%. The yields of EL were 66.68, 77.41, 78.33, and 45.32%, respectively. With the increase in ChCl dosage under these conditions, the FA conversion rate and EL yield increased first, but the increase was not significant when the amount of ChCl increased from 0.035 to 0.07 g. When the amount of ChCl exceeded 0.07 g, the conversion rate of FA increased slightly but the yield of EL decreased greatly because EL was converted into other byproducts during the reaction. Therefore, the optimal amount of ChCl was 0.035 g (0.25 mmol), for which the FA conversion rate was 84.66% and EL yield was 77.41% at 100 °C for 1.5 h.

In addition, the influence of catalyst dosage on FA alcoholysis was studied at 100 °C for 1.5 h (Figure 2). When only 0.032 g 5-SSA was added, the conversion rate of FA

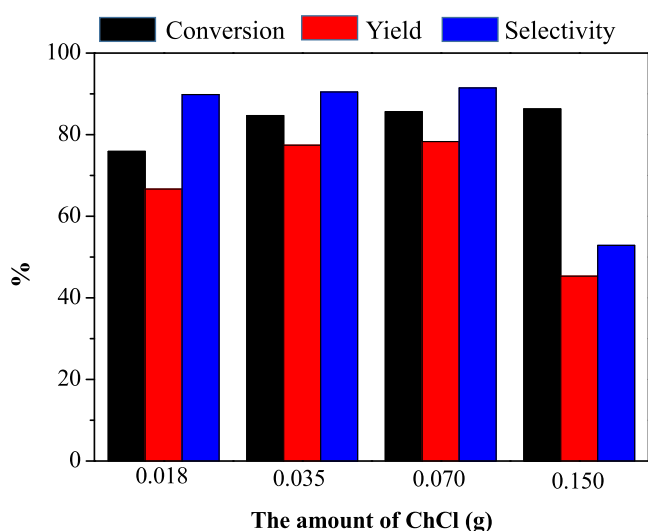


Figure 1. Effect of the amount of ChCl on the conversion of FA to EL. Reaction conditions: FA (0.098 g, 1 mmol), 5-SSA (0.064 g, 0.25 mmol), and ethanol (10 mL) at 100 °C for 1.5 h.

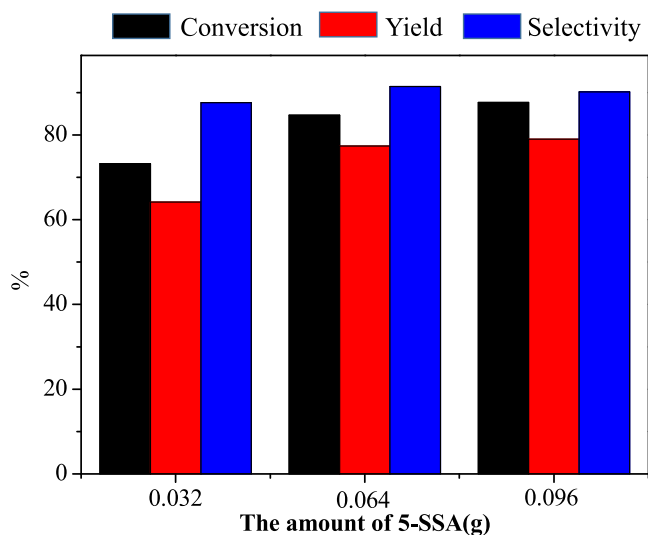


Figure 2. Effect of the amount of 5-SSA on the conversion of FA to EL. Reaction conditions: FA (0.098 g, 1 mmol), ChCl (0.035 g, 0.25 mmol), and ethanol (10 mL) at 100 °C for 1.5 h.

was 73.25%, and the yield of EL was 64.17%. After adding 0.064 g 5-SSA, FA conversion rate and EL yield reached 84.66 and 77.41%. When 0.096 g 5-SSA was added, the conversion rate of FA was 87.65%, and the yield of EL was 79.02%. Based on overall consideration, 0.064 g of 5-SSA was selected for the parallel experiment.

3.1.3. Effects of Reaction Temperature and Time on the Catalytic Reaction. Effects of the reaction temperature and reaction time on EL synthesis by the alcoholysis of FA in 5-SSA and DES were investigated. With the increase in temperature, the FA conversion rate and EL yield increased using only 5-SSA as the catalyst at 90–110 °C for 1–2 h, reaching 93.86 and 89.33%, respectively (Figure 3). When ChCl and 5-SSA were added into the reaction in a 1:1 ratio at 110 °C for 1.5 h, the FA conversion rate and EL yield reached the maximum of 93.91 and 88.17%, respectively. However, with the increase in reaction time to 2 h, the increase rate of FA conversion and EL yield decreased significantly to 95.45 and 90.70%, respectively. With the increase in reaction time from 1 to 2 h at 100 °C, the FA conversion rate and EL yield increased rapidly to 94.91 and 88.82%, respectively. These values were slightly less than the conversion and yield of the reaction conducted at 110 °C for 2 h. Therefore, from the perspective of energy savings, a reaction time of 2 h at 100 °C was selected as the best reaction condition in DES with ChCl/5-SSA = 1:1. In addition, the experimental results showed that the FA conversion rate and EL yield were 91.98 and 80.24% using only 5-SSA as the catalyst at 100 °C for 2 h. These values were significantly less than the FA conversion rate (94.91%) and EL yield (88.82%) under the catalysis of 5-SSA and ChCl at 100 °C for 2 h. This result indicated that the addition of ChCl promoted the reaction, especially at low temperatures.

3.2. Plausible Mechanism. According to previous studies,²¹ the mechanism of DES catalysis of the alcoholysis of FA to form EL is proposed, as shown in Scheme 1. In DES and 5-SSA, the reaction starts with the hydroxyl group on the FA connecting to the acid center in the solution.

On the basis of the experimental study on the alcoholysis of FA into EL under acidic conditions, the related mechanism was investigated through density functional theory (DFT) calculations.

First, the oxygen atom on the hydroxyl group in FA was linked with H⁺, affording intermediate A and water (Figure 4). The hydrogen of the hydroxyl group in ethanol coupled with

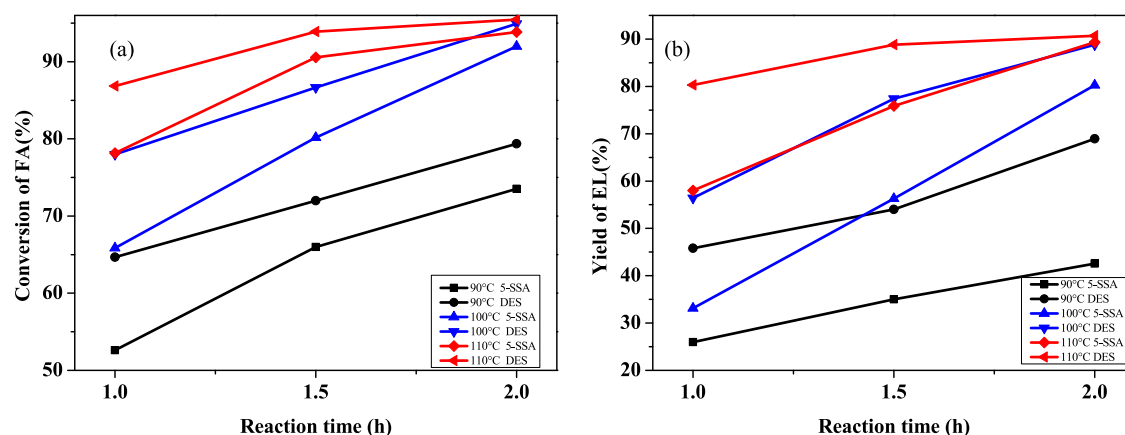


Figure 3. Effects of different reaction temperatures and times on (a) FA conversion and (b) EL yield by the addition of 5-SSA and DES, respectively. Reaction conditions: FA (0.098 g, 1 mmol), 5-SSA (0.064 g, 0.25 mmol), ChCl (0.035 g, 0.25 mmol), and ethanol (10 mL).

Scheme 1. Schematic for the Conversion of FA into Protonated EL

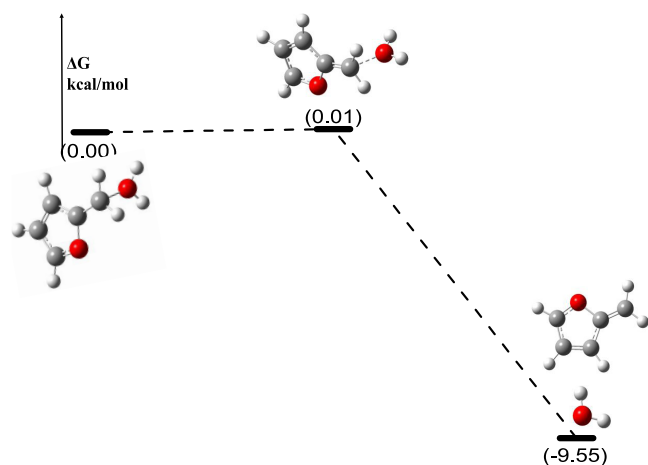
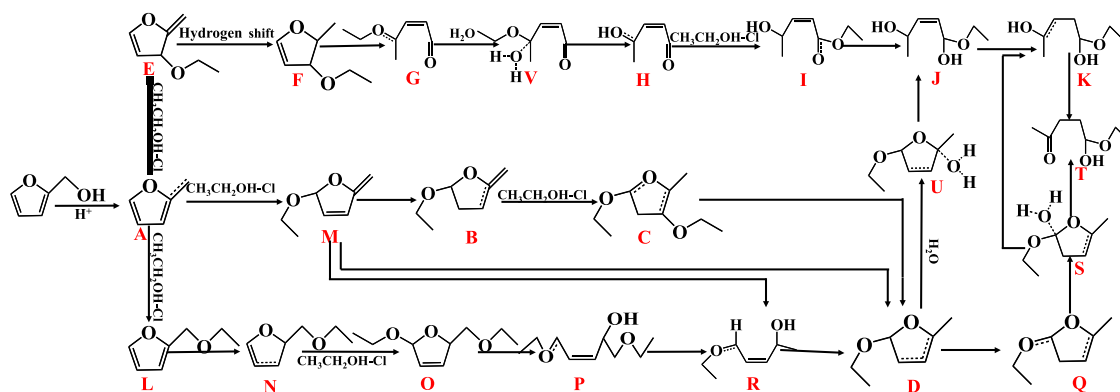


Figure 4. Calculated Gibbs free-energy profile using M062X/def2tzvp with schematic geometries of FA to intermediate A along the stepwise pathway.

Cl in ChCl to form DES and promote the formation of ethoxyl group. Then, intermediate A reacted with ethoxyl group in DES via three reaction paths under acidic conditions, which were denoted as A, B, and C, respectively. In all pathways, the protonation of the hydroxyl group was the initial step. At 373.15 K, the free-energy barrier of FA to generate intermediate A was 0.01 kcal/mol.

The intermediate A may react with ethanol under acidic conditions to form humin and ethyl acetate propionate.²² Since humin is a byproduct and its structure is complex, the reaction energy barrier during its formation was not calculated. The energy barrier and transition state of intermediate A to EL are shown in Figure 5.

In route A, intermediate A reacted to generate intermediate R, which was converted to intermediate D, and then product T was synthesized in three possible steps.

In the first path (see the Supporting Information (SI): Figure S1a–b) of intermediate A to R, the positively charged intermediate A attracted the negatively charged oxygen atoms of ethanol to form intermediate L; the free-energy barrier for this process was -25.75 kcal/mol. Intermediate L rearranged to form intermediate N, with a free-energy barrier of 6.47 kcal/mol. The intermediate N reacted with ethoxyl group in DES, affording a product with a possible structure of intermediate O that required an energy barrier of -17.43 kcal/mol. This hydrogen shift from intermediate O to intermediate P had a free-energy barrier of 3.42 kcal/mol. An energy of 13.80 kcal/

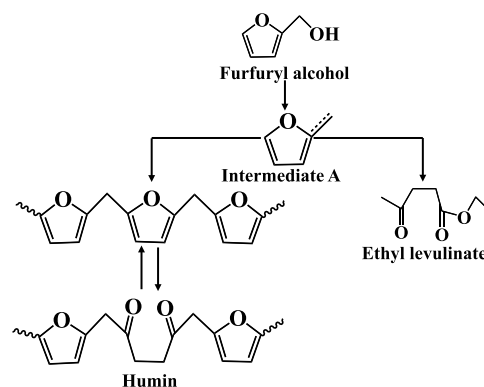


Figure 5. Proposed formation pathways of humin and ethyl levulinate from the acid-catalyzed conversion of furfuryl alcohol in ethanol with 5-SSA.

mol was required for the transfer of hydrogen from the carbon connected with the hydroxyl group to the ethyl group connected to the adjacent carbon of intermediate P to form intermediate R and ethanol. The intermediate R continued to a pathway in the presence of ethanol, which will be described later.

Route B shows three possible reaction paths for the conversion of intermediate A to D in DES (see SI: Figure S2). The first path of intermediate A to D involved the attraction of positively charged intermediate A to the ethoxyl group in DES to form intermediate M, requiring a free energy of -20.45 kcal/mol. Under the action of ethanol, intermediate M underwent hydrogen transfer to form intermediate B overcoming an energy barrier of 11.72 kcal/mol. Intermediate B overcame a reaction energy barrier of -10.14 kcal/mol to generate intermediate C. Intermediate C lost ethanol molecules to form intermediate D, overcoming a reaction energy barrier of 4.63 kcal/mol.

In the second path of intermediate A to D, intermediate A went through the same path as the first one to intermediate M. Intermediate M generated intermediate R under acidic conditions, requiring the energy of -1.96 kcal/mol to undergo hydrogen transfer to form intermediate R. Intermediate R rearranged to form intermediate D and ethanol molecules, requiring an activation energy of 12.65 kcal/mol.

The third possible reaction path for intermediate A to form intermediate D involved a reaction between reaction intermediate A and ethoxyl group in DES to form the same intermediate M as above. Intermediate M directly generated

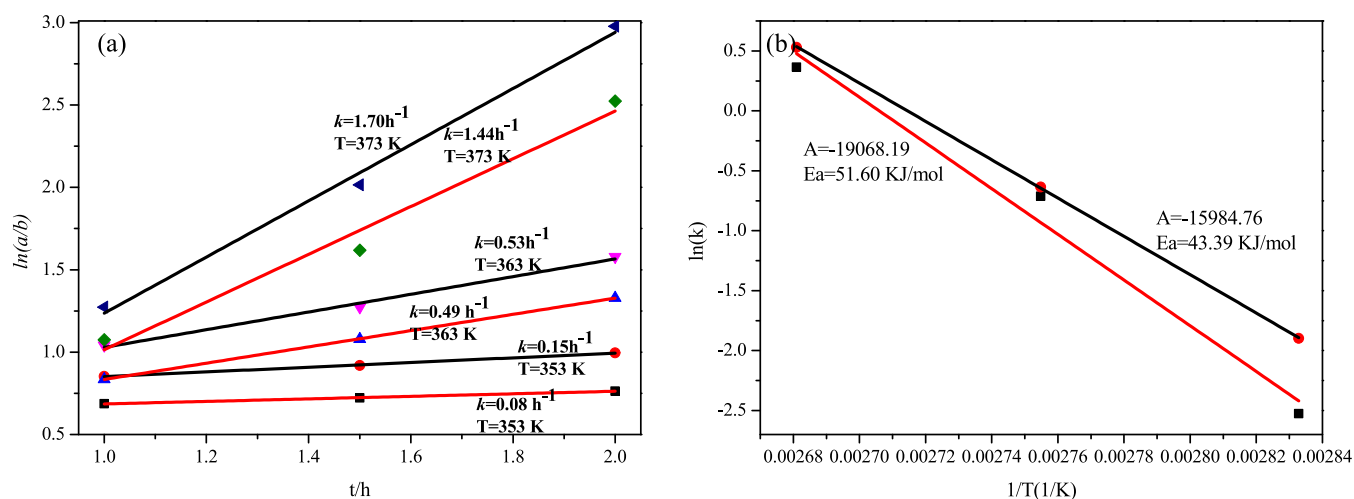


Figure 6. (a) First-order kinetic curves of FA to EL; (b) Arrhenius equation at different temperatures. Reaction environments: FA (0.098 g, 1 mmol), 5-SSA (0.064 g, 0.25 mmol), ChCl (0.034 g, 0.25 mmol), ethanol (10 mL), and temperatures: 80–100 °C.

intermediate D under the action of ethanol molecules, overcoming a reaction energy barrier of 1.77 kcal/mol.

The intermediate D then continued to react to form protonated EL T through three possible reaction paths (see SI: Figure S3a–b). The first reaction path involved the rearrangement of intermediate D to form intermediate Q, and the energy required for this process was 22.06 kcal/mol. The carbocation in intermediate Q connected to an oxygen ion in water to form intermediate S, overcoming an energy barrier of 1.07 kcal/mol. After overcoming an energy barrier of 16.62 kcal/mol, the intermediate S directly generated protonated EL (intermediate T).

In the second reaction path, the reaction of intermediate D to S was the same as before. Under the action of ethanol, the generated intermediate S underwent hydrogen transfer to form intermediate K, and the energy barrier of this process was 15.07 kcal/mol less than that of the directly generated intermediate T.

The third reaction path of intermediate D to form intermediate T involved the initial combination of intermediate D and water to generate intermediate U, requiring an energy barrier of 8.30 kcal/mol to be overcome. The second step involved the conversion of intermediate U into intermediate J, having an energy barrier of 5.18 kcal/mol. With an energy barrier of 23.99 kcal/mol, the intermediate J continued to transform into intermediate K. Then, the reaction of intermediate K to intermediate T was the same as mentioned before.

In route C, intermediate A was transformed into intermediate E with an energy barrier of -0.64 kcal/mol (see SI: Figure S4). Intermediate E was converted into intermediate F by hydrogen shift, and the energy barrier of this process was 5.65 kcal/mol.

Under the action of ethanol, intermediate F continued to react to generate intermediate G via two possible reaction paths. First, the positive C ion on intermediate G combined with water to generate intermediate V, thereby generating intermediate H through hydrogen transfer. The energy barriers of the three reaction processes were -3.95 , 3.79 , and 8.96 kcal/mol, respectively. Second, intermediate F lost ethanol molecules under the action of water to form intermediate H

directly. The reaction energy barrier of this process was -0.45 kcal/mol (see SI: Figure S5).

The positive C ion on intermediate H combined with ethoxy group in DES to form intermediate I, and the reaction energy barrier for this step was -14.06 kcal/mol. Hydrogen transfer occurred in intermediate I under the action of ethanol, with the reaction energy barrier of -3.03 kcal/mol. The reaction path of intermediate J to intermediate T was as described above (see SI: Figure S6).

From the comparison of the activation energy of all possible pathways of intermediate A to intermediate T, it is seen that the reaction energy barriers of all reaction paths are relatively small, and reactions occur spontaneously. This result further indicates that all reaction paths may occur in the conversion of FA to EL under acidic conditions, but the path requiring the lowest energy barrier in the reaction process revealed a higher proportion of each product. In acidic DES, the highly electronegative chlorine ion is coupled with the hydrogen on the hydroxyl group of ethanol to form a structure similar to HCl, promoting the formation of ethoxyl group in the reaction. The conversion rate of FA and the yield and selectivity of EL were improved by the addition of ChCl into the reaction system.

3.3. Plausible Mechanism. To examine the effect of adding ChCl on the transformation of FA to EL from the perspective of reaction kinetics, the reaction kinetics of systems with 5-SSA and ChCl at 80, 90, and 100 °C were investigated. Ethanol was used as the solvent in the whole reaction system, and the effect of ethanol concentration on reaction kinetics was not considered during the reaction process. Therefore, the transformation of FA to EL is assumed to be a quasi-first-order reaction (Figure 6). The first-order reaction rate equation is $\ln(a/b) = kt$, where a is the concentration of reactants at the start of the reaction, and b is the concentration of reactants at time t . Quasi-first-order kinetics was observed at all of the investigated reaction temperatures. According to the experimental results, the values of rate constant k were 0.08, 0.49, and 1.44 h^{-1} with the addition of only 5-SSA, and E_a for conversion of FA to EL was 51.60 kJ/mol. In acidic DES, the values of rate constant k were 0.15, 0.53, and 1.70 h^{-1} , and E_a was 43.39 kJ/mol, which was favorable for the reaction because it was less than that without ChCl.

4. CONCLUSIONS

In this paper, FA conversion to EL was investigated in a DES formed by adding ChCl into ethanol with 5-SSA as the catalyst. With the addition of ChCl and 5-SSA, the selectivity of EL was significantly higher than that with only 5-SSA under the same reaction conditions. This was because Cl^- in ChCl can be coupled with H from the hydroxyl group of ethanol to form a structure similar to HCl, which is more conducive to the formation of ethoxyl group and hydrogen transfer in the reaction process. DFT results showed that the energy barrier to be overcome in each step of the FA alcoholysis reaction was relatively low under the catalytic action of Brønsted acid for the formation of EL, which could be spontaneously generated. In addition, the theoretical calculation results further indicated that Brønsted acid is mainly responsible for the dehydration of FA, which is the switch of the whole reaction. The concentration of H^+ determines whether the reaction can be carried out and the reaction conditions. The formation of ethoxyl also facilitates subsequent alcoholysis reactions. In short, DES has potential application prospects for biomass conversion in the future because of its pollution-free feature and low cost.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c03424>.

The density functional theory (DFT) calculation method is used to simulate all possible reaction paths of FA alcoholysis to EL in acidic DES (PDF)

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Notes

The authors declare no competing financial interest.

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