Remarkably efficient hydrolysis of cinnamaldehyde to natural benzaldehyde in amino acid ionic liquids

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Abstract−The hydrolysis of cinnamaldehyde to natural benzaldehyde was investigated systematically using tetramethylammonium-based amino acid ionic liquids as homogeneous catalysts. The results indicated that tetramethylammonium prolinate ($[N_{1111}][Pro]$) can be a powerful catalyst for the highly efficient hydrolysis of cinnamaldehyde, in which natural benzaldehyde was obtained with almost 94% yield and over 99% selectivity in 1 h. Moreover, kinetic study showed that compared with other catalysts, the catalytic system of $[N_{1111}][Pro]$ has a lower activation energy of $38.30 \ kJ \cdot mol^{-1}$ in the hydrolysis reaction, indicating superior catalytic performance of $[N_{1111}][Pro]$. Quantum-mechanical calculations further manifested that such high performance originates from the cooperative catalysis of the secondary amino and carboxyl group in the anion [Pro].

Keywords: Natural Benzaldehyde, Cinnamaldehyde, Hydrolysis, Ionic Liquids

INTRODUCTION

Benzaldehyde is the second most utilized flavor compound worldwide and used extensively in the fields of food, beverages, cosmetics, and pharmaceutical industries, etc [1]. With an increased interest in food safety and natural flavor essence, natural benzaldehyde is widely accepted and is becoming more popular. Thus, the demand for natural benzaldehyde is growing rapidly, and much attention has been paid to the production of natural benzaldehyde in recent years [2].

The conventional preparation of natural benzaldehyde is by alkaline hydrolysis of laetrile. However, this technology could inevitably form highly toxic hydrogen cyanide as a byproduct, which would require costly removal methods for safety. With the principle of green and sustainable processes, the synthesis of natural benzaldehyde from cinnamon oil, which contains about 80% of cinnamaldehyde, is considered to be an alternative route. But the key problem is that cinnamon oil and cinnamaldehyde are poorly soluble in water, resulting in a relatively low yield of natural benzaldehyde. Thus, several strategies such as near-critical water, modified natural polymers, and basic hydrotalcite catalyst have been reported to promote the reaction [3-5]. For example, near-critical water was reported to be an excellent solvent to improve the solubility of cinnamaldehyde and accelerate the hydrolysis reaction [5]. Furthermore, β-cyclodextrin and 2-hydroxypropyl-β-cyclodextrin were developed as catalysts for the oxidation of cinnamaldehyde, respec-

tively [6,7]. The Al-Mg hydrotalcite catalyst was also demonstrated to produce natural benzaldehyde with a considerable yield [8]. In spite of the preliminary success, these results are not entirely satisfactory because of low reaction selectivity and product yield, harsh reaction conditions (high temperature of 553 K, high pressure of 15 MPa), and too complex catalyst preparation. Therefore, many more investigations are still required to develop green catalysts with high efficiency under mild conditions for obtaining natural benzaldehyde.

Ionic liquids (ILs) have increasingly attracted attention as promising catalysts and green solvents [9]. Most ILs have many specific physical-chemical properties such as structural variability, low volatility, high thermal and chemical stability, remarkable solubility, and effortless reusability. Thus, these features can afford many opportunities for the applications of ILs in many fields such as gas absorption, catalysis, biotransformation, electrochemistry, etc [10-13]. However, to the best of our knowledge, there is no study investigating the application of ILs as catalysts and solvents for the hydrolysis of cinnamaldehyde to obtain natural benzaldehyde. Among the varieties of ILs, amino acids ionic liquids (AAILs) derived from bioresources are considered to be of low toxicity, high biocompatibility and biodegradable characteristics [14-18]. Then the AAILs would have great potential for preserving the highest possible natural essence of benzaldehyde.

Hence, in this work, a series of tetramethylammonium-based AAILs ($[N_{1111}][AA]$) have been used as catalysts for the hydrolysis

Scheme 1. Hydrolysis of cinnamaldehyde catalyzed by $[N_{1111}][AA]$.

of cinnamaldehyde to natural benzaldehyde (Scheme 1). The effect of different reaction parameters such as reaction time, temperature, catalyst loading, and molar ratio of reactants were studied in detail. The kinetics for the hydrolysis reaction were explored to obtain the kinetics parameters (reaction rate constant, activation energy), and a plausible reaction mechanism involving the cooperative catalysis of $[N_{1111}][Pro]$ was also proposed.

EXPERIMENTAL METHODS

1. Materials

Tetramethylammonium hydroxide (25 wt% aqueous solution) was obtained from Shanghai Macklin Biochemical Co. Other reagents such as amino acid, triethylamine, Na_2CO_3, and NaOH were of analytical grade and used without further purification. Four AAILs $[N_{1111}][Pro]$, $[N_{1111}][Gly]$, $[N_{1111}][Ala]$, and $[N_{1111}][Val]$ were synthesized via the simple neutralization reaction similar to the reported procedures [19]. The detailed preparation methods and characterization results of these AAILs are listed in the Supplementary data.

2. General Reaction Procedures

Typically, cinnamaldehyde (2 mmol, 0.264 g), deionized water (10 g), and 5 wt% of $[N_{1111}][Pro]$ (0.5132 g) were charged into a round-bottomed glass flask equipped with a magnetic stirrer and condenser. Then, the reaction mixture was stirred at 333 K for 1 h. Samples were taken from the reactor at regular intervals and analyzed by GC-MS and GC. For the kinetic study, duplicate experiments at least three times were run to obtain averaged values of natural benzaldehyde yield and selectivity. The averaged uncertainty of the kinetic data in this work was well within ±1%. In addition, large-scale hydrolysis of cinnamaldehyde to natural benzaldehyde was also carried out under optimal conditions as follows: cinnamaldehyde (40 mmol, 5.28 g), deionized water (200 g), and 5 wt% of $[N_{1111}][Pro]$ (10.264 g).

3. Analysis

Qualitative analyses of products were examined by a Thermo Trace 1300 GC-ISQ, and quantitative analyses were carried out by a GC-FID (Agilent 7890B). A capillary column HP-5 (methyl polysiloxane, 30 m×0.32 mm×1 μm) was used to determine the composition of the samples with nitrogen as the carrier gas at a flow rate of 3 mL/min. Naphthalene used as the internal standard to calculate the conversion of cinnamaldehyde and the selectivity of nature benzaldehyde. The temperature of the column, the inlet and the detector was kept at 453, 473, and 523 K, respectively.

4. Computational Methods

The geometry optimizations and natural bond orbital (NBO) charge analysis were performed using density functional theory (DFT) at the B3LYP/6-311++G(d,p) level in the Gaussian 09 program package [20]. Each final optimized structure of $[N_{1111}][Pro]$, cinnamaldehyde and their complexes was checked to be a true minimum through frequency calculation at the corresponding levels.

RESULTS AND DISCUSSION

1. Catalyst Screening

The hydrolysis of cinnamaldehyde to natural benzaldehyde in the presence of four AAILs $[N_{1111}][AA]$ as catalysts was conducted

Table 1. Results of hydrolysis of cinnamaldehyde using different catalysts[a]

Entry	ILs	Cinnamaldehyde conversion (%)	Benzaldehyde yield (%)
1	$[N_{1111}][Pro]$	94	94
2	$[N_{1111}][Gly]$	37	34
3	$[N_{1111}][Ala]$	8	7
4	$[N_{1111}][Val]$	Trace	Trace
5	$[P_{4444}][Pro]$	74	66
6	$[N_{1111}][Ace]$	<2	<2
7	$[Emim][Pro]$	80	72
8	NaOH	50	35
9	Na_2CO_3	Trace	Trace
10	Et_3N	<3	<2

[a]Reaction conditions: cinnamaldehyde (2.0 mmol), catalyst (5 wt%), deionized water (10 g), reaction time (1 h), reaction temperature (333 K)

to test their catalytic activities. The results are summarized in Table 1. $[N_{1111}][Pro]$ catalyzed the hydrolysis reaction smoothly, giving natural benzaldehyde in a good yield (entry 1). However, the other three $[N_{1111}][AA]$ ILs catalysts gave unsatisfactory results, with incomplete conversion and low yields of natural benzaldehyde (entries 2-4). To gain insight into the catalysis of $[N_{1111}][Pro]$, we calculated the natural bond orbital (NBO) charges in the free cinnamaldehyde, [Pro], and the complexes of cinnamaldehyde with [Pro]. As shown in Fig. 1, compared with the free [Pro], the negative charge of the nitrogen atom in the complexes of cinnamaldehyde with [Pro] decreases obviously (from −0.054 to −0.01). Meanwhile, both the NBO positive charge of the hydrogen atom H (1) and the NBO negative charge of the oxygen atom O (1) increase, indicating a strong interaction between secondary amino and aldehyde group. On the other hand, the carbon atom C (3) and the hydrogen atom
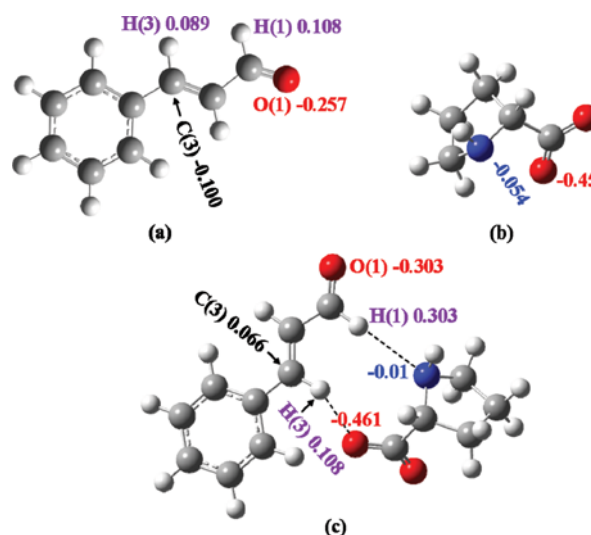

Fig. 1. Optimized structures and NBO charge analysis of (a) free cinnamaldehyde, (b) free [Pro], and (c) the complexes of cinnamaldehyde with [Pro].

H (3) in the complexes of cinnamaldehyde with [Pro] are found to possess more NBO positive charges because of the electron-withdrawing effect of the carboxylate group in the anion [Pro]. This shows that the electrophilicity of C (3) could improve effectively, which is in favor of the nucleophilic attack by water. Consequently, the AAIL [N$_{1111}$][Pro] containing secondary amino and carboxyl group can smoothly interact with cinnamaldehyde, thus enabling water to nucleophilic attack and hydrolyze the C=C double bond of cinnamaldehyde to obtain a high yield of natural benzaldehyde. We also studied the hydrolysis reaction in other three ILs 1-ethyl-3-methylimidazolium prolinate ([Emim][Pro]), tetrabutylphosphonium prolinate ([P$_{4444}$][Pro]), and tetramethylammonium acetate ([N$_{1111}$][Ac]). It is found that [Emim][Pro] and [P$_{4444}$][Pro], which has the same anion of [Pro] as that of [N$_{1111}$][Pro], also exhibited good catalytic performance, yielding 72% and 66% of natural benzaldehyde, respectively, whereas a very low yield was obtained in the catalysis of [N$_{1111}$][Ac] (entries 5-7). This further confirms that the presence of an amino and a carboxyl group in one molecule is essential for the hydrolysis of cinnamaldehyde.

For comparison, several traditional alkaline catalysts such as NaOH, Na$_2$CO$_3$, and triethylamine were studied for the hydrolysis of cinnamaldehyde. All of these basic catalysts were found to perform very low selectivity and yield of natural benzaldehyde (entries 8-10). This implies that too strong alkaline is detrimental to the hydrolysis reaction. Moreover, we compared the catalytic activity of [N$_{1111}$][Pro] with the performance of other catalysts published in the literature [6-8,21]. The catalyst 2-HP-β-CD/Na$_2$CO$_3$/H$_2$O$_2$ was reported to show the best catalytic activity so far and induced a 81% yield of natural benzaldehyde [22], which is much less than the catalysis performance of [N$_{1111}$][Pro]. Therefore, [N$_{1111}$][Pro] can be considered a promising catalyst for the highly efficient synthesis of nature benzaldehyde. [N$_{1111}$][Pro] was chosen as the catalyst for further studies.

2. Effect of Reaction Temperature

The effect of reaction temperature on hydrolysis of cinnamalde-

hyde was investigated. As seen from Fig. 2, the reaction temperature had an obvious influence on the hydrolysis rate. The conversion of cinnamaldehyde at 1 h could improve rapidly as the reaction temperature increased from 303 K to 333 K. For example, the benzaldehyde yield was 46% at the temperature of 303 K, while the benzaldehyde yield was 94% in the case of 333 K. Nevertheless, the yield of benzaldehyde could not be further enhanced when the temperature was increased to 343 K. Thus, the optimal reaction temperature should be at 333 K. Moreover, compared with the reaction conditions in the previous literature [5,8], it is demonstrated that the favorable temperature in this work is much lower and this is especially beneficial for retaining the natural essence of natural benzaldehyde.

3. Effect of Water Amount

The amount of water is crucial to the hydrolysis of cinnamaldehyde because of the bad solubility of cinnamaldehyde in water. The effect of water amount was then studied ranging from 2.5 g to 15 g (Fig. 3). It was found that the reaction rate of hydrolysis of cinnamaldehyde could be effectively accelerated with water dosage rising from 5 to 10 g. However, the yield of natural benzaldehyde did not improve too much with the extra increase to 15 g water. This shows that the increase of water concentration can facilitate the dissolution of cinnamaldehyde in water and thus speeds up the reaction rate. This finding is matched well with the results in the previous report [23]. Therefore, the amount of water is preferred to be 10 g.

4. Effect of Catalyst Loading

Fig. 4 shows the effect of catalyst loading on the hydrolysis reaction. It is found that catalyst loading is crucial to the enhancement of yield of natural benzaldehyde. With an increase in the relative amount of [N$_{1111}$][Pro], the rate of hydrolysis reaction was speeded up and thus a higher yield was obtained. For example, when the dosage of [N$_{1111}$][Pro] increased from 1% to 5%, the yield significantly increased from 70% to 93% in 1 h. However, only a slight increase in the yield was examined when the catalyst dosage was
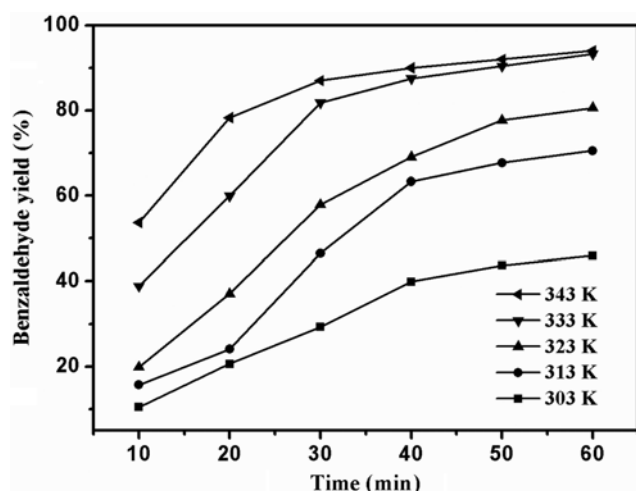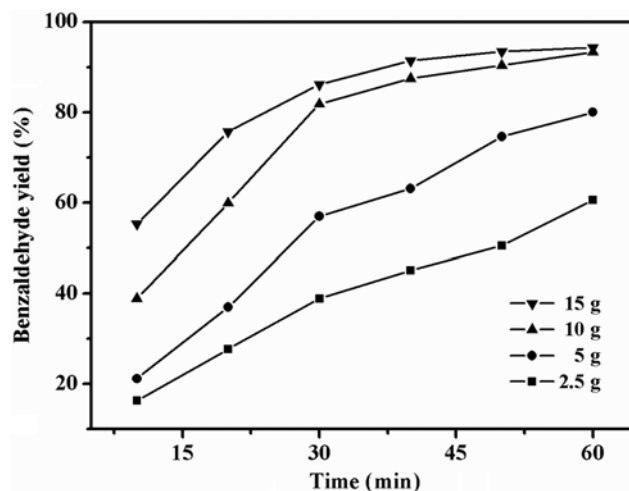

Fig. 2. Effect of reaction temperature on the yield of natural benzaldehyde. Cinnamaldehyde (2 mmol, 0.264 g), deionized water (10 g), [N$_{1111}$][Pro] catalyst, catalyst loading (5 wt%), reaction time (1 h).

Fig. 3. Effect of water amount on the yield of natural benzaldehyde. Cinnamaldehyde (2 mmol, 0.264 g), [N$_{1111}$][Pro] catalyst, catalyst loading (5 wt%), reaction temperature (333 K), reaction time (1 h).
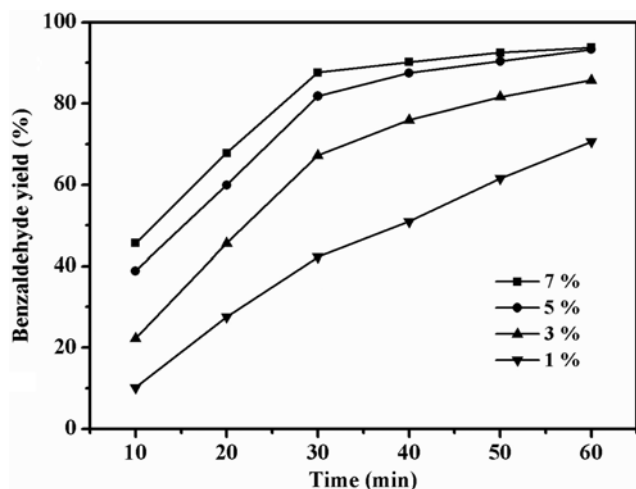
Fig. 4. Effect of catalyst loading on the yield of natural benzaldehyde. Cinnamaldehyde (2 mmol, 0.264 g), deionized water (10 g), [N$_{1111}$][Pro] catalyst, reaction temperature (333 K), reaction time (1 h).

further added to 7%. This indicates that beyond a certain catalyst loading, too much catalyst amount is not necessary. Thus, in consideration of the cost of catalyst, 5 wt% is taken as the optimum catalyst loading and used in most of the hydrolysis experiments.

5. Reusability of Catalyst

For potential application in industry, the reusability and stability of a catalyst are the two key influential factors. After the completion of a reaction, the reaction system with the catalyst [N$_{1111}$][Pro] was cooled to room temperature and extracted with ethyl acetate (10 mL×3), and the system thus formed a liquid-liquid biphase, and the aqueous phase containing [N$_{1111}$][Pro] could be easily separated by simple decantation. After that, the catalyst [N$_{1111}$][Pro] was further in a vacuum oven at 90 °C for 6 h to remove water and the residual reactants. [N$_{1111}$][Pro] was therefore recycled four times
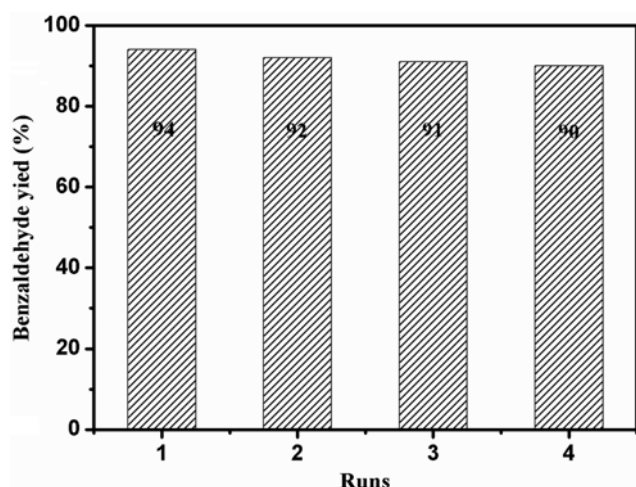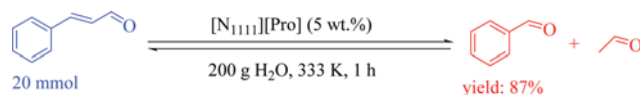

Fig. 5. The recycle test of [N$_{1111}$][Pro] catalyst. Cinnamaldehyde (2 mmol, 0.264 g), deionized water (10 g), [N$_{1111}$][Pro] catalyst, catalyst loading (5 wt%), reaction temperature (333 K), reaction time (1 h).

Scheme 2. Large-scale hydrolysis of cinnamaldehyde catalyzed by [N$_{1111}$][Pro].

for testing its activity as well as stability. From Fig. 5, no significant decrease in the yield of natural benzaldehyde was examined during these four successive recycles. Thus, the catalyst [N$_{1111}$][Pro] was stable enough to be recycled for the hydrolysis of cinnamaldehyde. [N$_{1111}$][Pro] was considered to be steadily recycled for the hydrolysis reaction.

6. Large-scale Experiment

A large-scale experiment for the hydrolysis of cinnamaldehyde was performed under the optimal reaction conditions (Scheme 2). It is found that the experiment does not show an apparent scaling effect. The yield of natural benzaldehyde could still reach 87%, even though the quantity of reactants increased twenty-fold. This implies that this process shows great potential for the production of natural benzaldehyde in an industrial scale.

7. Hydrolysis of other Cinnamaldehydes

To further investigate the wide applicability of [N$_{1111}$][AA] ILs, the activity of [N$_{1111}$][Pro] was tested in a series of hydrolysis of various cinnamaldehyde and the results are listed in Table 3. The electron donating/withdrawing substituent in the benzene ring of cinnamaldehyde derivatives had a significant effect on the hydrolysis

Table 2. The reaction rate constants at different temperatures

T (K)	K (min^{-1})	Correlation coefficient (R^2)
303	0.01122	0.9823
313	0.02152	0.9916
323	0.02793	0.9956
333	0.04704	0.9949

Table 3. Results of hydrolysis of different cinnamaldehydes

Entry	Cinnamaldehyde	Product	Yield (%)
1			94
2			<5 80[a]
3			<3 99[b]
4			30 94[c]

Reaction conditions: cinnamaldehyde (2.0 mmol), catalyst (5 wt%), deionized water (10 g), reaction time (1 h), reaction temperature (333 K)
[a]Catalyst (30 wt%), reaction time (18 h), reaction temperature (373 K)
[b]Catalyst (10 wt%), reaction time (12 h), reaction temperature (353 K)
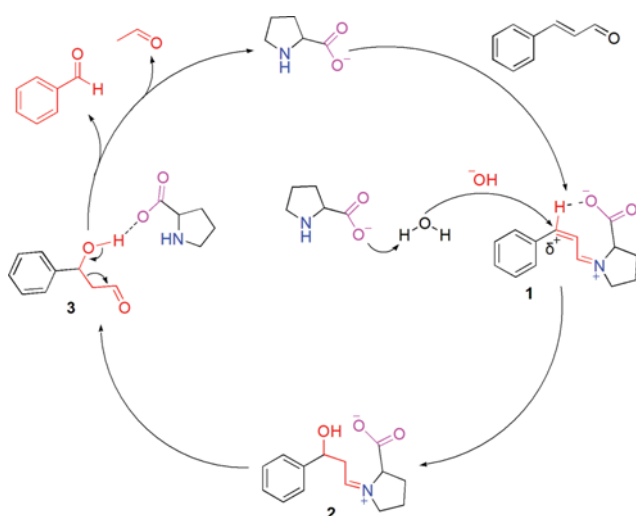[c]Catalyst (10 wt%), reaction time (2 h), reaction temperature (353 K)

Fig. 6. The plausible reaction mechanism for [N$_{1111}$][Pro] promoted hydrolysis of cinnamaldehyde.

reaction. The electron withdrawing group -NO$_2$ and electron donating groups -N(CH$_3$)$_2$ and -OCH$_3$ on the aromatic ring remarkably decreased the yields. To obtain considerable yields, harsh reaction conditions such as high temperature, more time and catalyst loading must be provided. Therefore, it was demonstrated that all the substrates had good yields (80-99%) of corresponding products by simply tuning the reaction conditions, indicating the wide applicability of [N$_{1111}$][Pro] in the hydrolysis of various cinnamaldehyde.

8. Reaction Mechanism

The mechanism of alkaline hydrolysis of cinnamaldehyde to benzaldehyde is considered as retro-Aldol condensation reaction. Thus, on the basis of the above-mentioned DFT results and iminium catalysis [23-25], a plausible mechanism involving the cooperative catalysis of [N$_{1111}$][Pro] was proposed and illustrated in Fig. 6. Initially, cinnamaldehyde is transformed into iminium salt **1** by the interaction of the secondary amino group in [Pro]. Hydroxide ion (OH$^-$) is also formed from water under alkaline conditions. Subsequently, nucleophilic OH$^-$ attacks the β-carbon atom of α,β-unsaturated carbocation on iminium salt **1** to give intermediate **2**. The carboxyl group of [Pro] further forms a hydrogen bridge with the hydroxyl group of hydrated molecule **2**, resulting in intermediate **3**. Finally, deprotonation of intermediate **3** leads to carbon-carbon double bond cleavage and release of benzaldehyde and abstraction of proton to give acetaldehyde, and then the catalyst [N$_{1111}$][Pro] is regenerated.

9. Kinetic Model

It was obvious that the water amount was much higher than the mass of cinnamaldehyde. Then the hydrolysis of cinnamaldehyde was taken without considering the reverse reaction. The hydrolysis reaction equation is written as:

$$A+B \xrightarrow{\ k_1\ } C+D \qquad (1)$$

where A, B, C, and D are cinnamaldehyde, water, benzaldehyde, and acetaldehyde, respectively. k_1 is the forward reaction rate constant. According to the pseudo-first order law [8], the reaction kinetics can be expressed as:

$$-\frac{dC_A}{dt} = k_1 C_A C_B \qquad (2)$$

where t is reaction time, C_A and C_B are the molar concentration of cinnamaldehyde and water, respectively. Because the concentration of reactant water was much higher than that required for the hydrolysis of cinnamaldehyde, the molar concentration of water (C_B) in the whole process of the reaction could be considered as a constant. Let $k_1 C_B = K$, Eq. (2) thus can be further simplified:

$$-\frac{dC_A}{dt} = KC_A \qquad (3)$$

where $C_A = C_{A0}(1-x_A)$, C_{A0} is the molar concentration of cinnamaldehyde at time t=0, x_A is the conversion of cinnamaldehyde. Eq. (3) can be rewritten as:

$$\frac{dx_A}{dt} = K(1-x_A) \qquad (4)$$

Integrals were taken for both sides of Eq. (4):

$$-\ln(1-x_A) = Kt \qquad (5)$$

with the use of Eq. (5), plotting $-\ln(1-x_A)$ versus time t at different temperatures generates a straight line with a slope of K (Fig. 7). The values of K at different temperatures are listed in Table 2. It is demonstrated that these are straight lines passing through origin, which confirms the pseudo-first order behavior of the reaction very well.

The temperature dependency of the reaction rate constant K can be expressed by the Arrhenius equation:

$$K = K_0 e^{-E_a/RT} \qquad (6)$$

Eq. (6) can be rewritten as:

$$\ln K = \ln K_0 - \frac{E_a}{RT} \qquad (7)$$

By plotting lnK versus 1/T, straight lines with the slope of $-E_a/R$ can be obtained from Eq. (7) and are shown in Fig. 8. From the
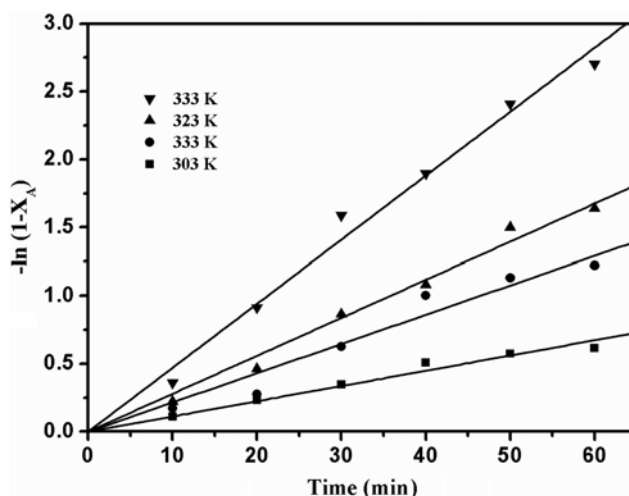

Fig. 7. Kinetic plots for various temperatures. Cinnamaldehyde (2 mmol, 0.264 g), deionized water (10 g), [N$_{1111}$][Pro] catalyst, catalyst loading (5 wt%), reaction time (1 h).
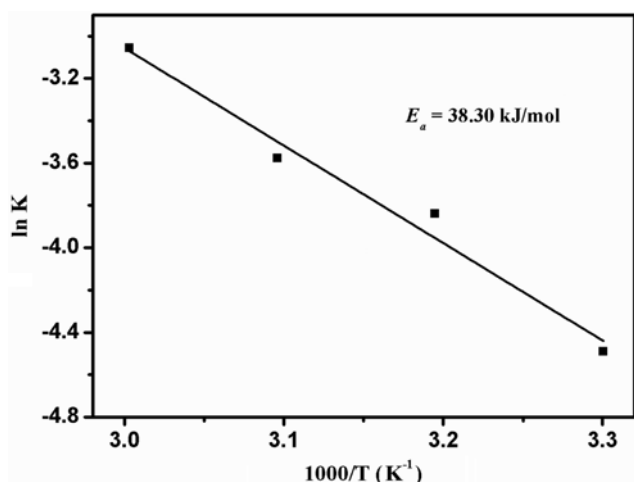
Fig. 8. Arrhenius plots of the rates constants for hydrolysis of cinnamaldehyde.

$E_a = 38.30$ kJ/mol

Table 4. The values of activation energy (E_a) for hydrolysis of cinnamaldehyde in the presence of various catalyst systems

Catalysts	E_a (kJ·mol^{-1})	Ref.
β-CD/NaOH	45.27	[3]
2-HPβ-CD/NaOH	41.72	[4]
Al-Mg hydrotalcite	41.84	[8]
[N$_{1111}$][Pro]	38.30	This work

slope of the straight line, the apparent activation energy (E_a) is found to be 38.30 kJ mol^{-1}. For comparison, the activation energies for other catalytic systems reported in the previous literature [3,4,8] are also listed in Table 4. The results show that the catalytic system of [N$_{1111}$][Pro] has the lowest activation energy of 38.30 kJ·mol^{-1} in the hydrolysis reaction. It is evident that the AAIL, [N$_{1111}$][Pro], is an excellent catalyst for the alkaline hydrolysis of cinnamaldehyde to natural benzaldehyde.

CONCLUSIONS

AAIL, [N$_{1111}$][Pro], has been proven to be a powerful catalyst for alkaline hydrolysis of cinnamaldehyde to natural benzaldehyde with 94% yield and over 99% selectivity of natural benzaldehyde achieved under optimized conditions. Further investigation of a kinetic study demonstrated that compared with other catalysts, the catalytic system of [N$_{1111}$][Pro] had a lower activation energy of 38.30 kJ·mol^{-1} in the hydrolysis reaction. Thus, this efficient catalytic system could be a beneficial reference for further production of natural benzaldehyde from the abundant and renewable cinnamon oil.

ACKNOWLEDGEMENTS

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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APPENDIX A. SUPPLEMENTARY DATA

Synthesis details for four $[N_{1111}][AA]$, FTIR, NMR spectra, ESI-MS, elemental analysis and a table of thermal property data. This material is available free of charge via the Internet at.

Supporting Information

Remarkably efficient hydrolysis of cinnamaldehyde to natural benzaldehyde in amino acid ionic liquids

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1. Preparation of [N$_{1111}$][AA]

In the experiment, the preparation of AAILs started with tetramethylammonium hydroxide ([N$_{1111}$][OH]) aqueous solutions of 25% (w/w), purchased from Shanghai Macklin Biochemical Co. Ltd.. They were storage in the dark and cool condition. All of amino acids were of analytical grade (99.9%) and purchased from the Sinopharm Chemical Reagent Co. Ltd.. [N$_{1111}$][AA] ILs were produced by the neutralization of a slight excess of amino acid with [N$_{1111}$][OH] aqueous solution at room temperature for 2-4 hours. After the reaction completed, water was distilled off at 60 °C under reduced pressure. The crude product was added into ethanol, and filtrated to remove excess amino acid. After filtration, ethanol was removed by evaporation. The AAILs were dried in high vacuum for 12 h at 80 °C.

2. Characterization Results

The structure of [N$_{1111}$][AA] ILs was confirmed using ^{1}H NMR spectra (Bruker Ascend 400), ESI-MS (Shimadazu LC-MS 2020),

FTIR spectra (NEXUS870 spectrometer), and CHN elemental analysis (Elementar Vario El III). The amount of water was measured to be less than 0.05 wt% by Karl Fisher coulometric titration (Brinkmann Metrohm 756 KF Coulometer). The melting temperature (T$_m$) and decomposition temperature (T$_{dec}$) were determined from TGA (PerkinElmer Diamond TG/DTA) in the rang of (−100 to 100) °C and (25 to 600) °C, respectively, at a scan rate of 10 °C/min under N$_2$ atmosphere.

[N$_{1111}$][Pro]: 90% yield based on the amount of [N$_{1111}$][OH]. ^{1}H NMR (300 MHz, DMSO, TMS): δ=1.36 (m, 1H, CH$_2$CH$_2$CH$_2$), 1.47 (dt, 1H, CH$_2$CH$_2$CH$_2$), 1.55 (d, 1H, CH$_2$CH), 1.70 (m, 1H, CH$_2$CH), 2.18 (s, 1H, NH), 2.89 (dd, 1H, CH$_2$NH), 2.96 (m, 1H, CH$_2$NH), 3.13 (s, 12H, CH$_3$N), 3.38 (d, 1H, CH). ESI-MS: 74.12 for [N$_{1111}$] (calculated: 74.10), 114.10 for [Pro] (calculated: 114.06). Elemental analysis (%) calculated: C 57.06, H 10.64, N 14.79; Found: C 57.42, H 10.71, N 14.88.

[N$_{1111}$][Ala]: 90% yield based on the amount of [N$_{1111}$][OH]. ^{1}H NMR (300 MHz, DMSO, TMS): δ=1.005 (d, 3H, CH$_3$CN), 2.798

Table S1. Thermal properties of four [N$_{1111}$][AA] ILs

AAILs	T$_m$/°C	T$_{dec}$/°C
[N$_{1111}$][Pro]	ND	194
[N$_{1111}$][Gly]	ND	181
[N$_{1111}$][Ala]	42	219
[N$_{1111}$][Val]	40	223

ND=not detected
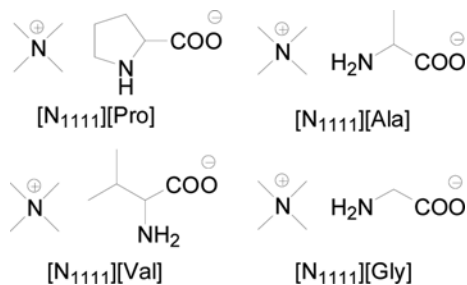
Fig. S1. The chemical structures of [N$_{1111}$][AA].
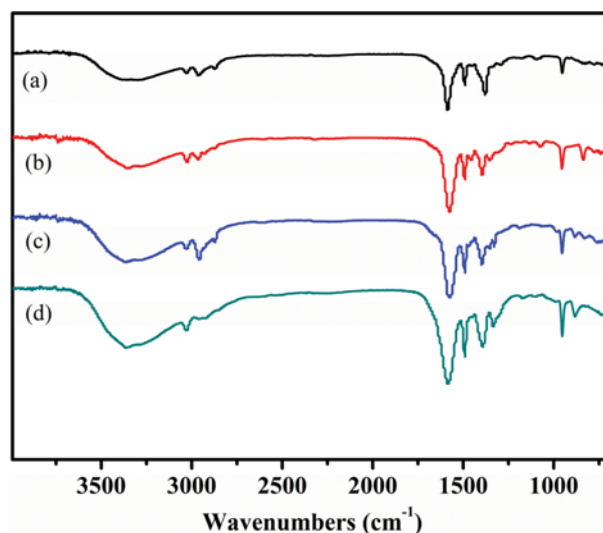
Fig. S2. FTIR spectra of (a) [N$_{1111}$][Pro], (b) [N$_{1111}$][Ala], (c) [N$_{1111}$][Val], and (d) [N$_{1111}$][Gly].

(q, 1H, CH), 3.110 (s, 12H, CH$_3$N). ESI-MS: 74.12 for [N$_{1111}$] (calculated: 74.10), 88.15 for [Ala] (calculated: 88.04). Elemental analysis (%) calculated: C 51.82, H 11.18, N 17.27; Found: C 51.58, H 10.46, N 17.06.

[N$_{1111}$][Val]: 89% yield based on the amount of [N$_{1111}$][OH]. ^{1}H NMR (300 MHz, DMSO, TMS): δ=0.662 (d, 3H, CH$_3$CH), 0.793 (d, 3H, CH$_3$CH), 1.890 (q, 1H, CHCH$_3$), 2.503 (t, 1H, CHNH$_2$), 3.111 (s, 12H, CH$_3$N). ESI-MS: 74.12 for [N$_{1111}$] (calculated: 74.10), 116.14 for [Val] (calculated: 116.07). Elemental analysis (%) calculated: C 56.81, H 11.65, N 14.72; Found: C 56.61, H 11.76, N 14.62.

[N$_{1111}$][Gly]: 91% yield based on the amount of [N$_{1111}$][OH]. ^{1}H NMR (300 MHz, DMSO, TMS): δ=2.696 (s, 2H, NCH$_2$COO), 3.130 (s, 12H, CH$_3$N). ESI-MS: 74.12 for [N$_{1111}$] (calculated: 74.10), 74.09 for [Gly] (calculated: 74.02). Elemental analysis (%) calculated: C 48.63, H 10.88, N 18.90; Found: C 48.48, H 10.76, N 18.84.

3. Molecular Coordinates

[Pro]:

C	−1.64190800	0.36886600	−0.91025200
C	−0.61624900	1.34503900	−0.28512200
C	0.19901200	0.45724200	0.69399900
C	−1.67725500	−0.84362300	0.07346900
H	−2.62708500	0.83542600	−1.02663900
H	−1.30698700	0.03904800	−1.89557500
H	−1.13604500	2.13301100	0.27697700
H	0.01830400	1.83169000	−1.02969200
H	0.60038200	1.03474200	1.52951100
H	−1.27642600	−1.72607600	−0.42334100
H	−2.68708800	−1.06544300	0.43848100
N	−0.79587700	−0.51435900	1.21215800
H	−1.35178200	−0.02500500	1.91019700
C	1.41268900	−0.19391700	−0.05609100
O	2.49458300	0.42861900	0.07771100
O	1.16543400	−1.21093500	−0.74784200

Cinnamaldehyde:

C	2.79955700	−0.99584700	−0.00002700
C	1.43602900	−1.27348600	−0.00001500
C	0.48561800	−0.23877000	0.00000700
C	0.94737000	1.08990000	0.00002100
C	2.30775200	1.36674300	0.00000700
C	3.23966800	0.32587200	−0.00001800
H	3.51642700	−1.80889600	−0.00004600
H	1.09621500	−2.30402600	−0.00002200
H	0.23886500	1.90949700	0.00004100
H	2.64658400	2.39649200	0.00001700

H	4.30093100	0.54677300	−0.00002800
C	−0.93374100	−0.58655200	0.00002200
H	−1.14291600	−1.65584400	−0.00000900
C	−1.99468200	0.24345000	0.00004400
H	−1.90176200	1.32434600	0.00005800
C	−3.35765800	−0.28855000	0.00055700
H	−3.42620600	−1.39828300	0.00022500
O	−4.36345200	0.39167100	−0.00010400

The complexe of cinnamaldehyde with [Pro]:

C	−4.91140700	−0.31887600	0.48246200
C	−4.27534300	−1.16122800	−0.65655600
C	−2.83204200	−0.61078700	−0.81998800
C	−3.77004400	0.62586600	0.93631300
H	−5.76527300	0.26131400	0.11319800
H	−5.26836600	−0.94429600	1.30481300
H	−4.83933600	−1.04186500	−1.58874900
H	−4.24347600	−2.22005900	−0.40041000
H	−2.53602200	−0.50817400	−1.86636300
H	−3.22839100	0.17374300	1.77005600
H	−4.11816600	1.61534700	1.24771000
N	−2.84309000	0.74488800	−0.20128800
H	−3.24435900	1.39459200	−0.87395500
C	−1.74193100	−1.49247400	−0.11321700
O	−0.57322700	−1.34458200	−0.56611600
O	−2.12185300	−2.22857900	0.82236400
C	2.49964100	−1.31181000	−0.05180900
C	3.58968100	−2.17775700	0.01609700
C	4.88619300	−1.67692100	0.12193200
C	5.09408700	−0.29483700	0.16006900
C	4.01226600	0.57458000	0.09491000
C	2.69880200	0.08086700	−0.01054300
H	1.47797900	−1.68212100	−0.13695500
H	3.42155700	−3.24923600	−0.01328600
H	5.73251500	−2.35461200	0.17447400
H	6.10155100	0.10084300	0.24073900
H	4.18713100	1.64439100	0.12425600
C	1.51301300	0.93965700	−0.07578700
H	0.57412400	0.39317400	−0.19671200
C	1.48022900	2.28820800	−0.00812100
H	2.36956400	2.90395200	0.10157300
C	0.20780100	2.99868400	−0.08120300
H	−0.68738500	2.35131900	−0.15556400
O	0.10286900	4.21921800	−0.05664200