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Synthetic and theoretical study on proline-catalyzed Knoevenagel condensation in ionic liquid

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Abstract

The Knoevenagel condensation of diethylmalonate and various aldehydes catalyzed by proline in a common ionic liquid was achieved. Mild reaction conditions, enhanced rates, improved yields, recyclability of ionic liquids containing proline, and reagents' reactivity which is different from that in conventional organic solvents are the remarkable features observed in ionic liquids. The ionic liquid containing catalyst was recycled in four subsequent runs with no decrease in activity. In addition, the results of calculations with the Gaussian 98 suite of program are in good accordance with the experimental outcomes.

Keywords: L-proline; Ionic liquid; Gaussian 98; Solvation energies; The Knoevenagel condensation

1. Introduction

Knoevenagel condensation is one of the most pivotal preparation methods of substituted alkenes. Thus, this synthetic method is of much interest and a variety of reaction systems have been developed. Many of these conditions are associated with one or more disadvantages such as hazardous and carcinogenic solvents, and non-recovery of the catalysts, which limit the use of these reactions in industrial processes [1]. In order to avoid the disadvantages mentioned above, some new conditions have been reported such as the use of inorganic solid supports as catalysts [2], and new techniques exploiting solvent free microwave assisted conditions [3]. Although these routes decrease reaction time, they produce desired alkenes in poor yields (3–86%). During the past few years, ionic liquids (ILs) have been emerging as potential "greener" alternatives to volatile organic solvents and being used as environmentally benign media for many important organic reactions [4]. For example, Morrison et al. used glycine to catalyze the Knoevenagel condensation of malononitrile and benzaldehyde in IL [6-mim][PF_6] (1-hexyl-3-methylimidazolium hexafluorophosphate), but the yield of product was only 77% after 22 h of reaction [5]. Harjani et al. have synthesized electrophilic alkenes via the Knoevenagel condensation in Lewis acidic ILs [bmim]Cl·$XAlCl_3$ and [bpy]Cl·$XAlCl_3$, which were moisture sensitive and readily hydrolyzed. This route has two reactions (Knoevenagel and Michael) competing to give different ratios of two products [6], which would lead to undesirable by-product.

Recently, the commercially available amino acid proline has been elegantly used to catalyze many kinds of reactions such as Mannish reaction and the direct asymmetric aldol reaction [7]. The proline function has been proposed to act like a "microaldolase" that facilitates each step of the mechanism, including the formation of the intermediate imine and the carbon–carbon bond.

In this paper, an effective and green preparation method where catalytic activity of proline in imidazolium-based ILs for the Knoevenagel condensation along with its regenerability was established for the first time (Scheme 1). Obviously the chirality of the catalyst is not necessary for the described procedure, but the cheapness of L-proline in comparison with the corresponding racemic amino acid, makes it the catalyst of choice. Furthermore, calculations by the Gaussian 98 suite of program was carried out to study into the experimental results of the Knoevenagel condensation.

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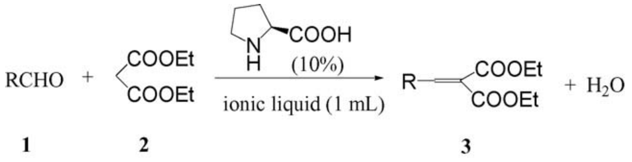


Scheme 1. L-proline-catalyzed Knoevenagel condensation in ionic liquid.

2. Experimental

2.1. Materials

Ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) were prepared by the procedures given in the literature [8]. All other chemicals and reagents were of analytical grade and used as obtained.

2.2. General experimental procedure for the L-proline catalyzed Knoevenagel condensation of aldehydes and diethylmalonate in neutral ionic liquids

To 11.25 mmol of diethylmalonate **2**, 7.5 mmol of the substrate **1** was added. To this, 1 ml IL and 0.1 equivalent of L-proline were added. The reaction mixture was stirred at different temperatures for several hours. The reactions were monitored by thin layer chromatography (TLC). After the reaction, the mixture was extracted with ether (3× 15 mL) to leave the IL containing L-proline. The ether extract was dried with sodium sulfate, filtered and evaporated to dryness in vacuo to give the crude product. The product was purified by column chromatography. All the products are properly characterized by their ^{1}H NMR and GC–MS. Furthermore, the reaction conducted in H_2O, DMSO, CH_3OH, CH_3CH_2OH, CH_2ClCH_2Cl, C_7H_{14}, respectively, was compared with that in ILs.

2.2.1. Representative data

2.2.1.1. (2-methylpropylidene)malonic acid diethyl ester. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 0.97–0.99 (d, 8 Hz, 6H), 1.18–1.25 (m, 6H), 2.55–2.64 (m, 1H), 4.11–4.22 (m, 4H), 6.67–6.69 (d, 8 Hz, 1H). GC–MS (*m/z*): 214 (M^+), 169, 122, 94.

2.2.1.2. Benzylidenemalonic acid diethyl ester. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.27–1.36 (m, 6H), 4.29–4.37 (m, 4H), 7.38–7.39 (t, 2 Hz, 3H), 7.45–7.47 (t, 4 Hz, 2H), 7.75 (s, 1H). GC–MS (*m/z*): 248 (M^+), 203, 158, 130, 102.

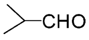
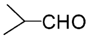
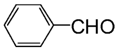
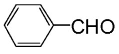
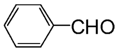
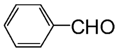
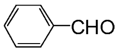
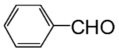
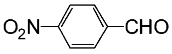
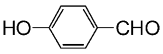
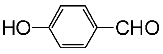
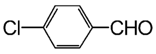
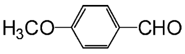
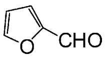
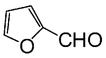
2.2.1.3. (2-Furanylmethylene)malonic acid diethyl ester. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.32–1.41 (m, 6H), 4.28–4.33 (q, 2H), 4.40–4.45 (q, 2H), 6.51–6.52 (q, 1H), 6.78–6.79 (d, 4 Hz, 1H), 7.47 (s, 1H), 7.54 (s, 1H). GC–MS (*m/z*): 238 (M^+), 210, 193, 164.

Table 1
L-proline-catalyzed Knoevenagel condensation of diethylmalonate and benzaldehyde in various ionic liquids at different temperature

Entry	Ionic liquid	Time (h)	Temperature (°C)	Conversion (%)[a,b]
1	[emim][BF_4]	24	15	46
2	[bmim][BF_4]	24	15	51
3	[bmim][PF_6]	24	15	25
4	[bmim][BF_4]	12	35	89
5	[bmim][BF_4]	12	50	93
6	[bmim][BF_4]	12	65	51
7	[bmim][BF_4]	12	80	81

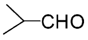
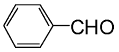
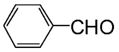
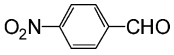
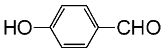
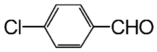
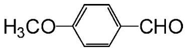
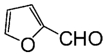
[a] Conversion of the reaction for each sample was determined by GC.
[b] All the products characterized by ^{1}H NMR spectroscope and GC–MS.

Table 2
L-proline-catalyzed Knoevenagel condensation of diethylmalonate and various aldehydes in [bmim][BF_4]

Entry	Aldehyde	Time (h)	Temperature (°C)	Conversion (%)[a,b]
1		12	35	89
2		12	50	97
3		48	50	0[c]
4		12	50	93
5		22–48	50	93
6		12	50	93[d]
7		12	50	92[e]
8		12	50	92[f]
9		22	50	27
10		12	35	6
11		12	50	63
12		12	50	45
13		12	50	60
14		12	35	86
15		6	50	100

[a] Conversion of the reaction for each sample was determined by GC.
[b] All the products characterized by ^{1}H NMR spectroscope and GC–MS.
[c] The reaction was carried out without proline in IL.
[d] The second run.
[e] The third run.
[f] The fourth run.

Table 3
L-proline-catalyzed Knoevenagel condensation of diethylmalonate and various aldehydes in [emim][BF_4]

Entry	Aldehyde	Time (h)	Temperature (°C)	Conversion (%)[a,b]
1		12	50	95
2		12	50	90
3		22–48	50	90
4		22	50	27
5		22	50	56
6		12	50	56
7		12	50	94
8		6	50	100

[a] Conversion of the reaction for each sample was determined by GC.
[b] All the products characterized by ^1H NMR spectroscope and GC–MS.

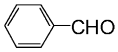
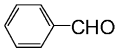
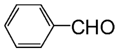
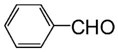
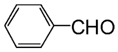
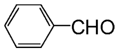
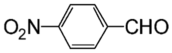
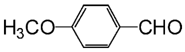
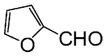
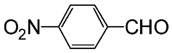
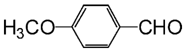
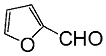
2.3. General experimental procedure for the recycling ionic liquid and L-proline

The system of IL and L-proline was thoroughly extracted with ether to move all organic impurities. Successive reuse of the recovered proline-IL system in the same reaction yielded amounts of product as high as the last cycle. As shown in Table 2, no considerable decrease in reactivity and yield was observed after four cycles when the same reaction time was strictly maintained (entries 3, 5, 6, 7).

3. Calculation methods

All calculations were performed with the GAUSSIAN 98 program package [9]. The geometries of all the stationary points were fully optimized at the B3LYP/6-31G* [10] level of theory. The B3LYP functional is composed of Becke's three-parameter hybrid exchange functional (B3) [11,12], as implemented in Gaussian 98 [13], and the correlation functional of Lee, Yang, and Parr (LYP) [14]. The total energies and the solvation energies for reactants, products and intermediates were computed using a polarizable continuum model with the permittivities of 78.39,

Table 4
Solvent effect on L-proline-catalyzed Knoevenagel condensation of diethylmalonate and various aldehydes at 50 °C

Entry	Aldehyde	Solvent	Time (h)	Conversion (%)[a,b]
1		H_2O	12	82
2		DMSO	12	80
3		CH_3OH	12	76
4		CH_3CH_2OH	12	75
5		CH_2ClCH_2Cl	12	66
6		C_7H_{14}	12	66
7		DMSO	12	22
8		DMSO	12	20
9		DMSO	12	16
10		H_2O	12	25
11		H_2O	12	87
12		H_2O	12	62

[a] Conversion of the reaction for each sample was determined by GC.
[b] All the products characterized by ^1H NMR spectroscope and GC-MS.

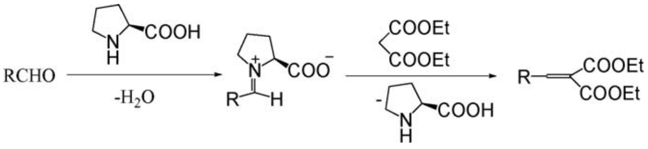


Fig. 1. The mechanism of the Knoevenagel condensation.

Table 5
The calculated energies (Hatree) of the reactants, intermediates and products in six distinct solvents

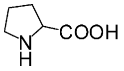
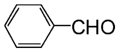
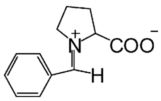
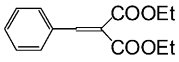
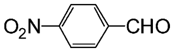
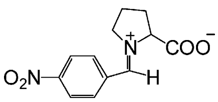
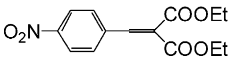
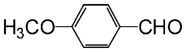
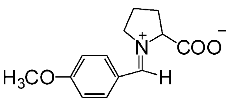
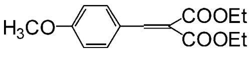
		H_2O	DMSO	CH_3OH	CH_3CH_2OH	CH_2ClCH_2Cl	C_7H_{14}
1		−401.1662252	−401.1656144	−401.1654574	−401.1651023	−401.1633648	−401.1542994
2	H_2O	−76.4211516	−76.4209687	−76.4207761	−76.4205687	−76.4194731	−76.4132713
3		−345.583779	−345.5835363	−345.5834141	−345.5831987	−345.5822133	−345.5769589
4		−670.3110174	−670.3099638	−670.3096478	−670.3088826	−670.3055244	−670.2874243
5		−844.0349319	−844.0338451	−844.0339807	−844.0334909	−844.0317255	−844.0233421
6	ΔH_f (4 + 2 − 3 − 1)	0.0178352	0.0182182	0.0184476	0.0188497	0.0205806	0.0305627
7	ΔH_f (5 + 2 − 3 − 43)	0.0304443	0.0308317	0.0307709	0.0308956	0.0314080	0.0336743
8		−550.086139	−550.0857162	−550.0856203	−550.0852881	−550.0839107	−550.0764101
9		−874.8105567	−874.8092432	−874.8090285	−874.8081592	−874.8043993	−874.7850117
10		−1048.5378363	−1048.5363808	−1048.5367396	−1048.5361137	−1048.5338606	−1048.523748
11	ΔH_f (9 + 2 − 8 − 1)	0.0206559	0.0211187	0.0212733	0.0216625	0.0234031	0.0324265
12	ΔH_f (10 + 2 − 8 − 43)	0.0298999	0.0304759	0.0302182	0.0306622	0.0309671	0.0327196
13		−460.1102615	−460.1098600	−460.1097897	−460.1095376	−460.1084119	−460.1025849
14		−784.8386829	−784.8374516	−784.8372383	−784.8364134	−784.8328100	−784.8138341
15		−958.5620695	−958.5604566	−958.5608008	−958.5601896	−958.5582473	−958.5493831
16	ΔH_f (14 + 2 − 13 − 1)	0.0166522	0.0170541	0.0172327	0.0176578	0.0194936	0.0297789

Table 5 (*Continued*)

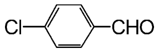
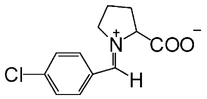
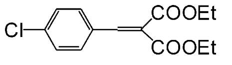
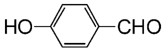
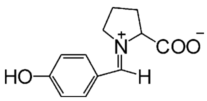
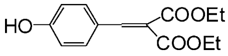
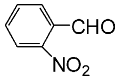
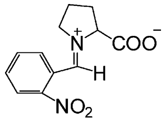
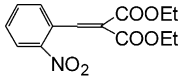
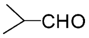
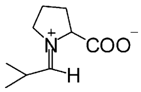
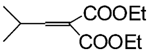
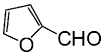
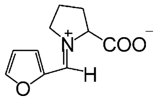
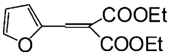
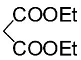
		H_2O	DMSO	CH_3OH	CH_3CH_2OH	CH_2ClCH_2Cl	C_7H_{14}
17	ΔH_f (15 + 2 − 13 − 43)	0.0297892	0.0305439	0.0303264	0.0305358	0.0310816	0.0332593
18		−805.1794076	−805.1791226	−805.1790206	−805.1788003	−805.1777967	−805.1724423
19		−1169.2316783	−1169.2311178	−1169.2310873	−1169.2308356	−1169.2294638	−1169.2226534
20		−1303.6307594	−1303.6295117	−1303.6297910	−1303.6291420	−1303.6274552	−1303.6192447
21	ΔH_f (19 + 2 − 18 − 1)	−39.3071971	−39.3073495	−39.3073854.	−39.30750172	−39.3077754	−39.3091830
22	ΔH_f (20 + 2 − 18 − 43)	0.0302454	0.0307514	0.0305671	0.0308461	0.0312585	0.0332551
23		−420.8123494	−420.8118245	−420.8115661	−420.8111162	−420.8091038	−420.7986017
24		−745.5409957	−745.5394068	−745.5390815	−745.5380214	−745.5334843	−745.5097593
25		−919.2642137	−919.2625502	−919.2627993	−919.2618946	−919.2590256	−919.2455045
26	ΔH_f (24 + 2 − 23 − 1)	0.0164273	0.0170634	0.0171659	0.0176284	0.0195112	0.0298705
27	ΔH_f (25 + 2 − 23 − 43)	0.0297329	0.0304148	0.0301043	0.0304094	0.0309952	0.0331547
28		−550.077537	−550.077044	−550.0769636	−550.0766542	−550.0753528	−550.0683928
29		−874.8171393	−874.8162185	−874.8162821	−874.8157740	−874.8140412	−874.8046486
30		−1048.4195907	−1048.41785063	−1048.4181611	−1048.4173445	−1048.4149579	−1048.403567
31	ΔH_f (29 + 2 − 28 − 1)	0.0054713	0.0054712	0.0053628	0.0054138	0.0052033	0.0048023
32	ΔH_f (30 + 2 − 28 − 43)	0.1395435	0.14033387	0.1401400	0.1404975	0.1413119	0.1448866

Table 5 (*Continued*)

		H_2O	DMSO	CH_3OH	CH_3CH_2OH	CH_2ClCH_2Cl	C_7H_{14}
33		−232.4657476	−232.465549	−232.4654935	−232.4653557	−232.4647281	−232.461482
34		−557.2086615	−557.2082733	−557.2081419	−557.2078881	−557.2067686	−557.2007568
35		−730.9336547	−730.9324828	−730.9327227	−730.9322518	−730.9309738	−730.9249104
36	ΔH_f (34 + 2 − 33 − 1)	0.0021596	0.0019214	0.0020329	0.0020032	0.0018512	0.0017533
37	ΔH_f (35 + 2 − 33 − 43)	0.0136901	0.0142055	0.0141083	0.0142917	0.0146713	0.0166291
38		−343.3587583	−343.3585679	−343.358399	−343.3582193	−343.3572493	−343.3518075
39		−668.0928687	−668.0918349	−668.0915366	−668.0909526	−668.0874353	−668.0693118
40		−841.8223104	−841.8213697	−841.8214509	−841.8209997	−841.8192113	−841.8105447
41	ΔH_f (39 + 2 − 38 − 1)	0.0109632	0.0113787	0.0115437	0.0118003	0.0137057	0.0235237
42	ΔH_f (40 + 2 − 38 − 43)	0.0180451	0.0183387	0.0182856	0.0184074	0.018955	0.0213203
43		−574.9027488	−574.9021092	−574.9021136	−574.9017565	−574.9003901	−574.8933288

46.7, 32.63, 24.55, 10.36 and 1.92, for H_2O, DMSO, CH_3OH, CH_3CH_2OH, CH_2ClCH_2Cl, and C_7H_{14}, respectively. These calculations involve the solvation model PCM as implemented in Gaussian 98.

4. Results and discussion

The successful results of experiments were found that proline-catalyzed Knoevenagel condensation in ILs is substantially faster than the corresponding reaction in conventional organic solvents. The reaction of diethylmalonate with furfural was completed within less than 6 h at 50 °C in [bmim][BF_4] (Table 2). As presented in Table 1, these reactions in [bmim][BF_4] are faster than those in other ILs such as [emim][BF_4], [bmim][PF_6]. However, When 4-methoxylbenzaldehyde or 4-chlorobenzaldehyde is reactant, the yield of product in [emim][BF_4] is higher than that in [bmim][BF_4]. When aromatic aldehyde with electron-donating groups are reactant, the yield of product is higher than that with electron-withdrawing group, which is contrary to the Knoevenagel condensation in conventional organic solvents (Tables 2–4). Some blank experiments were also carried out to demonstrate the catalysis of proline. As shown in Table 2, when the reaction was performed without L-proline, no product was obtained after 2 days (entry 3). We speculate that the enhanced rates result from IL-based stability of the imine electrophiles, and electron-donating groups of aromatic aldehyde can promote the stability of imine electrophile. An alternative lower energy reaction pathway is utilized when the ionizing solvent is present to assist in the formation and stabilization of separated charges.

Table 6
The solvation energies (kcal/mol) of the reactants, intermediates and products in six distinct solvents

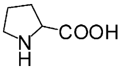
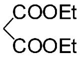
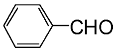
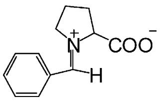
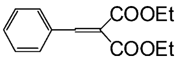
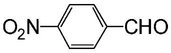
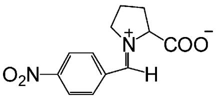
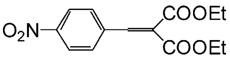
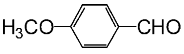
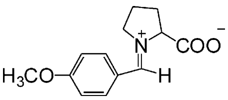
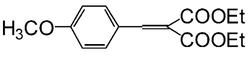
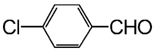
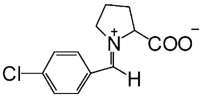
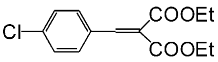
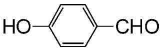
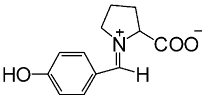
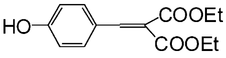
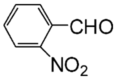
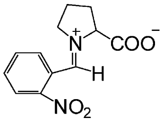
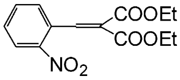
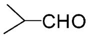
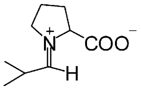
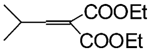
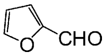
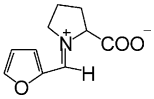
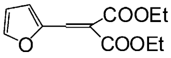
	H_2O	DMSO	CH_3OH	CH_3CH_2OH	CH_2ClCH_2Cl	C_7H_{14}
	−12.82	−12.36	−12.23	−11.95	−10.62	−4.05
	−10.25	−9.74	−9.73	−9.44	−8.33	−3.04
H_2O	−8.47	−8.33	−8.19	−8.03	−7.21	−2.81
	−7.81	−7.59	−7.48	−7.29	−6.45	−2.35
	−28.03	−27.11	−26.80	−26.12	−23.14	−8.44
	−12.98	−12.08	−12.16	−11.75	−10.22	−3.63
	−10.97	−10.62	−10.53	−10.25	−9.10	−3.37
	−30.30	−29.16	−28.91	−28.13	−24.75	−8.94
	−15.46	−14.25	−14.52	−13.99	−12.13	−4.40
	−8.65	−8.32	−8.25	−8.04	−7.10	−2.64
	−29.37	−28.31	−28.09	−27.37	−24.20	−8.92
	−14.08	−12.74	−13.01	−12.49	−10.83	−3.91
	−7.88	−7.63	−7.54	−7.35	−6.50	−2.38
	−9.97	−9.55	−9.50	−9.30	−8.20	−3.11
	−12.76	−11.71	−11.92	−11.37	−9.94	−3.57

Table 6 (*Continued*)

	H_2O	DMSO	CH_3OH	CH_3CH_2OH	CH_2ClCH_2Cl	C_7H_{14}
	−15.39	−14.93	−14.70	−14.31	−12.58	−4.42
	−36.39	−35.04	−34.71	−33.79	−29.84	−10.85
	−20.76	−19.37	−19.54	−18.76	−16.29	−5.70
	−10.32	−9.95	−9.86	−9.61	−8.55	−3.23
	−13.83	−13.15	−13.16	−12.77	−11.39	−4.33
	−18.25	−16.77	−16.99	−16.28	−14.16	−4.98
	−4.93	−4.75	−4.70	−4.58	−4.02	−1.45
	−8.70	−8.39	−8.27	−8.07	−7.16	−2.64
	−9.55	−8.62	−8.78	−8.41	−7.34	−2.69
	−8.08	−7.92	−7.77	−7.62	−6.79	−2.54
	−28.43	−27.54	−27.23	−26.71	−23.55	−8.62
	−13.56	−12.76	−12.80	−12.41	−10.82	−3.87

So the energies of the reactants, intermediates and products were calculated according to the mechanism of the Knoevenagel condensation.

The mechanism of the Knoevenagel condensation, as depicted in Fig. 1 is widely accepted. It has two steps and the formation of the intermediate (imine) is the key step [15]. The total energies and solvation energies of eight reactants, their intermediates and their products in six distinct solvents are collected, respectively, in Tables 5 and 6. In Table 5, entries 6, 11, 16, 21, 26, 31, 36, 41 present ΔH_{298} of the first step in the reaction, entries 7, 12, 17, 22, 27, 32, 37, 42 present ΔH_{298} of the whole reaction. Because ILs are formed from cations and anions, it is difficult to calculate the interaction of ILs with chemical compounds with the Gaussian 98 suite of program. Therefore, the theoretical explanation for ILs' effect on the reactions can only be done based on the tendency obtained from the calculation for some selected solvents other than directly with calculations.

As can be seen from Table 6, the solvation energy (negative value) decreases with increasing polarity of the solvent. This clearly indicates that the reactants, intermediates and products are more stabilized when polarity of solvent increases. Thus, the reactants, intermediates and products in IL are more stable compared with those in other organic solvents. This can be rationalized by considering that the polarity of IL is the highest among all solvents used and that ILs are formed from large organic cations and inorganic anions, which can promote the stability of intermediates possessing partial charges. Solvents play a crucial role in the reaction by stabilizing ionic charges and providing an alternative lower energy pathway by which the reaction may proceed. Hence, the Knoevenagel condensation in ILs can be definitely promoted by proline. The results of calculations present that ΔH_{298} of the first step in the reaction is less than that of the corresponding whole reaction, which indicates that the formation of the intermediate can reduce the reaction energy barrier. This may explain that proline catalyzes the reaction. The reaction is endothermic, which indicates a higher temperature can promote the reaction, but the temperature should not exceed a certain range (Table 1). In addition, in stronger polar H_2O solvent, the free energy of reaction (ΔG_{298}) of aromatic aldehyde with electron-withdrawing groups (4-nitrobenzaldehyde) is higher than that of aromatic aldehyde with electron-donating moieties (4-methoxylbenzaldehyde), which is different from those in other solvents. Accordingly, aromatic aldehyde with electron-donating group reacts more easily than with electron-withdrawing moiety in stronger polar solvents. The calculation results are presented in Table 5. Furthermore, the calculation results were verified by experiments on solvent effect (Table 4). It must be noted that the value of free energy (ΔG_{298}) is approximately represented by the value of enthalpy (ΔH_{298}) for explaining the reaction equation, since the term of TS is commonly little, which makes the value of enthalpy (ΔH_{298}) close to the value of free energy (ΔG_{298}).

5. Conclusion

In summary, the L-proline-catalyzed Knoevenagel condensation reaction has been successfully carried out in imidazolium-based ILs with increased rate and yield. Study on the recycling of the catalyst has revealed that L-proline in an ionic liquid can be reused at least four times with comparable yields. These results created a 'green' class of Knoevenagel condensation wherein both solvent and catalyst are readily recycled and reaction time is minimized. These reactions can be performed on a multi-gram scale under operationally simple and safe conditions. Moreover, enhanced rate resulting from IL-based activation of the imine electrophiles was supposed and proved by calculations with the Gaussian 98 suite of program, as well as the reactivity of reagents, which is different from that in traditional organic solvents. Further studies aimed at exploring the scope of organocatalytic reactions in ILs are in progress.

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