Esterification of aliphatic acids with olefin promoted by Brønsted acidic ionic liquids

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Abstract

Addition reactions of aliphatic acids with olefins to give corresponding esters have been investigated using SO_3H-functionalized ionic liquids as dual catalyst–solvent. The isolation of the desired products could be achieved via simple decantation and ionic liquids could be reused continuously after dried in vacuum (5–12 mmHg) at ca. 80 °C.
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Keywords: Ionic liquid; Esterification; Acid catalysis; Olefin

1. Introduction

It is well known that olefins can react with lower aliphatic acids to form the corresponding esters, which avoids the use of expensive alcohols and removal of co-produced water to promote the reaction [1]. A number of acidic catalysts such as ion exchange resins [2,3], heteropoly acids [4,5], silica-supported sulphuric acid [6], zeolite [7], *p*-toluenesulfonic acid [8], $BF_3 \cdot Et_2O$ [9], etc. were reported previously. However, many problems could not be solved in above processes, which inhibited their industrial application [6]. Silica-supported sulfonic acid is a typical gas phase reaction catalyst, which suffers from intense volatilization and dissolving-away of the effective catalytic components during the reaction, and therefore, it is not possible to carry out a continuous operation for a long time. At the same time, the recovery of liquid phase homogeneous catalysts from the products and the regeneration of the catalysts are still quite difficult to be recovered although good results are obtained from some liquid phase reactions. Therefore, it is necessary to develop a new class of substitute for conventional liquid and solid acids to promote the addition of olefins with aliphatic acids.

Ionic liquid is a new class of solvent entirely composed of ions. Their use as an environmentally friendly alternative for conventional solvents has received much attention recently [10–14]. Our specific interest in ionic liquids is its designability, thus giving us ability to manipulate the structure (with respect to the organic cation, inorganic anion and the length of the side chain attached to the organic cation) and consequently their properties. When an alkane sulfonic acid group is covalently tethered to the IL cation, the IL would be a strong Brønsted acid [15]. These SO_3H-functionalized ionic liquids have exhibited great potential in replacement of conventional homogenous and heterogeneous acidic catalysts because they are fluxible, nonvolatile, non-corrosive and immiscible with many organic solvents [16] (Fig. 1).

In this paper, we report an efficient and environmentally friendly addition of aliphatic acids with olefins using SO_3H-functionalized ionic liquids as a substitute for conventional homogenous and heterogeneous acidic catalysts.

2. Experimental

2.1. Materials and reagents

All solvents and chemicals used were commercially available and used without further purification unless otherwise stated. N-methylimidazole; 1,4-butane sulfone; trifluoromethanesulfonic acid; 1-hexene; 2-methyl-2-butene; dicyclopentadiene; 1-methyl cyclohexene and 1-amylene were purchased from Aldrich. Norbornene, cyclopentene, cyclohexene, crotonic acid, valeric acid and iso-octanoid acid were obtained from Strem Chemicals. Acetic acid,

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I: R = CH₃
II: R = CH₂CH₃
III: R = CH₂CH₂CH₂CH₃
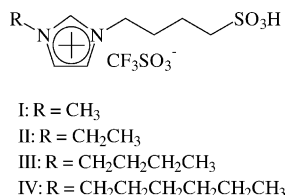IV: R = CH₂CH₂CH₂CH₂CH₂CH₃

Fig. 1. The SO₃H-functionalized ionic liquids used in this study.

acrylic acid, bromethane, 1-chlorobutane, 1-bromohexane and propionic acid were received from Shanghai Chemicals Co. Ethylene, propylene and 1-butene were purchased from Lanzhou Petroleum Refinery and its purities are all more than 99%.

2.2. Preparations of ionic liquids

The SO₃H-functionalized ionic liquids I–IV were synthesized according to literature [15]. 1-Ethylimidazole, 1-butylimidazole and 1-hexylimidazole were prepared from imidazole and halogenated hydrocarbon in ethanol using slightly excess of sodium as a sacrificial reagent according to literature [17].

2.2.1. Preparations of 1-alkyl-3-(butyl-4-sulfonate) imidazolium betaines [18]

N-alkylimidazole (10 mmol) is stirred solvent free with 1,4-butanesultone (1361 mg, 10 mmol) at room temperature for 3 days. After solidification of the mass, it was washed three times with toluene and dried under high vacuum. The white solid was readily soluble in water, less readily soluble in organic solvents. (Yield of 1-methyl-3-(butyl-4-sulfonate) imidazolium betaine: 2100 mg, 96%.)

2.2.2. Preparations of SO₃H-functionalized ionic liquids [15]

A stoichiometric amount of trifluoromethanesulfonic acid was added to 1-alkyl-3-(butyl-4-sulfonate) imidazolium obtained and stirred for 2 h at 40 °C to form the ionic liquid. The IL phase was then washed repeatedly with toluene and ether to remove non-ionic residues, and dried in vacuum (80 °C, 5–12 mmHg). The product was formed quantitatively and in high purity as assessed by mass balance and NMR

spectroscopy. Spectroscopic data for ionic liquid I: ^{1}H NMR (400 MHz, D₂O, neat 25 °C); δ 9.161 (s, 1H), 7.782 (s, 1H), 7.748 (s, 1 H), 4.210 (t, $J = 7.2$, 2H), 3.891 (s, 3H), 2.685 (t, $J = 7.2$, 2H), 1.903 (q, $J = 7.6$, 2H), 1.605 (q, $J = 4.6$, 2H), C₉H₁₅F₃O₆N₂S₂ (368.36): calcd. C 29.34, H 4.10, N 7.61, S 17.41; found C 29.39, H 4.28, N 7.54, S 17.27.

2.3. Esterification of aliphatic acids with olefins in SO₃H-functionalized ionic liquids

All reactions were conducted in a 90 ml autoclave with a glass tube inside equipped with magnetic stirring. In each reaction, 10 mmol ionic liquid, 15 mmol aliphatic acid and 15–45 mmol olefin were successively introduced and allowed to react at 90–150 °C for 2.5–6 h. After the reaction, the autoclave was cooled to room temperature, and then the upper organic phase containing the esters was simply separated from the ionic liquid by decantation. The dissolved organic species in ionic liquid can be extracted by toluene (5 ml × 3), and the extract was combined with upper organic phase followed by GC analysis. The ionic liquid could be reused in the next run by a 30 min of heat treatment under vacuum (80 °C, 5–12 mm Hg).

2.4. Qualitative and quantitative analysis

Qualitative and quantitative analyses were conducted with a HP 6890/5973 GC/MS and a HP 1790 GC equipped with a FID detector. The concentration of reactant and product was directly given by the system of GC chemstation according to the area of chromatograph peak.

3. Results and discussion

3.1. Optimization of reaction conditions

The esterification of acetic acid (AcOH) was firstly tested in ionic liquid IV at 120 °C. However, the reaction rate was slow and only 57% of AcOH conversion was obtained after 4 h reaction using 1 eq. of 1-heptene as an alkyl donor (Table 1, entry 1). Fortunately, the desired reaction was

Table 1
Esterification of AcOH with 1-heptene in different ionic liquids and reaction conditions[a]

Entry	ILs	1-heptene/AcOH	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)		
1	IV	1	120	4	57	55	40	5
2	IV	3	120	4	99	53	41	6
3	IV	3	90	4	70	70	25	5
4	IV	3	120	2.5	74	55	40	5
5	I	3	120	4	75	83	14	3
6	II	3	120	4	89	77	20	3
7	III	3	120	4	92	67	28	5

[a] Reaction conditions: 10 mmol ionic liquid, 15 mmol aliphatic acid.

efficiently accomplished when the reaction was carried out using 3 eq. of 1-heptene (entry 2). The subsequent experiments revealed that 4 h and 120 °C were necessary to achieve a good result because the conversion only reached 74 and 70% respectively with shorter reaction time or lower reaction temperature, such as 2.5 h and 90 °C (entries 3 and 4).

In subsequent studies, other three SO_3H-functionalized ionic liquids were further investigated under the above-mentioned optimized conditions (Table 1, entries 5–7). Slight decrease in AcOH conversion and increase in selectivity to (1-methyl)hexyl acetate were observed as the carbon number of the alkyl substituent of imidazolium cation decreased. The decrease in AcOH conversion in ionic liquids I–III was presumably attributable to the less dissolution of 1-heptene because of the increasing lipophilicity of the ionic liquid with increasing carbon number of the alkyl substitutent in imidazolium cation. In a similar way, in ionic liquid IV, the carbon chain isomerization of 1-heptene to internal olefins could be easier than in other three ionic liquids; therefore, the selectivity to (1-methyl)hexyl acetate was very poor in ionic liquid IV.
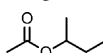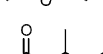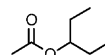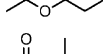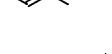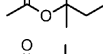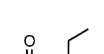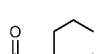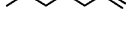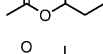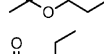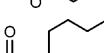
3.2. Esterificartion of various linear olefins with acetic acid in ionic liquid IV

Table 2 shows the results of esterificartion of various linear olefins with acetic acid in ionic liquid IV. Ethylene, propylene and 1-butene all underwent the addition of acetic acid to give corresponding acetate with nearly 100% selectivity (entries 1–3). The acid catalyzed oligomerization of olefin was not observed in this ionic liquid condition and as a result, the ester selectivity obtained under our ionic liquid conditions was higher than that reported in previous papers [4,6]. In the case of 1-pentene, the (1-methyl)butyl acetate and (1-ethyl)propyl acetate were detected in selectivity of 66 and 34%, respectively (entry 4). Similarly, the addition of 1-hexene with AcOH provided the (1-methyl)amyl acetate and (1-ethyl)butyl acetate in 55 and 45% selectivity (entry 5). The esterification of 2-methyl-2-butene with AcOH was very successful affording the (1,1-dimethyl)propyl acetate with complete AcOH conversion and 100% selectivity (entry 6). The product distribution in esterification between 1-octane and AcOH was similar to that of 1-heptene and the main esters were methyl and ethyl substituted alkyl acetates and propyl substituted alkyl acetates were less than 10% (entries 7 and 8). Comparing the conversions of AcOH, it can be seen that the reactivity of α-olefins is increased with lengthening its alkyl chain till 1-heptene. However, further increase in alkyl chain of olefin to 1-octane was not beneficial to the improvement of AcOH conversion. It should be pointed out that when ethylene and propylene were used the conversions of AcOH were 78 and 89%, respectively, indicating the usefulness of this esterification method.

Additionally, all the produced esters were less soluble to insoluble in the SO_3H-functionalized ionic liquids. Therefore, the products can be simply decanted out from the ionic liquid after reaction, so, the recycling and reuse of ionic liquid is viable. In the reaction of acetic acid and propylene using ionic liquid IV, the reaction was carried out four times in consecutive runs with slight decrease in activity (Table 2, entry 9).

Table 2
Esterification of linear olefins with acetic acid in ionic liquid IV[a]

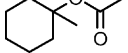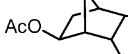| Entry	Olefins	Conversion (%)[b]	Products (selectivity %)[d]		
1		78	~100		
2		89	~100		
3		91	~100		
4		96	66	34	
5		97	55	45	
6		92	~100		
7		99	53	41	6
8		95	51	41	8
9[c]		86	~100		
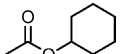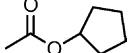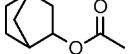
[a] *Reaction conditions*: 4.3 g (10 mmol) ionic liquid IV, 15 mmol acetic acid, 45 mmol olefin, 120 °C, 4 h.
[b] Conversion of acetic acid.
[c] Reused four times.
[d] Selectivity to ester based on acetic acid.

Table 3
Esterification of cycloolefines with acetic acid in ionic liquid IV[a]

Entry	Olefin	Conversion (%)[b]	Products (selectivity %[c])	
1		82		~100
2		94		~100
3		~100		~100
4		~100		~100
5		~100		~100

[a] *Reaction conditions*: 4.3 g (10 mmol) ionic liquid IV, 15 mmol acetic acid, 45 mmol cycloolefin, 120 °C, 4 h.
[b] Conversion of acetic acid.
[c] Selectivity to ester based on acetic acid.

3.3. Esterificartion of various cycloolefins with acetic acid in ionic liquid IV

Table 3 shows the results of esterificartion of various cycloolefins with acetic acid in ionic liquid IV. All cycloolefins reacted with acetic acid smoothly in good to high AcOH conversions and near 100% selectivity to ester. Reaction of dicyclopendiene with acetic acid quantitatively gave monoesterification product in exo-form without any by-product. When cyclopentene was used as alkyl donor, dimerization products were distinctly detected by GC/MS analysis (Fig. 2). Based on cyclopentene, 54% of cyclopentene dimer was detected besides cyclopentyl acetate. They are composed of 35% of tricyclo[4.4. 0. 0 (2, 8)] decane (1), 10% of 3-cyclopentylcyclopentene (2) and 9% of 1-methylenespiro [4.4] nonane (3).

3.4. Esterificartion of various aliphatic acids with propylene in ionic liquid IV

Furthermore, increasing the length of alkyl chain of aliphatic acid at constant conditions led to a slight decrease in aliphatic acid conversion when propylene was used as alkyl donor (Table 4). For example propionic acid was converted to isopropyl propionate in conversion of 88%; however, under the same conditions, conversions of valeric acid and iso-octanoic acid were 80 and 77%, respectively (entries 2–4). This esterification method was also effec-
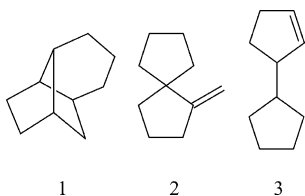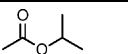
Table 4
Esterification of different aliphatic acids with propylene in ionic liquid IV[a]

Entry	Aliphatic acid	Conversion (%)[b]	Products (selectivity %)	
1		89		~100
2		88		~100
3		80		~100
4		77		~100
5		89		~100
6		85		~100

[a] *Reaction conditions*: 4.3 g (10 mmol) ionic liquid IV, 15 mmol aliphatic acid, 45 mmol propylene, 120 °C, 4 h.
[b] Conversion of aliphatic acid.

tive in α,β-unsaturated aliphatic acids. For example acrylic acid and crotonic acid were esterified in ionic liquid IV by propylene in 89 and 85% conversions, respectively (entries 5 and 6).

4. Conclusion

In summary, the SO₃H-functionalized ionic liquids have been demonstrated to be a new class of substitute for conventional liquid and solid acids in the addition of olefins with aliphatic acids. Although the reaction was accomplished in homogeneous model, isolation of the desired products as well as ionic liquids could be achieved via a simple decantation and the ionic liquids could be reused repeatedly after a treatment in vacuum (5–12 mmHg) at ca. 80 °C. The analogous addition etherifications between olefins and alcohols in these SO₃H-functionalized ionic liquids are being investigated.

Fig. 2. Dimerization products of cyclopentene in the ionic liquid IV.

References

[1] H.A. Bruson, T.W. Riener, J. Am. Chem. Soc. 67 (1945) 723.
[2] A. Heidekum, M.A. Harmer, W.F. Hoelderich, J. Catal. 181 (1999) 217.
[3] M. Gruffaz, O. Micaelli, USP(4275228), 1981.
[4] K. Sano, M. Nishiyama, T. Suzuki, S. Wakabayashi, K. Miyahara, USP(5189201), 1993.
[5] K. Inoue, M. Iwasaki, K. Matsui, USP(5241106), 1993.
[6] I.J. Dijs, H.L.F. van Ochten, C.A. van Walree, J.W. Geus, L.W. Jenneskens, J. Mol. Catal. A: Chem. 188 (2002) 209.

[7] R.A. Crane, S.H. Brown, L. De Caul, USP(5973193), 1999.

[8] D.R. Cova, C.W. Roos, Ind. Eng. Chem. Prod. Res. Dev. 7 (1968) 301.

[9] L.O. Raeth.er, A.J. Lauck, H.R. Gamrath, Ind. Eng. Chem. Prod. Res. Dev. 2 (1963) 133.

[10] T. Welton, Chem. Rev. 99 (1999) 2071.

[11] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772.

[12] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667.

[13] C.M. Gordon, Appl. Catal. A: Gen. 222 (2002) 101.

[14] H. Olivier, J. Mol. Catal. 146 (1999) 285.

[15] A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weave, D.C. Forbes, J.H. Davis, J. Am. Chem. Soc. 124 (2002) 5962.

[16] J. Fraga-Dubreuil, K. Bourahla, M. Rahmouni, J.P. Bazureau, J. Hamelin, Catal. Commun. 3 (2002) 185.

[17] P. Bonhôte, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168.

[18] W.A. Herrmann, M. Elison, J. Fischer, C. Kocher, USP(5663451) 1997.