

Ionic liquid as a green catalytic reaction medium for esterifications

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Received 12 April 2000; accepted 11 September 2000

Abstract

Esterifications of alcohols with carboxylic acids in the room temperature ionic liquid 1-butylpyridinium chloride–aluminium(III) chloride as green reaction medium in catalytic quantities have been investigated. Excellent conversion and selectivities were achieved, and the most of resultant esters could be easily recovered due to immiscibility with the ionic liquid. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ionic liquid; Esterification; Catalyst

1. Introduction

Organic esters are valuable intermediates in chemical industry. Recently, effort has been made in order to replace the traditional inorganic acid, e.g. sulfuric acid and to develop clean catalytic method such as supported sulfuric acid or solid superacid for the syntheses of organic esters [1–3]. On the other hand, although many organic reactions, including oligomerization, polymerization, alkylation and acylation, have been reported to be proceeded in room temperature ionic liquids with excellent yields and selectivities [4–13], to date, the esterification of carboxylic acids with alcohols in room temperature ionic liquids as a catalyst and reaction media, however, have not been reported in literatures yet, probably due to strong and detrimental interactions between the organic acids or water and the aluminium chloride based ionic liquid, such as 1-butylpyridinium chloride–aluminium(III) chloride ionic liquids. With a view

towards developing clean esterification method, a number of esterification reactions using the 1-butylpyridinium chloride–aluminium(III) chloride ionic liquids as catalyst and reaction media have been investigated in our laboratory. This letter is to show that such ionic liquid could be used as an efficient and clean catalytic technology for the esterifications of alcohols and carboxylic acids.

2. Experimental

For each esterification the amount of aluminium chloride 1-butylpyridinium chloride–aluminium(III) chloride ionic liquid containing 0.005 M aluminium(III) chloride (1 ml of ionic liquid), was used. For the purpose of comparison, same esterification reactions were also carried out with equivalent of concentrated sulfuric acid (0.25 ml) as catalyst.

During the experiments, there are two key factors for a successful esterification. (1) The molar ratio of aluminium chloride/butylpyridine chloride must be <1. It is well known that the aluminium chloride

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based ionic liquids are usually degraded rapidly by even small amount of water with formation of solid aluminium hydroxide species. However, we found that the aluminium chloride based ionic liquids could be stable enough to resist degradation by water as long as the molar ratio of aluminium chloride/butylpyridine chloride was <1 . Therefore, in this study the molar ratio of aluminium chloride/butylpyridine chloride was chosen as $1/2$. (2) Alcohol must be added into the ionic liquid first, and then the organic acid was introduced into the reaction system.

Alcohols (0.25 mol) and equivalent carboxylic acid (indicated in Table 1) were successively added into a 100 ml round-bottomed flask equipped with magnetic stirring, a flux condenser and thermometer and charged with appropriate amount of ionic liquid mentioned above. The esterification reaction was typically allowed to proceed for 2 h with stirring and fluxing at 30 – 110°C , depending upon each specific esterification. After reaction, the reactant and products were directly analyzed with HP6890/5973 GC-MS with cross-linked 5% PH ME siloxane column, $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$.

3. Results and discussion

The esterification results of several alcohols with acetic or anchoic acids in the ionic liquid and concentrated sulfuric acid, respectively, are outlined in Table 1. For the esterification of *iso*-propyl, *iso*-pentyl, and benzyl alcohols with acetic acid, although the conversions varied with different alcohols, the catalytic activities of ionic liquid were obviously higher than that of the corresponding sulfuric acid, and it seems that there was not much difference in selectivities. For esterifications of benzyl alcohol, some by-products, i.e. benzyl chloride ($\sim 3\%$) in ionic liquid and phenymethylether ($\sim 4\%$) in sulfuric acid were found, respectively. The experimental results also indicated that the ionic liquid as esterification catalyst could be reused (Table 1, entry 3–5) although the conversion was slightly decreased after the first esterification was conducted. The result of esterification of *iso*-octanol with anchoic acid (entry 6) suggested that the catalytic performance of the ionic liquid could be much better than that of the concentrated sulfuric acid under same reaction conditions. In comparison to sul-

furic acid, there were two obvious advantages for ionic liquid as catalyst: (1) the resultant esters were not dissolved in the ionic liquid and therefore could be isolated easily; (2) the ionic liquid could be recovered and reused again only just evacuate the reactor system containing ionic liquid at about 110°C for ca. 10 min. so as to remove the water produced during the reaction.

In order to compare the catalytic performances between the ionic liquid and the sulfuric acid further, the esterification of glycerol with acetic acid was also conducted since the reaction of glycerol with acetic acid to produce triacetin is relatively difficult due to three hydroxyls in glycerol. Reactions between glycerol and acetic acid resulted in five esters, i.e. monoacetins (monoacetin-1 and monoacetin-2), diacetins (diacetins-1,3 and diacetins-1,2) and triacetin. At lower reaction temperature, i.e. 30°C , the glycerol was almost completely converted into esters with the ionic liquid used as catalyst, and the corresponding yield of triacetin was higher than that with sulfuric acid as catalyst. The yields of total monoacetins and triacetin reached a minimum and maximum, respectively, at ca. 75°C for ionic liquid as catalyst. While the yields of total monoacetins and triacetin kept decreases and increases, respectively, with the increases of temperature for sulfuric acid. Furthermore, it can be seen that the yields of 1,3-diacetins from ionic liquid was always higher than that from sulfuric acid, while the yields of 1,2-diacetins from ionic liquid was always lower than that from sulfuric acid. It is well known that the aluminium chloride based ionic liquids can be Lewis acidic or Lewis basic if the mol ratio of aluminium chloride/butylpyridine chloride is greater or less than 1.0. Obviously, the ionic liquid used in this study was Lewis basic, and therefore we conjecture that the mechanism of esterification in ionic liquid may be different from that in sulfuric acid.

Although detailed reaction mechanism of esterification in ionic liquid is not clear at this stage, the preliminary experimental results showed that esterification in the ionic liquid as a novel environmental friendly catalyst is not only possible but also quite satisfactory. The outstanding advantage is that the resultant esters may not dissolved in the ionic liquid and therefore they could be isolated easily. The ionic liquid as a catalyst and reaction medium is particularly suitable to those esterifications between aliphatic acids and alcohols at mild reaction conditions.

Table 1
Comparison of esterification performances between ionic liquid and concentrated sulfuric acid catalysts

Entry	Alcohols	Carboxylic acids	Molar ratios of alcohol/carboxylic acid	Reaction temperature (°C)	Products	Ionic liquid		Sulfuric acid	
						Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
1	<i>iso</i> -Propyl alcohol	Acetic acid	1/1	68	<i>iso</i> -Propyl acetate	71.3	98.0	66.2	98.0
2	<i>iso</i> -Pentyl alcohol	Acetic acid	1/1	80		87.1	98.0	71.5	97.0
3 ^a	Benzyl alcohol	Acetic acid	1/1	80	Benzyl acetate	79.6	97.0	71.1	94.0
4 ^b	Benzyl alcohol	Acetic acid	1/1	80	Benzyl acetate	65.4	97.0	–	–
5 ^c	Benzyl alcohol	Acetic acid	1/1	80	Benzyl acetate	66.5	98.0	–	–
6	<i>iso</i> -Octanol	Anchoic acid	2/1	100	Diisooctyl azelate	80.3	99.0	55.8	98.0
7	Glycerol	Acetic acid	1/3	30	Monoacetin-1	99.9	43.7	98.3	42.3
					Monoacetin-2		2.0		0.8
					Diacetins-1,3		31.9		31.4
					Diacetins-1,2		18.8		20.9
					Triacetin		3.6		2.9
					Monoacetin-1	100	16.9	100	15.6
					Monoacetin-2		0.2		0.3
8	Glycerol	Acetic acid	1/3	75	Diacetins-1,3		39.5		36.8
					Diacetins-1,2		19.3		23.8
					Triacetin		24.0		23.7
					Monoacetin-1	100	17.5	100	13.0
					Monoacetin-2		0.4		0.2
					Diacetins-1,3		38.8		34.2
					Diacetins-1,2		23.1		26.2
9	Glycerol	Acetic acid	1/3	110	Triacetin		20.2		26.4

^a The first esterification.

^b The second esterification.

^c The third esterification.

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