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Microwave-accelerated esterification of salicylic acid using Brönsted acidic ionic liquids as catalysts

Hua Shi, Wenshuai Zhu, Huaming Li *, Hua Liu, Ming Zhang, Yongsheng Yan, Zhigao Wang

College of Chemistry and Chemical Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, PR China

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ABSTRACT

A variety of Brönsted acidic ionic liquids were screened as catalysts for the esterification of salicylic acid. The experimental results indicated that SO_3H-functionalized ionic liquids with HSO_4^- performed high catalytic activity under microwave irradiation, and the yields can reach 91.9–93.6%. Furthermore, ionic liquids can be easily separated by simple decantation and have a fair reusability. The Brönsted acidity–catalytic activity relationships were also investigated and the results showed that the activity of the acidic ionic liquids is in excellent agreement with their acidity order.

1. Introduction

As fine chemicals, methyl salicylate (MS) has been widely used as flavor and fragrance agent, cosmetic and dye carrier, as well as ultraviolet (UV)-light stabilizer in acrylic resins [1]. Fisher esterification is one of the simplest methods to obtain this ester. However, these reactions usually employ mineral acids, such as H_2SO_4, HF and H_3PO_4. It is well-known that these catalysts suffer from inherent problems of corrosiveness, more byproducts, environmental hazards, difficulty in catalyst recovery and reuse, and high susceptibility to water. Additionally, solid acid catalysts such as mesoporous materials [2,3], zeolites [4,5], and anion-modified metal oxides [6] are also used as esterification catalysts. Although above-mentioned shortcomings can be overcome, these catalysts have their own disadvantages, for example, high mass transfer resistance, easy to deactivation, adsorption of products, which limit their applications.

Ionic liquids (ILs) have been revealed as green reaction media owing to their negligible volatility, excellent thermal stability, and the variety of structures available [7–9]. So applications of ILs have been extensively studied with high yields, among which esterification is hot topic. The majority of research has focused primarily on $[BMIM][PF_6]$ and $[BMIM][BF_4]$ as catalysts and reaction media for esterification [10,11]. However, these ILs contain halogen atom, which may cause serious concerns under certain conditions. Therefore, the development of halogen-free ILs is highly desirable. Imidazolium salts with HSO_4^- and $H_2PO_4^-$ as anion, and protic pyridinium ILs have been synthesized [12,13]. These ILs showed excellent catalytic activity. Furthermore, Cole et al. [14] first synthesized Brönsted acidic ILs that bear an alkane sulfonic acid group in the cation. These ILs can be used as dual solvent–catalysts in esterification. Since then, SO_3H-functionalized ILs were widely used in esterification, for instance, esterification of acetic acid [15], benzoic acid [16] and aliphatic acids [17]. So far, only one report regarding synthesis of salicylate using ILs has been published [18]. However, the reaction time is long.

Esterification under microwave irradiation, besides being environmentally friendly, is also marked by a considerable reduction in reaction time in comparison to conventional esterification [19,20]. Furthermore, to the best of our knowledge, esterification of salicylic acid in ILs has not yet been achieved under microwave irradiation. In this paper, several Brönsted acidic ILs were prepared and used in the microwave-accelerated synthesis of salicylate. Two SO_3H-functionalized ILs showed high catalytic activity in a very short period of time. Additionally, the stability and reuse performance of these ILs were also examined.

2. Experimental section

2.1. Chemicals and instruments

All the chemicals were commercially available and were used without further purification.

* Corresponding author. Tel.: +86 0511 88791800; fax: +86 0511 88791708.
E-mail address: lihm@ujs.edu.cn (H. Li).

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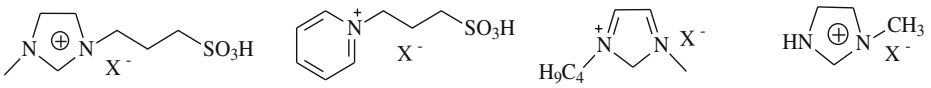

I $X^- = HSO_4^-$
II $X^- = H_2PO_4^-$
III $X^- = HSO_4^-$
IV $X^- = HSO_4^-$
V $X^- = H_2PO_4^-$
VI $X^- = HSO_4^-$

Fig. 1. Ionic liquids used in this paper.

UV–vis spectra were recorded on a UV-2450 spectrophotometer (Shimadzu Corporation, Japan) in H_2O. NMR spectra were recorded on an AV-400 spectrometer (Bruker Corporation, Germany) in D_2O. FT-IR spectra were performed on a Nicolet FT-IR spectrophotometer (Nexus 470, Thermo Electron Corporation) using KBr pellets at room temperature. TG/DSC was done on STA-449C Jupiter (NETZSCH Corporation, Germany).

2.2. General preparation of Brönsted acidic ionic liquids

The ionic liquids (ILs) used in this paper (Fig. 1) were synthesized according to previous literatures [12,16,21]. The ILs were analyzed by ^1H, ^{13}C NMR spectroscopies, and the spectral data agreed with their structures.

Spectral data for $[PSPy][HSO_4]$: ^1H NMR (400 MHz, D_2O): δ 2.28 (m, 2H), 2.80 (t, 2H), 4.59 (t, 2H), 7.90 (t, 2H), 8.38 (t, 1H), 8.70 (s, 1H); ^{13}C NMR (100 MHz, D_2O): δ 26.06, 47.00, 59.84, 128.37, 144.32, 145.89.

2.3. Esterification under microwave irradiation

The reactions were carried out in Microwave Synthesis System (MAS-I, Sineo Microwave Chemical Technology Co. Ltd., Shanghai, China) equipped with a magnetic stirrer and a water-cooled condenser. Temperature was controlled by automatic adjusting of an infrared temperature sensor. In a typical procedure, a solution of the substrates consisting of 0.02 mol salicylic acid, 0.05–0.08 mol methanol, and 4–12 mmol ILs were prepared and irradiated for 10–30 min. After the reaction, the mixture became biphasic, and diethyl ether was added to dissolve the unreacted salicylic acid (SA). The upper layer consisting of the produced ester and some unreacted SA was isolated by simple decantation, while the lower layer, viscous ILs, could be used in next reaction after removal of water at 90 °C for 6 h. Produced methyl salicylate was analyzed by ^1H NMR (^1H NMR (400 MHz, acetone-d 6): δ 3.95 (s, 3H), 6.91 (t, 1H), 6.97 (d, 1H), 7.50 (t, 1H), 7.81 (d, 1H), 10.79 (s, 1H)).

The composition of the products was analyzed by GC-FID (Agilent 7890A, HP-5 column, 30 m × 0.32 mm i.d. × 0.25 μm film thickness). The GC process started at 70 °C and the temperature was raised to 170 °C at 15 °C/min. The products were identified by comparing with the standards, and GC results showed that the major product was methyl salicylate and the minor side product was phenol. The conversion and selectivity were calculated according to the area of chromatograph peak [4].

$$\text{Conversion of salicylic acid (SA)}/\% = 100 - \frac{[\text{salicylic acid}]}{[\text{salicylic acid}] + [\text{methyl salicylate}] + [\text{phenol}]} * 100 \quad (1)$$

$$\text{Selectivity for methyl salicylate (MS)}/\% = \frac{[\text{methyl salicylate}]}{[\text{methyl salicylate}] + [\text{phenol}]} * 100 \quad (2)$$

$$\text{Yield of methyl salicylate (MS)}/\% = \text{conversion of SA} * \text{selectivity for MS} \quad (3)$$

2.4. UV–vis acidity determination

According to previous work [17], the Brönsted acidity was evaluated from the determination of the Hammett acidity function, using UV–vis spectroscopy. In the present case, ILs and the indicator 4-nitroaniline were dissolved in H_2O at concentrations of 3.2×10^{-2} mol/L and 2.9×10^{-3} mol/L, respectively.

3. Results and discussion

3.1. The effect of conventional and microwave heating on the synthesis in ILs

For the purpose of comparison, methyl salicylate was synthesized under conventional conditions and under microwave irradiation. Some data under conventional conditions (entries 5–7) are not given here by reason that it cannot be determined for its low catalytic activity. Other results are listed in Table 1.

According to the obtained data under microwave irradiation, the catalytic activity of SO_3H-functionalized ILs $[PSPy][HSO_4]$ and $[MIMPS][HSO_4]$ (Table 1, entries 1 and 2) was better than that of non-functionalized ILs (entries 3, 4 and 6). The yields can reach 91.9–93.6%. Under conventional conditions, the yields ranged from 2.2% to 36.6%, respectively, thereby, highlighting the role of microwave irradiation in promoting the esterification. Additionally, blank experiment (without catalyst) under the same microwave irradiation manifested that the application of SO_3H-functionalized ILs could effectively promote the reaction.

3.2. Optimization of reaction conditions

$[PSPy][HSO_4]$ was used as catalyst to define the optimal reaction parameters of the synthesis under microwave irradiation. The effect of varying the concentration of the $[PSPy][HSO_4]$ was explored (Table 2, entries 2, 8 and 9). The maximum yield was obtained when 10 mmol of ILs was added. An excess of ILs resulted in a decrease of yield. The optimal molar ratio of methanol to salicylic

Table 1
The effect of conventional and microwave heating on the synthesis in ILs.

Entry	Ionic liquid	Yield (%)		Selectivity(%)[b]	
		MH[c]	CH[d]	MH[c]	CH[d]
1	$[PSPy][HSO_4]$	93.6	36.6	99.9	99.9
2[a]	$[MIMPS][HSO_4]$	91.9	33.1	99	99.9
3	$[Bmim][HSO_4]$	17.6	4.5	99.9	99.9
4	$[Hmim][HSO_4]$	7.4	2.2	99.9	99.9
5	$[MIMPS][H_2PO_4]$	4.2	–	99.9	–
6	$[Bmim][H_2PO_4]$	1.7	–	99.9	–
7	Blank	1.0	–	99.9	–

Reaction conditions: ratio of methanol to salicylic acid = 3:1; ILs 10 mmol; refluxed for 20 min at 105 °C.
[a] Refluxed at 95 °C.
[b] Selectivity for methyl salicylate (base on salicylic acid).
[c] MH: microwave heating.
[d] CH: conventional heating.