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Koch carbonylation of tertiary alcohols in the presence of acidic ionic liquids

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Abstract

Koch carbonylation of tertiary alcohol with CO was carried out in decane in the presence of acidic ionic liquid, which presents a novel application of acidic ionic liquid as well as a novel reaction system for Koch reaction that can offer good reusability and easy separation of product. Used as the probe reaction, carbonylation of *tert*-butyl alcohol with CO to pivalic acid was investigated under varying reaction conditions. A negative effect of air or water as additives on the yield of product was observed, while increasing the CO pressure from 4 to 8 MPa could remarkably benefit the reaction. Increasing reaction temperature from 120 to 160 °C also played a positive role, but a further elevation to 170 °C will lead to the decrease of product yield.

Keywords: Koch carbonylation; Ionic liquid

1. Introduction

The carbonylation of carbon monoxide with alcohols or olefins and water to form carboxylic acids, known as Koch reaction, is one of the most important synthetic routes to manufacture tertiary acids [1]. Generally, this reaction is carried out in a homogenous way in the presence of excessive strong acids such as H_2SO_4, BF_3 or HF at high pressure of CO. In the late 1980s, a new process that could be operated at room temperature and atmospheric CO for Koch reaction was developed by using a $Cu(CO)^+$ or $Ag(CO)^+$ catalyst dissolved in H_2SO_4 [2].

Form the point of environmental view, the usage of strong acids in a large scale will cause a series of problems such as the need for corrosion resistant materials, a complicated wash and separation section to isolate tertiary acid from the strong acids and the disposal of huge amount of waste acids.

To overcome these disadvantages, an alternative method is to perform this reaction in a heterogeneous way by using solid catalyst, and a variety of solid acids, such as Nafion-H, silver trifluoromethanesulfonate, H-zeolites, sulfated zirconia and Amberlyst 36, have been examined as catalysts for Koch reaction [3a,3b,3c,3d,3e].

Meanwhile, room temperature ionic liquids (RTILs) have gained more and more recognition as green and promising solvents for synthetic chemistry [4a,4b,4c,4d,4e]. We reported previously that the Brönsted acidic ionic liquids, as well as their sulfonyl chloride derivatives, could behaved as effective catalysts for alkylation, nitration and Beckmann rearrangement [5a,5b,5c]. As a continuous attempt to expand their application in synthetic chemistry, we report in this paper another novel application of these acidic ionic liquids. It was found that Koch carbonylation of tertiary alcohols with CO could be successfully carried out in decane in the presence of acidic ionic liquids to offer the corresponding carboxylic acid in good yields. The reaction is carried out in a biphasic mode; therefore the separation of product is becoming easy, similar to the previous study of solid catalyst. These acidic ionic liquids also show good performance in reusability.

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2. Experimental

Preparation of the acidic ionic liquids could be found in the previous literatures [5]. In a typical experiment, tertiary alcohol, decane and ionic liquid were charged successively into a self-made autoclave equipped with magnetic stirrer. After the autoclave was purged with CO for 3 times, CO was introduced and raised to the desired pressure, ranged from 4 to 8 MP at room temperature. Then the autoclave was held in oil bath at desired temperature for 22 h. After the reaction, the upper organic layer was separated and the remaining ionic liquid phase was washed with decane (1 ml) for 2 times. Then the organic phase was combined and analyzed by a gas chromatograph equipped with a FID detector using toluene as internal standard (Shimadzu GC-2014, ULBON HR-52 capillary column 25 m × 0.32 mm).

To examine the reusability of acidic ionic liquid, the decane-washed ionic liquid phase was dried in vacuo at 50 °C for 2 h and then reused in the same way as described above.

3. Results and discussion

3.1. Koch carbonylation of tertiary alcohols in the presence of acidic ionic liquids

Results of Koch carbonylation of alcohol with CO in the presence of acidic ionic liquids were summarized in Table 1. Firstly the conversion of *tert*-butyl alcohol (*t*-BA) to pivalic acid was employed as the probe reaction. It should be noted that in all of the experiments concerning *tert*-butyl alcohol its peak totally disappears after reaction, which means a 100% conversion of *tert*-butyl alcohol. The complete conversion of *tert*-butyl alcohol in Koch reaction was also observed in other catalyst systems, Nafion-H, for example, could offer a complete conversion of *tert*-butyl alcohol from the beginning of 383 K [3a] which could be attributed the relative severe reaction conditions of Koch reaction in the presence of acidic catalyst that involved high temperature and long reaction time. As can be seen from the table, when Koch carbonylation of *tert*-butyl alcohol with CO was carried out in the presence of **1a**–**2b** with a mole ratio of ionic liquid/alcohol at 1:1, yields of product pivalic acid ranged from 6.3% to 26.5% are achieved (Runs 1–4). Our primary results showed that the sulfonyl chloride modified Lewis acidic ionic liquids have better activity than that of the Brönsted ones, indicating the difference in the acidity type can affect carbonylation of *tert*-butyl alcohol with CO in some degree (see Scheme 1).

Table 1
Koch carbonylation of alcohols in the presence of acidic ionic liquids[a]

Run	Substrate	IL	IL/alcohol	Yield[d] (%)
1	*t*-BA	**1a**	1:1	26.5
2	*t*-BA	**1b**	1:1	16.9
3	*t*-BA	**2a**	1:1	12.3
4	*t*-BA	**2b**	1:1	6.3
5	*t*-BA	**2a**	0.5:1	7.3
6	*t*-BA	**2a**	1.5:1	23.4
7	*t*-BA	**2a**	2.5:1	20.9
8[b]	*t*-BA	**2a**	1.5:1	2.9
9[c]	*t*-BA	**2a**	1.5:1	<0.5
10	*t*-AA	**2a**	1.5:1	32.4
11	adamantanol	**2a**	1.5:1	55.8
12	2-butanol	**2a**	1.5:1	–

[a] Reaction conditions: 1.4 mmol alcohol, 8 MPa CO, 423 K, 22 h reaction time.

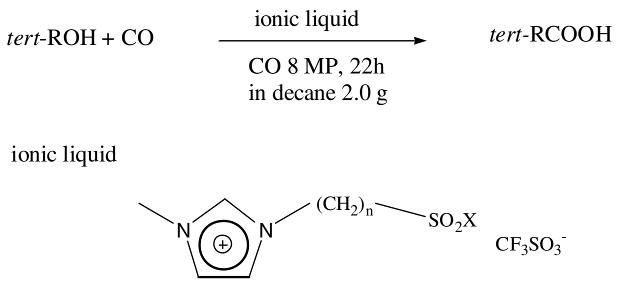
[b] Air: 0.1 MPa.

[c] Water: 5 mmol.

[d] GC yield (toluene as internal standard).

The yields of pivalic acid were also significantly affected by the mole ratio of ionic liquid/alcohol. Take **2a** as reaction medium, for example, when the mole ratio of **2a** to *tert*-butyl alcohol increased from 0.5:1 to 1.5:1, a corresponding increment of yield of pivalic acid from 7.3% to 23.4% is observed (Runs 3, 5 and 6). A further increasing of the ratio to 2.5: 1, however, causes a slight decrement in the yield of product to 20.9% (Run 7). The classical reaction mechanism for Koch carbonylation is well established,[3] which involved the dehydration of alcohol to form carbon cation at first over acidic catalyst and then followed by addition of CO with carboncation and water to generate corresponding acid, accompanying with dehydration and oligomerization reactions as side reactions. Although the detail of Koch carbonylation of *tert*-alcohols to corresponding tertiary acids in the presence of acidic ionic liquid is not clear at this stage, based upon the molecular structure of acidic ionic liquids and their applications in other reactions,[5,6] which almost always behave like normal acids, we are inclined to believe that the traditional reaction mechanism also functions here. Therefore, our explanation to the observed decreasing yields of pivalic acid at a high ionic liquid/*tert*-butyl alcohol ratio is that side reactions are probably more favored when too much ionic liquid was used.

Additives such as air and water also play an important role in carbonylation of *tert*-butyl alcohol with CO. It was already known that either air or water can significantly promote Koch carbonylation in the case of using catalyst such as silver trifluoromethanesulfonate [3b]. Therefore, the effect of air and water on carbonylation of *tert*-butyl alcohol in the presence of **2a** was examined. Unfortunately,



1a.n=3, X=Cl, **1b**. n=4, X=Cl
2a. n=3,X=OH, **2b**. n=4, X=OH

Scheme 1. Koch carbonylation of tertiary alcohol in the presence of acidic ionic liquids.