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Imidazolium-Based Ionic Liquids Catalyzed Formylation of Amines Using Carbon Dioxide and Phenylsilane at Room Temperature

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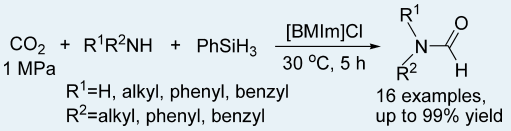
Supporting Information

ABSTRACT: The CO_2-involved synthesis of chemicals is of significance. In this work, we found that 1-alkyl-3-methylimidazolium ionic liquids (ILs) had high efficiency for catalyzing the formylation of amines using CO_2 and phenylsilane at room temperature, producing the corresponding formylated products in excellent yields under the metal-free condition. The ILs acted as bifunctional catalysts, which activated the Si−H bond of phenylsilane to react with CO_2 to form the formoxysilane intermediate and simultaneously activated the amine substrate through the hydrogen bond. Moreover, the imidazolium cation and the anions of the ILs showed an excellent synergistic effect on catalyzing the formylation of amines.



KEYWORDS: *carbon dioxide, ionic liquid, formylation, room temperature, conversion*

The metal-free catalytic process can reduce cost and avoid the pollution caused by metals and is thus regarded as a green process, which has been paid much attention in chemical synthesis.[1] The CO_2-involved chemical synthesis has been widely investigated in the past decades because CO_2 is a cheap, renewable, abundant, and green C1 resource.[2] However, due to the inherent thermodynamic and kinetic stability of CO_2, it is challenging to activate CO_2 and achieve its transformation under mild conditions, especially at room temperature. So far, much work has focused on exploring efficient catalysts or catalytic systems for CO_2 conversion.[3] Metal-based catalysts have been widely applied in the CO_2-involved chemical synthesis.[4] Recently, metal-free catalytic systems have been reported, showing promising potential for the CO_2 transformation.[5] For example, N-heterocyclic carbenes (NHCs) can activate CO_2 and catalyze CO_2 conversion at room temperature and atmospheric pressure.[5a] However, compared with the metal catalysis, the nonmetal-catalyzed CO_2 conversion is still in an early stage.

Ionic liquids (ILs), composed of organic cations and organic/inorganic anions, possess unique features such as high thermal and chemical stability, negligible vapor pressure, easy separation and tunable properties. Notably, most of the ILs are nonmetallic salts, which have displayed promising applications in many areas, especially in catalysis.[6] For example, task-specific ILs have realized the CO_2 capture and conversion under mild and metal-free conditions. Protic IL (e.g., [DBUH][TFE]) served as a bifunctional catalyst and achieved the CO_2 conversion at atmospheric pressure and room temperature in the synthesis of quinazoline-2,4(1H,3H)- diones from CO_2 and 2-aminobenzonitriles.[6d] ILs are designable via selecting cations and anions and thus can provide the ILs specific functions as a result of the cooperative or synergistic effects between the ions.[7] As nonmetal catalysts, ILs are promising due to their advantages such as easy separation, recyclability, stability to air and water, and so on.

Formamides are versatile chemicals and important building blocks, which are generally produced via the formylation of amines. Using CO_2 instead of toxic CO for the N-formylation reaction is an attractive and green alternative for the production of formamides.[4c,5a,b,8] However, the reported routes generally suffered from drawbacks such as requiring metal catalysts, inert gas atmosphere, complicated reaction system, high temperature and pressure, and difficulty in catalyst separation, among others. Therefore, exploring simple, recyclable, green catalytic systems is still highly desirable.

Herein, we carried out the initial work to use ILs as the catalysts for the N-formylation reactions of different amines with CO_2 and phenylsilane. It was discovered that imidazolium-based ILs (as listed in Table 1) could catalyze the reactions at room temperature, producing the formamides in excellent yields. It was indicated that the ILs served as bifunctional catalysts, which activated phenylsilane to react with CO_2 to form the formoxysilane intermediate and simultaneously activated the substrate through hydrogen bond, leading to the production of formamides. Moreover, it was found that the cations and anions of the ILs had excellent synergistic effect on catalyzing the formylation of amines. In addition, the ILs can be easily recovered from the reaction solution and can be reused for five times without activity loss.

In our initial experiments, the formylation of *N*-methylaniline (1a) with CO_2 and phenylsilane as a model reaction was performed in the presence/absence of 1-alkyl-3-methylimidazolium-based ILs, and the results are listed in Table 1. The

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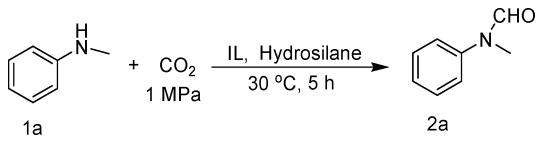
Table 1. IL-Catalyzed Formylation of 1a with CO_2 and Hydrosilanes[a]



1a 2a

entry	catalyst	hydrosilane [n][b]	yield [%][c]
1	--	$PhSiH_3$[2]	0
2	[BMIm]Cl	$PhSiH_3$[2]	93
3[d]	[BMIm]Cl	$PhSiH_3$[2]	10/25[e]
4	[BMIm]Br	$PhSiH_3$[2]	94
5	[BMIm]NO_3	$PhSiH_3$[2]	83
6	[BMIm]PF_6	$PhSiH_3$[2]	0
7	[BMIm]BF_4	$PhSiH_3$[2]	0
8	[HMIm]Cl	$PhSiH_3$[2]	92
9	[BMIm]Cl	PMHS[5]	0
10	[BMIm]Cl	Ph_2SiH_2[3]	5
11	[BMIm]Cl	Et_2SiH_2[3]	0
12[f]	[BMIm]Cl	$PhSiH_3$[2]	92

[a]Reaction conditions: IL (1 mmol), 1a (1 mmol). [b]*n* refers to mmol of hydrosilane. [c]Determined by GC analysis using dodecane as the internal standard. [d]CO_2 pressure (1 atm). [e]Reaction time (24 h). [f]Reused for the fifth time.

reaction did not occur without ILs (Table 1, entry 1). To our delight, 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) was very effective for this reaction, affording *N*-methylformanilide in a yield of 93% within 5 h at room temperature (Table 1, entry 2). Moreover, this reaction could proceed even at atmospheric pressure in spite of providing product in a lower yield (Table 1, entry 3). The other four ILs with the same cation (i.e., $[BMIm]^+$) were examined for catalyzing this reaction (Table 1, entries 4−7). Both [BMIm]Br and [BMIm]NO_3 were also active, whereas [BMIm]PF_6 and [BMIm]BF_4 were not effective. These findings indicated that anions of the ILs had a significant influence on the activity of the ILs, which may be ascribed to the different interactions between the ILs and the reactants. For comparison, 1-hexyl-3-methylimidazolium chloride ([HMIm]Cl) was used, and it showed the same catalytic activity as [BMIm]Cl (Table 1, entry 8), indicating that the alkyl substituent on the 1-alkyl-3-methylimidazolium cation had limited effect on the catalytic activity of the ILs. The effects of different hydrosilanes demonstrated the priority of phenylsilane ($PhSiH_3$) for this reaction (Table 1, entries 9−11). For example, the reaction did not proceed using poly(methylhydrosiloxane) (PMHS) or diethylsilane (Et_2SiH_2), and the product yield was only 5% with diphenylsilane (Ph_2SiH_2). In addition, the reusability of [BMIm]Cl was studied as well, and the yield of *N*-methylformanilide remained unchanged after [BMIm]Cl was used for five times (Table 1, entry 12), indicating that the IL was stable in this catalytic system and it can be reused without activity loss.

Among the tested ILs, [BMIm]Cl, [BMIm]Br, and [HMIm]Cl showed excellent activity for catalyzing the formylation of *N*-methylaniline with CO_2 and phenylsilane at room temperature. Moreover, a catalytic amount of [BMIm]Cl (10 mol %) could efficiently catalyze the formylation of *N*-methylaniline, affording product in a high yield of 91%; however, it showed low activity for catalyzing some of the other amines (Supporting Information, Table S1). Therefore, using equivalent [BMIm]Cl to substrate as the catalyst, we explored the scope of the reactive amine substrates, and the results are listed in Table 2. It was demonstrated that different kinds of amines were formylated to the corresponding formamides in moderate to excellent yields at 30 °C within 5 h. For each secondary amine, sole formylated product was obtained without any other byproduct (Table 2, entries 1−5 and 7−11). *N*-Methylanilines with electron-donating or electron-withdrawing groups including methyl, methoxy, 4-chloro-, and 4-fluoro- were well tolerated (Table 2, entries 2−5).

However, when the substituent group was nitro-, a strong electron-withdrawing group, the substrate was unreactive (Table 2, entry 6). Dibenzylamine exhibited good reactivity, producing dibenzylformamide in a yield of 69% (Table 2, entry 7), and cyclic secondary amine and secondary amine with ether functional group could convert to the corresponding formamides in excellent yields (Table 2, entries 8 and 9). Secondary amines with alkyl chains showed lower activity compared to *N*-methylanilines and aliphatic primary amines, and longer alkyl chains seemed to be more favorable for the formylation reaction (Table 2, entries 10 and 11, 13 and 14). It is worthwhile to mention that the yield of *N*,*N*-dipropylformamide could be increased to 99% after a longer reaction time (Table 2, entry 10). For most of primary amines, both N−H bonds of the amines were reactive for formylation, and mono- and diformylated products were obtained (Table 2, entries 12−14). Moreover, prolonging reaction time resulted in the increase in the yield of the diformylated product (Table 2, entry 14). Different from the formylation of the above primary amines, the formylation of aniline and *p*-methylaniline only yielded monoformylated products, and *p*-methylaniline showed higher activity than aniline, affording corresponding product in a yield of 97% (Table 2, entries 15 and 16).

To gain deep insight into the role of the ILs and the reaction pathway, NMR analysis was performed on [BMIm]Cl and its mixtures with CO_2, phenylsilane and *N*-methylaniline, respectively. No new signal or chemical shift was observed in the ^1H and ^{13}C NMR spectra of the mixture of [BMIm]Cl and CO_2, indicating that this IL cannot activate CO_2 noticeably. From the ^1H NMR spectra of [BMIm]Cl and its mixture with phenylsilane (Figure 1), it was found that the ^1H signal of a-H in [BMIm]Cl shifted downfield from 9.31 to 9.63 ppm due to mixing with phenylsilane; meanwhile, the signal assigning to Si−H (b) of phenylsilane in the mixture shifted from 4.15 to 4.11 ppm. A chemical shift of Si in phenylsilane was also observed in the ^{29}Si NMR spectrum of the mixture (Figure S1). These shifts demonstrated that there was interaction between [BMIm]Cl and phenylsilane and that this IL activated the Si−H bond of phenylsilane, which might make it more favorable for the insertion of CO_2. To confirm this, the solution of phenylsilane, CO_2, and [BMIm]Cl was prepared at 1 MPa and 30 °C, and was examined by NMR analysis after being stirred for 5 h and CO_2 release. In the ^{13}C NMR spectrum of the mixture, a new signal appeared at δ = 163.0 ppm (Figure 2), and a new one also appeared in the ^1H NMR spectrum at δ = 8.27 ppm (Figure S2). These two signals were ascribed to formoxysilane, suggesting that the reaction of phenylsilane with CO_2 occurred catalyzed by [BMIm]Cl. This result was in agreement with those reported employing other catalysts such as transition metals or NHCs.[3a,8d] From the ^1H NMR spectra of *N*-methylaniline and its mixture with [BMIm]Cl, the obvious shift of the signal ascribing to N−H in amine was observed (Figure S3), probably due to the hydrogen bond between the

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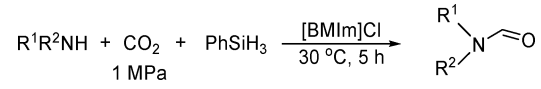
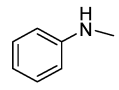
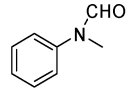
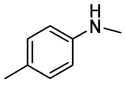
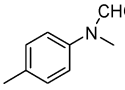
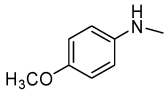
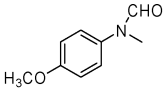
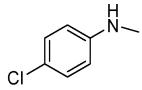
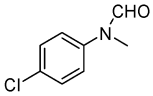
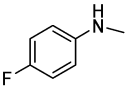
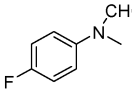
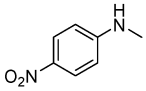
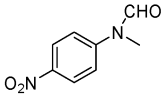
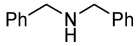
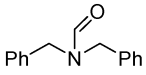
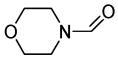
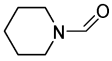
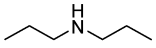
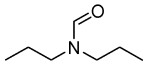
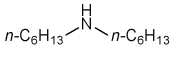
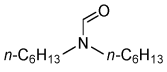
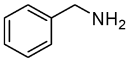
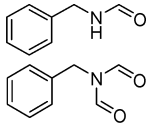
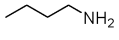
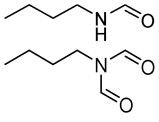
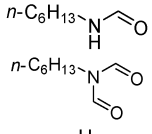
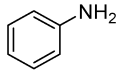
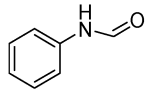
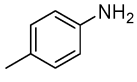
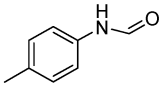
Table 2. Formylation of Various Amines Using CO_2 and Phenylsilane[a]



Entry	Substrate	Product	Yield [%][b]
1			95/93[c]
2			91
3			90
4			90
5			89
6			0
7			69
8			99
9			98
10			62/99[d]
11			82
12			60 10
13			62 28
14	n-C_6H_{13}–NH_2		70/14[e] 29/84[e]
15[c]			76
16			97

[a]Reaction conditions: [BMIm]Cl (1 mmol), substrate (1 mmol), $PhSiH_3$ (2 mmol). [b]Determined by ^1H NMR using an internal standard of mesitylene. [c]Yield was determined by GC analysis using dodecane as the internal standard. [d]Reaction time (10 h). [e]$PhSiH_3$ (4 mmol), 10 h.

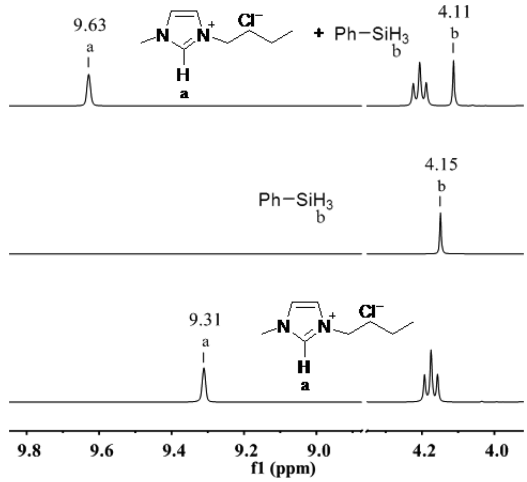


Figure 1. ^1H NMR spectra of the [BMIm]Cl, phenylsilane and their mixture ([D_6]DMSO, 298 K).

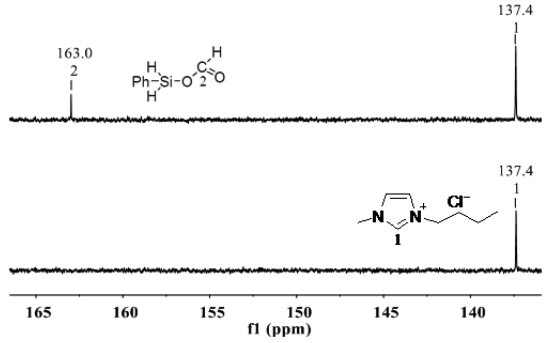


Figure 2. ^{13}C NMR spectra of the formoxysilane intermediate and [BMIm]Cl ($CDCl_3$, 298 K).

anion of the IL and the amine.[7a] That is, the IL, [BMIm]Cl, could activate *N*-methylaniline. As *N*-methylaniline was added into the reaction solution of phenylsilane, CO_2, and [BMIm]Cl at room temperature, excitingly, *N*-methylformanilide was obtained. This result indicated that formoxysilane was the key intermediate in the formylation of *N*-methylaniline with CO_2 and phenylsilane, which further reacted with the amine, producing the final product. The above findings indicated that the IL acted as a bifunctional catalyst, which activated phenylsilane to react with CO_2 to form formoxysilane, and simultaneously activated the amine via hydrogen bond. These results can also explain the influence of CO_2 pressure on the product yield. At higher pressure (e.g., 1 MPa), more CO_2 could dissolve in the reaction solution and react with the IL-activated phenylsilane to form formoxysilane, thus forming the product in a higher yield after formoxysilane further reacted with the amine (Table 1, entry 3).

In a control experiment using *N*-methylimidazole instead of [BMIm]Cl as the catalyst, *N*-methylformanilide was also obtained, but in a yield of 51% under the same other conditions. This suggested that the $[BMIm]^+$ cation of the ILs played a crucial role in catalyzing the N-formylation of amines with CO_2 and phenylsilane. To further explore the reason for the activity difference of the ILs with the same cation, ILs with different anions including Cl^-, Br^-, NO_3^-, BF_4^- and PF_6^- were examined through ^1H NMR analysis. As illustrated in Figure S4, the ^1H signal of 2-H in imidazolium ring of the ILs appeared in a range of 9.31 to 9.08 ppm, following the order: Cl^- > Br^- >

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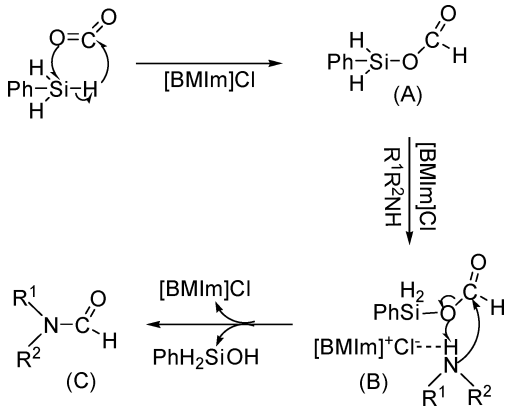
NO_3^- > PF_6^- > BF_4^-, which indicated that the properties of ILs were influenced by the interactions of $[BMIm]^+$ cation and different anions. In the ^1H NMR spectra of phenylsilane with [BMIm]Br and [BMIm]NO_3 (Figure S4), different degree of chemical shifts assigning to H of the imidazolium ring and Si−H in phenylsilane were observed, whereas in the spectra of phenylsilane with [BMIm]BF_4 and [BMIm]PF_6, no chemical shift was observed. Similar results on the chemical shift of N−H in *N*-methylaniline were obtained in the spectra of *N*-methylaniline and its mixture with ILs (Figure S3). These results indicated that ILs with $[BMIm]^+$ cation and Cl^-, Br^-, NO_3^- anions were able to activate phenylsilane and the amine substrate, while [BMIm]BF_4 and [BMIm]PF_6 were ineffective, which was in accordance with the experimental results in Table 1. On the basis of these results, it can be deduced that the cations and anions of the ILs generated synergistic effect, thus leading to different activities on catalyzing the formylation reaction studied in this work.

In the NHC catalytic system, there were two viewpoints on the formation of formoxysilane intermediate. Zhang and Ying reported that the primary activation process involved the reaction between NHC and CO_2, resulting in the formation of NHC−CO_2 adduct, which further reacted with hydrosilane to form formoxysilane.[9] The calculated results of Wang and co-workers indicated that NHC preferred to activate the Si−H bond of hydrosilane and transfer a nucleophilic hydride to CO_2 to form the intermediate.[10] In this work, we found that [BMIm]Cl activated Si−H bond of phenylsilane to react with CO_2, forming the formoxysilane intermediate. Our experimental results supported the calculated results by Wang and co-workers.[10]

On the basis of the above experimental results and previous reports,[3a,9−11] a possible mechanism for the [BMIm]Cl-catalyzed formylation of amines using CO_2 and phenylsilane to produce formamides was proposed, as illustrated in Scheme 1. First, the Si−H bond of phenylsilane is activated by the IL,

Scheme 1. Possible Reaction Mechanism



thus making the insertion of CO_2 much easier to form the key intermediate (A). Meanwhile, the N−H bond in amine is weakened through the hydrogen bond with [BMIm]Cl, and the nucleophilic N atom of the amine attacks the carbon atom of (A) to form (B), thus yielding the formamide product (C), together with the silanol byproduct (see Supporting Information).

In conclusion, a new metal-free approach to the formylation of amines using CO_2 and phenylsilane catalyzed by 1-alkyl-3-methylimidazolium-based ILs was demonstrated for the first time. Different kinds of formamides were synthesized in moderate to excellent yields under low CO_2 pressure and room temperature. It was found that the cations and anions of the ILs played synergistic role in catalyzing the formylation reactions. Moreover, the ILs (e.g., [BMIm]Cl) can be reused at least five times without loss in activity. We believe that these easily available, commonly used imidazolium-based ILs can find more applications in the transformation of CO_2 under mild conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01274.

Experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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