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Ionic liquids as benign catalysts for the carbonylation of amines to formamides

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ABSTRACT

1-Butyl-3-methylimidazolium hydrogen carbonate ([BMIm][HCO_3]), prepared from the reaction of [BMIm]Cl with K_2CO_3 in methanol, exhibits high activity for the carbonylation of amines to produce formamides.

Computational calculation results on the carbonylation reaction of methylamine implies that such high activity of [BMIm][HCO_3] could be ascribed to the bi-functional actions of $[HCO_3]^-$ as a hydrogen atom acceptor and a donor.

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1. Introduction

Formamides are being widely used as polar aprotic solvents for inorganic salts, high molecular mass polymers, natural products, and dyes due to their interesting physical and chemical properties such as low molecular mass, high dielectric constant, electron-donor characteristics, and ability to form complexes [1,2]. Formamides also find applications as extractants in many separation processes such as the recovery of acetylenes from olefins, butadiene from C_4 raffinates, sulfur dioxide from CO_2-containing gases, and aromatics from hydrocarbon mixtures [3].

Presently, two methods are commercially employed for preparing formamides: direct one-step and indirect two-step synthesis [4–6]. In the direct synthesis, carbon monoxide or a gas mixture containing carbon monoxide is reacted with amines in the presence of an alkali metal alkoxide dissolved in an alcohol (usually $NaOCH_3$ in CH_3OH). Although the direct synthesis is highly efficient to produce formamides in high yields, the handling of extremely reactive alkali metal alkoxides is rather problematic because alkali metal alkoxides are easily deactivated by water or S-containing compounds, generating insoluble salts like sodium formate.

In the two-step process, methylformate, prepared separately from CO and methanol, is reacted with an amine. The most important advantage of this process over one-step process is that insoluble salt is not produced because no catalyst is involved in the process. Nonetheless, the requirement of the additional process for manufacturing methylformate seems to reduce the economic value of this process.

To circumvent the problems associated with the above two processes, transition metal-catalyzed carbonylation reactions of amines have been extensively investigated. Accordingly, a number of group 4–10 organometallic compounds have been developed as catalysts for the carbonylation [7–13] reaction. Of these, however, only precious metal-based catalysts including Ru and Rh have shown promising results, but only at elevated temperatures and pressures [14–20]. For instance, in the presence of $RuCl_3$, the carbonylation reaction of *n*-butylamine produces *n*-butylformamide in yield of 93% at 200 °C and 45 MPa [20]. Although the advance with Ru catalysts has been significant, the development of inexpensive catalysts is highly desirable for practical reasons.

In a previous article [21–24], we have demonstrated that the reaction of $KSeO_2(OCH_3)$, prepared by reacting SeO_2 with K_2CO_3 in CH_3OH, with [BMIm]Cl produces [BMIm][$SeO_2(OCH_3)$], an highly active catalyst for the oxidative carbonylation of aromatic amines to corresponding disubstituted urea sans carbamates [21]. Likewise, we have anticipated that the reaction of [BMIm]Cl with TeO_2 and K_2CO_3 in CH_3OH would produce [BMIm][$TeO_2(OCH_3)$]. However, contrary to our expectation, [BMIm][HCO_3] instead of

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[BMIm][$TeO_2(OCH_3)$] was produced as a viscose liquid. Any Te-containing product was not observed on the basis of FAB-Mass spectrometric analysis, indicating that TeO_2 is not involved in the reaction. In fact, [BMIm][HCO_3] was obtained from the reaction of [BMIm]Cl with K_2CO_3 in methanol even in the absence of TeO_2.

Herein, we report on the synthesis of imidazolium-based ILs with a bicarbonate anion and their catalytic activities for the carbonylation of amines to produce formamides as well as on the activities of various ILs bearing an anion other than bicarbonate. The mechanistic investigation of the carbonylation of amines is also discussed on the basis of experimental and computational results.

2. Experimental

2.1. General

All of the chemicals used for the carbonylation reactions and for the preparation of ILs were purchased from Aldrich Chemical Co. and used as received. Solvents used were all reagent grades and were distilled from appropriate drying agents under a nitrogen atmosphere prior to use [25]. Carbon monoxide (99% pure) was obtained from Air Liquide Korea Co. ILs, 1-butyl-3-methylimidazolium chloride ([BMIm]Cl), 1-butyl-3-methylimidazolium acetate ([BMIm][AcO]), 1-butyl-2,3-dimethylimidazolium acetate ([BDMIm][AcO]), 1-butyl-3-methylimidazolium dimethylphosphate ([BMIm][Me_2PO_4]), 1-butyl-3-methylimidazolium methylphosphite ([BMIm][$MePHO_3$]), 1-butyl-3-methylimidazolium methylsulfate ([BMIm][$MeSO_4$]), and 1-butyl-3-methylimidazolium methylsulfonate ([BMIm][$MeSO_3$]), were prepared according to the literature procedures [3,26–29]. Gas chromatographic analysis of liquid samples for the carbonylation experiments were made on an Agilent 6890 gas chromatograph equipped with a FID and a DB-5 capillary column. Characterization of products was made using a 400 MHz Bruker NMR spectrometer and an Agilent 6890-5973 MSD GC–mass spectrometer equipped with a HP-MS capillary column.

2.2. Synthesis of ILs bearing a hydrogen carbonate anion

Four imidazolium-based ILs with a hydrogen carbonate anion were synthesized by reacting dialkylimidazolium chloride or trialkylimidazolium chloride with K_2CO_3 in CH_3OH.

2.2.1. Synthesis of 1-butyl-3-methylimidazolium hydrogen carbonate ([BMIm][HCO_3])

In a 100 mL one-neck flask, [BMIm]Cl (17.4 g, 0.1 mol) was reacted with K_2CO_3 (13.8 g, 0.1 mol) in CH_3OH (20 mL) for 6 h at room temperature. After the completion of the reaction, the solid precipitates were removed by filtration and the remaining solution was dried in vacuum to produce [BMIm][HCO_3] as a viscous pale yellow liquid (Yield: 86%).

Anal. Calcd for $C_9H_{16}N_2O_3$: C, 53.98; H, 8.05; N, 13.99; O, 23.97. Found: C, 54.12; H, 8.41; N, 13.81; O, 24.10. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.97 (t, 3H, CH_3); 1.37, 1.87 (m, 4H, CH_2); 4.03 (s, 3H, NCH_3); 4.27 (t, 2H, NCH_2); 7.42, 7.49 (d, 2H, CHN).

2.2.2. Synthesis of 1-ethyl-3-methylimidazolium hydrogen carbonate ([EMIm][HCO_3])

[EMIm][HCO_3] was prepared by reacting 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) with K_2CO_3 in a similar manner to that employed for the synthesis of [BMIm][HCO_3] (Yield: 84%).

Anal. Calcd for $C_7H_{12}N_2O_3$: C, 48.83; H, 7.02; N, 16.27; O, 27.88. Found: C, 49.24; H, 7.27; N, 16.11; O, 27.59. ^{1}H NMR (400 MHz, DMSO, 25 °C): δ = 0.96 (t, 3H, CH_3); 3.89 (s, 3H, NCH_3); 4.25 (t, 2H, NCH_2); 7.43, 7.48 (d, 2H, CHN).

2.2.3. Synthesis of 1,3-dimethylimidazolium hydrogen carbonate ([DMIm][HCO_3])

[DMIm][HCO_3] was prepared by reacting 1,3-dimethylimidazolium chloride ([DMIm]Cl) with K_2CO_3 in a similar manner to that employed for the synthesis of [BMIm][HCO_3] (Yield: 85%).

Anal. Calcd for $C_6H_{10}N_2O_3$: C, 45.57; H, 6.37; N, 17.71; O, 30.35. Found: C, 45.88; H, 6.09; N, 17.92; O, 30.29. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.92 (s, 6H, NCH_3); 7.69 (d, 2H, CHN); 9.06 (s, H, NCHN).

2.2.4. Synthesis of 1-butyl-2,3-dimethylimidazolium hydrogen carbonate [BDMIm][HCO_3]

[BDMIm][HCO_3] was prepared by reacting [BDMIm]Cl with K_2CO_3 in a similar manner to that employed for the synthesis of [BMIm][HCO_3] (Yield: 87%).

Anal. Calcd for $C_{10}H_{18}N_2O_3$: C, 56.06; H, 8.47; N, 13.07; O, 22.40. Found: C, 56.22; H, 8.52; N, 13.01; O, 22.46. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.96 (t, 3H, CH_3); 1.38, 1.80 (m, 4H, CH_2); 2.60 (s, 3H, CH_3); 4.02 (s, 3H, NCH_3); 4.22 (t, 2H, NCH_2); 7.54, 7.80 (d, 2H, NCH).

2.3. X-ray crystallographic study

Single crystals suitable for X-ray structural analysis were obtained by dissolving [BDMIm][HCO_3] in a mixed solvent (acetone/CH_2Cl_2 = 6/4) and stored at 0 °C in a refrigerator for several days. Single crystal with appropriate dimensions was mounted on a glass fiber in random orientation. X-ray data for [BDMIm][HCO_3] were collected on a Bruker SMART APEXII diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å). Preliminary orientation matrix and cell parameters were determined from three sets of ω scans at different starting angles. Data frames were obtained at scan intervals of 0.5° with an exposure time of 10 s per frame. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS. The structures were solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL program. All hydrogen atoms were calculated at idealized positions and refined with the riding models. Crystal data of [BDMIm][HCO_3]: Mw = 213.26, monoclinic, space group $P2_1/c$, a = 9.7547(18) Å, b = 8.7004(16) Å, c = 13.635(3) Å, β = 90.431(2)°, V = 1131.7(4) Å^3, Z = 4, D_{calc} = 1.252 g cm^{-3}, μ = 0.093 mm^{-1}, T = 100 K, 16,660 reflections collected, 2000 unique (R_{int} = 0.0388), $R1$ = 0.0604, $wR2$ = 0.1408 [$I > 2\sigma(I)$] and for all reflections, and relevant structure refinement parameters are listed in Table S1 in Supplementary data.

2.4. Catalytic carbonylation reaction

Carbonylation reactions were conducted in a 100 mL stainless steel reactor equipped with a magnetic stirrer and an electrical heater. The reactor was first charged with requisite amounts of an amine, solvent, an appropriate IL, and toluene (2 mL) as an internal standard. The reactor was pressurized with carbon monoxide at 2 MPa and then heated to a specified temperature. The pressure inside the reactor was maintained at 4 MPa throughout the reaction using a gas reservoir equipped with a high pressure regulator and a pressure transducer. After the reaction was completed, the reactor was cooled to room temperature and the reaction mixture was analyzed by means of GC and GC–MS.

2.5. Computational calculations

The carbonylation reaction of amine in the presence of an IL was theoretically investigated using Gaussian 09 program [30]. For simplicity, methylamine and 1-ethyl-3-methylimidazolium hydrogen carbonate ([EMIm][HCO_3]) were chosen as the amine and the IL. For a better modelling in consistent with the experimental results, one molecule of methanol was explicitly included in the calculation to take into account the hydrogen bonding between the solvent and the solute. The effect of bulk solvent was taken into account in the single point calculations through the self-consistent reaction field theory (SCRF) based on the Polarisable Continuum Model (IEFPCM-UFF) implemented in the Gaussian program [31,32].

2.6. Recycling experiment

The reactor was charged with cyclohexylamine (2.98 g, 30 mmol), CH_3OH 20 mL, [BMIm][HCO_3] (0.06 g, 0.3 mmol). The carbonylation reaction was performed at 140 °C and 4 MPa of CO for 4 h. After the reaction was completed, the reactor was cooled to room temperature. The reaction mixture was transferred to a 100 mL round bottomed flask and distilled under vacuum (1 mmHg) at 60 °C. The distillate was collected using a liquid nitrogen trap and the remaining [BMIm][HCO_3] was recovered for further use. The same procedure was repeated for the next four cycles with a fresh charge of amine and CH_3OH (20 mL).

3. Results and discussion

3.1. Synthesis of [BMIm][HCO_3]

Two methods are known for the synthesis of imidazolium-based RTILs bearing a hydrogen carbonate anion. One is the reaction of dialkylimidazolium-2-carboxyate with H_2CO_3 in a mixture of DMSO and water [33,34]. The decarboxylation is found to selectively produce corresponding dialkylimidazolium hydrogen carbonate in high yield, but the synthesis of dialkylimidazolium-2-carboxyate is a bit problematic because it requires long reaction time. The other method employed is the anion metathesis between imidazolium halide with alkali metal hydrogen carbonate ($NaHCO_3$ or $KHCO_3$) or ammonium hydrogen carbonate ([NH_4][HCO_3]) in an alcohol [26,35]. However, this method has also some drawbacks such as the long reaction time and low reaction yield.

During the course of our study to develop cost effective and water stable catalysts as alternatives to alkali metal alkoxides and precious metal catalysts, we have found that the carbonylation of amines can be effectively carried out in the presence of an imidazolium-based ionic liquid (IL) with a bicarbonate anion ($[HCO_3]^-$). [BMIm][HCO_3] was obtained from the reaction of [BMIm]Cl with K_2CO_3 in methanol. The pathway to the formation of [BMIm][HCO_3] is not clear at the moment, but it is assumed that $KOCH_3$ and H_2CO_3, possibly generated from the interaction of K_2CO_3 with CH_3OH, are responsible for the formation of [BMIm][HCO_3] (as shown in Eqs. (1)–(3)).

$$2CH_3OH + K_2CO_3 \rightleftharpoons 2CH_3OK + H_2CO_3 \quad (1)$$

$$CH_3OK + H_2CO_3 \rightleftharpoons CH_3OH + KHCO_3 \quad (2)$$

$$KHCO_3 + [BMIm]Cl \rightleftharpoons [BMIm][HCO_3] + KCl \quad (3)$$

The formation of [BMIm][HCO_3] was supported by a X-ray crystallographic analysis with the solid product obtained from the reaction of 1-butyl-2,3-dimethylimidazolium chloride ([BDMIm]Cl) with K_2CO_3. Single crystals were grown in a mixed solvent of acetone and CH_2Cl_2. The X-ray structural analysis data presented in Fig. 1 and Table 1 reveal that the solid product is

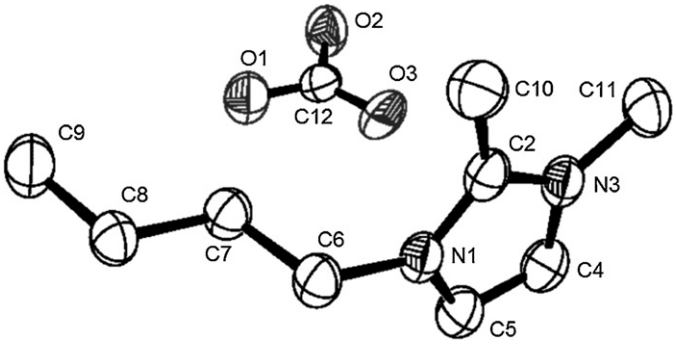

Fig. 1. Crystallographic structure (hydrogen atoms were omitted for clarity) of [BDMIm][HCO_3].

[BDMIm][HCO_3], where $[HCO_3]^-$ is located close to the $[BDMIm]^+$. The interaction of methyl group at C(2) carbon atom of the imidazolium ring is observed, implying that the methyl group possesses some acidity like the hydrogen atom at the same carbon atom. Dimeric structure of dimethylimidazolium hydrogen carbonate has already been reported as a hydrated form, where the $[HCO_3]^-$ anions form hydrogen-bonded dimers around crystallographic centers of inversion [33].

3.2. Activities of ILs for the carbonylation of amines

As an alternative to $NaOCH_3$, [BMIm][HCO_3] (entry 2) was tested as a catalyst for the carbonylation of amines to amides, due to the relatively strong basicity of $[HCO_3]^-$ ($pK_b = 7.65$) [36]. When the carbonylation of cyclohexylamine (CHA) was carried out for 4 h in the presence of [BMIm][HCO_3] at 140 °C and 4 MPa of CO, cyclohexyl formamide (CHF) was produced in yield of 88%. Being motivated by this result, the activities of other [BMIm]-based ILs were also evaluated for the carbonylation of CHA. However, as shown in Table 2, the ILs bearing an anion other than $[HCO_3]^-$ were found to exhibit much lower activities than that of [BMIm][HCO_3], producing CHF in yields of 15–40%. The formation of side products such as dicyclohexyl urea was not observed in all catalytic runs, suggesting that ILs are selective catalysts for the carbonylation reactions of amines.

As a whole, the catalytic activity of an IL was found to increase with increasing basicity of the anion: $[HCO_3]^-$ (entries 2–5, $pK_a = 6.35$) > $[CH_3CO_2]^-$ (entry 8, $pK_a = 4.76$) > $[(CH_3)P(H)O_3]^-$ (entry 7, $pK_a = 2.35$), $[(CH_3)_2PO_4]^-$ (entry 6, $pK_a = 1.29$), $[CH_3SO_4]^-$ (entry 9, $pK_a = 1.14$) > $[CH_3SO_3]^-$ (entry 10, $pK_a = -0.6$), $[BF_4]^-$ (entry 11, $pK_a = -4.9$). The pK_a values are those of the corresponding acids [37–39]. This is somewhat reasonable because more basic anion would interact more strongly with the amino group, thereby

Table 1
Selective bond lengths and angles of [BDMIm][HCO_3].

	Bond length (Å)		Bond angle (°)
C(5)–C(4)	1.339(3)	C(4)–C(5)–N(1)	107.02(17)
C(5)–N(1)	1.384(2)	C(5)–C(4)–N(3)	107.41(17)
C(4)–N(3)	1.373(2)	N(1)–C(2)–N(3)	107.29(16)
C(2)–N(1)	1.337(2)	N(1)–C(2)–C(10)	126.35(18)
C(2)–N(3)	1.339(2)	N(3)–C(2)–C(10)	126.33(17)
C(2)–C(10)	1.472(3)	C(2)–N(1)–C(5)	109.00(16)
C(11)–N(3)	1.466(2)	C(2)–N(1)–C(6)	125.67(16)
C(6)–N(1)	1.476(2)	C(5)–N(1)–C(6)	125.23(15)
C(12)–O(3)	1.216(2)	C(2)–N(3)–C(4)	109.27(16)
C(12)–O(1)	1.279(3)	C(2)–N(3)–C(11)	125.83(16)
C(12)–O(2)	1.324(3)	C(4)–N(3)–C(11)	124.86(17)
		O(3)–C(12)–O(1)	123.6(2)
		O(3)–C(12)–O(2)	119.6(2)
		O(1)–C(12)–O(2)	116.74(19)

Table 2
Activities of various ILs for carbonylation of CHA.[a]

Entry	Catalyst	CHA conversion (%)	CHF yield (%)
1	–	6	5
2	[BMIm][HCO_3]	89	88
3	[EMIm][HCO_3]	86	85
4	[DMIm][HCO_3]	84	83
5	[BDMIm][HCO_3]	85	83
6	[BMIm][Me_2PO_4]	20	19
7	[BMIm][$MeHPO_3$]	23	22
8	[BMIm][AcO]	41	40
9	[BMIm][$MeSO_4$]	24	22
10	[BMIm][$MeSO_3$]	23	22
11	[BMIm][BF_4]	16	15
12	$NaOCH_3$	85	83

[a] The reaction was conducted in CH_3OH (20 mL) for 4 h at 140 °C and at the molar ratio of CHA/IL = 100.

facilitating the insertion of CO into the N–H bond. Nonetheless, much higher activity of [BMIm][HCO_3] compared with those of other ILs is rather unusual. This can be primarily attributed to the stronger basicity of $[HCO_3]^-$ than those of other anions, but the planar structure of $[HCO_3]^-$ seems to play a certain role in enhancing the activity, possibly through the stabilization of transition state. The three oxygen atoms of $[HCO_3]^-$ are arranged in a way to simultaneously interact with amine, methanol, and C(2)–H through hydrogen bonds. Through such a favourable arrangement, hydrogen abstraction from the amine and hydrogen donation to the carbonyl group can take place in a concerted mechanism (see Section 3.4). It was anticipated that the catalytic activity of [BMIm][HCO_3] could be enhanced by increasing the electron density on the imidazolium ring through the substitution of C(2)–H with an electron donating alkyl group, but the replacement of C(2)–H with methyl group resulted in slight decrease of activity. Likewise, the variation of alkyl group on the nitrogen atoms of the imidazolium ring was also ineffective, implying that the catalytic activity is mostly governed by the type of anion, not by the electron density on the imidazolium cation.

3.3. Extension to other amines

The catalytic performances of [BMIm][HCO_3] were also tested for the carboxylation of different amines including *n*-butylamine, *n*-hexylamine, di-*n*-butylamine, *i*-butylamine, *t*-butylamine, and cyclic aliphatic amines. As listed in Table 3, primary amines, *n*-butylamine and *n*-hexylamine, produced corresponding formamides in yields over 85%. However, hindered primary amine, *i*-butylamine and *t*-butylamine, and a secondary amine, di-*n*-butylamine, gave much lower yields of corresponding formamides. If the first step for the carbonylation is the interaction between a hydrogen atom of the amino group and the $[HCO_3]^-$, the reactivity

Table 3
[BMIm][HCO_3]-promoted carbonylation reactions of various amines.[a]

Amine	Conversion (%)	Yield (%)
n-Butylamine	99	99
n-Hexylamine	89	85
i-Butylamine	67	65
t-Butylamine	61	60
Di-*n*-butylamine	45	42

[a]The reaction was conducted in CH_3OH (20 mL) for 4 h at 140 °C and at the molar ratio of amine/[BMIm][HCO_3] = 100.

Table 4
[BMIm][HCO_3]-promoted carbonylation of cyclic amines.[a]

Amine	Conversion (%)	Yield (%)
pyrrolidine	99	99
piperidine	99	98
piperazine	74	72
morpholine	67	64

[a]The reaction was conducted in CH_3OH (20 mL) for 4 h at 140 °C and at the molar ratio of amine/[BMIm][HCO_3] = 100.

of a secondary amine would be lower than that of a primary amine because the abstraction of the hydrogen atom from the less acidic secondary amine is more difficult than that from the primary amine with higher acidity. This is in good agreement with the experimental results. In addition, the lower reactivity of *t*-butylamine suggests that the steric hindrance around nitrogen atom is also an important factor in determining the reactivity of amines.

Unlike di-*n*-butylamine, 5- and 6-membered cyclic secondary amines, pyrrolidine and piperidine produced *N*-formylpyrrolidine and *N*-formylpiperidine, respectively, in almost quantitative yields (Table 4). This can be attributed to the lack of front strain caused by the ring structures. However, the reactivities of piperazine and morpholine are considerably lower than those of pyrolidine and piperidine. The presence of an additional electronegative atom in the heterocyclic ring should decrease the basicity of amino group, thereby limiting the interaction of CO with the amino group.

3.4. Computational calculations

To unveil the origin of the unique catalytic behaviour of [BMIm][HCO_3], the carbonylation reaction of amine in the presence of an IL was theoretically investigated using Gaussian 09 program.

Fig. 2 shows the optimized structures of the reactant, transition state and product for the interactions among methylamine, CO, [EMIm][HCO_3], and methanol. To better reflect the experimental results, the bulk solvent effect of MeOH was considered in the computational calculation and the result was compared with that obtained from the calculation without considering the solvent effect (see Supplementary data). The numbers in the

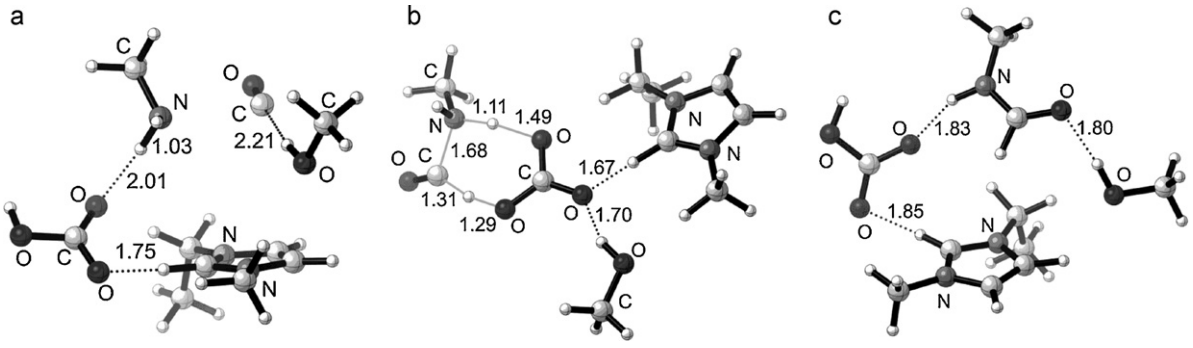

Fig. 2. Optimized structures of [EMIm][HCO_3]-promoted carbonylation reaction of methylamine: (a) reactant, (b) transition state ($\Delta G^{\ddagger}$ = +13.4 kcal^{-1} mol^{-1}), (c) product (ΔG = −26.6 kcal^{-1} mol^{-1}).

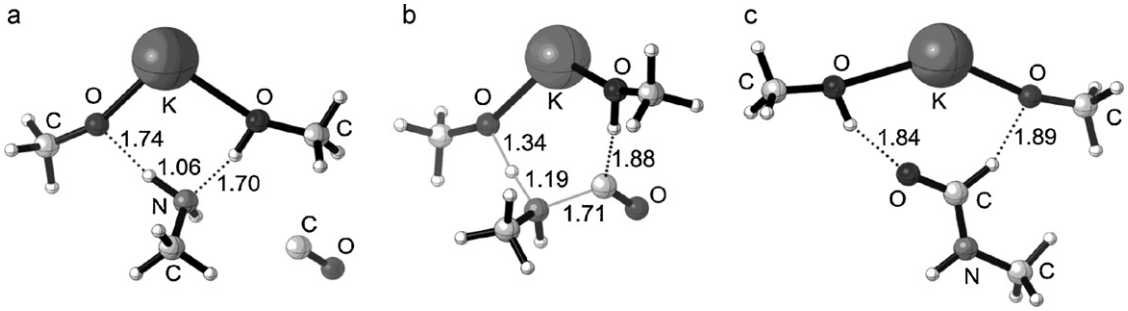

Fig. 3. Optimized structures of CH_3OK-promoted carbonylation reaction of methylamine: (a) reactant, (b) transition state ($\Delta G^{\ddagger}$ = +19.5 kcal^{-1} mol^{-1}), (c) product (ΔG = −10.6 kcal^{-1} mol^{-1}).

parentheses are energies relative to that of the ground state. To support the calculation results, a series of kinetic experiments were also conducted for the carbonylation reaction of cyclohexylamine in the presence of [BMIm][HCO_3]. The activation energy of +14.1 kcal mol^{-1} obtained from the experiments (see Supplementary data) is 5.5 kcal mol^{-1} lower than that of the calculated value without considering the solvent effect. However, when solvent effect is included, the experimental value is close to the calculation value (+13.4 kcal mol^{-1}). From these results, it is cautiously concluded that the experimental result is in good agreement with that of the calculation as long as the solvent effect is considered in the calculation. From the optimized structure of the transition state shown in Fig. 2(b), it is likely that the [HCO_3]$^-$-catalyzed carbonylation proceeds through a concerted mechanism, which involves the activation of methylamine by [HCO_3]$^-$, the formation of bonding between CO and the activated N atom to form carbamoyl species, and the hydrogen transfer from [HCO_3]$^-$ to the carbamoyl species. The activation of methylamine by [HCO_3]$^-$ is evident from the significant N–H bond lengthening of methylamine from 1.03 Å in the ground state to 1.11 Å in the transition state. The most interesting feature observed in the transition state is that [HCO_3]$^-$ functions as both a hydrogen acceptor and a donor. This is probably the reason for the higher activity of [BMIm][HCO_3] than those of other ILs.

For comparison, CH_3O^--catalyzed carbonylation of methylamine is also theoretically investigated. The optimized structure of the transition state shown in Fig. 3(b) demonstrates that CH_3O^--catalyzed carbonylation of methylamine also proceeds through a concerted mechanism, where CH_3O^- and CH_3OH are found to function as a hydrogen acceptor and a donor, respectively. This is a striking difference from the [HCO_3]$^-$-catalyzed carbonylation, where [HCO_3]$^-$ plays bi-functional roles as both a hydrogen acceptor and a donor. The comparison of the energies for the transition states ($\Delta G^{\ddagger}$) and products (ΔG) for both catalysis indicates that the carbonylation with [EMIm][HCO_3] is at least kinetically more favourable than that with $KOCH_3$. This is probably the reason why [BMIm][HCO_3] exhibits high activity similar to $NaOCH_3$ as listed in Table 2.

3.5. Recycle test

To investigate the recyclability of these IL catalysts, recycling experiments were conducted with cyclohexylamine as the substrate at 140 °C for 4 h in CH_3OH using [BMIm][HCO_3] as the catalyst. As listed in Table 5, the catalyst could be reused up to five times, with a moderate loss of initial activity. The reduced activity can be ascribed in part to the loss of the IL during transfer and recovery processes. Even though the catalytic activity was reduced by 20% after five uses, the selectivity of CHF remained almost unchanged.

Table 5
Catalytic recycling study with [BMIm][HCO_3].[a]

Cycle no.	CHA conversion (%)	CHF yield (%)	Selectivity (%)[b]
1	89	88	99
2	85	84	99
3	79	76	96
4	76	74	97
5	72	71	99

[a] The reaction was conducted in CH_3OH (20 mL) for 4 h at 140 °C and at the molar ratio of CHA/[BMIm][HCO_3] = 100.
[b] (CHF yield/CHA conversion) × 100.

4. Conclusion

Imidazolium-based ILs bearing a strongly basic anion such as hydrogen carbonate or acetate were shown to be efficient catalysts for the carbonylation of amines, producing corresponding formamides in moderate to excellent yields. In particular, [BMIm][HCO_3] exhibited comparable activity to $NaOCH_3$, suggesting that [BMIm][HCO_3] can be considered as promising alternatives to conventional alkali metal alkoxide and precious metal complexes.

Quantum mechanical calculations on the interactions among methylamine, CO, and [EMIm][HCO_3] suggest that [HCO_3]$^-$ plays bi-functional roles as both a hydrogen acceptor and a donor.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.07.016.

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