Ionic Liquids

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Demonstration of Chemisorption of Carbon Dioxide in 1,3-Dialkylimidazolium Acetate Ionic Liquids**

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Driven by increasing environmental concerns about greenhouse gas emissions (particularly carbon dioxide) and global warming, a growing amount of research has been carried out over the last decade on the use of ionic liquids (ILs), among other options, as a potential alternative to conventional processes based on aqueous amine solutions for CO_2 capture.[1] The tethering of an amine functional group to the cation was one of the initial possibilities investigated,[2] while more recently, absorption of CO_2 in ILs with amine functionality in the anion has also been reported.[3] Still, even without amine functionalization, ILs do generally dissolve CO_2 to a certain extent and CO_2 is generally much more soluble than other gases such as N_2 or O_2.[4] In most cases, solubilization of CO_2 in the nonfunctionalized IL occurs through physisorption, although chemisorption has been suggested for ILs with anions of remarkable basicity (e.g., carboxylate-derived anions).[5] The mechanisms proposed have typically involved an interaction between the acidic CO_2 and the basic anion; the only exception being a grant report by Maginn in 2005 where, to explain the absorption of CO_2 in 1-butyl-3-methylimidazolium acetate, he used NMR results to propose the abstraction of the proton at the C(2) position of the imidazolium ring by the basic acetate anion, followed by reaction of CO_2 with the carbene species thus formed.[5a] Interestingly, we could not find any further reference to this mechanism in the literature and we assume the idea was not pursued due to concerns about the lack of explanation for the presence of an a priori unstable N-heterocyclic carbene in a relatively stable IL.

The weak acidity of the proton at the C(2) position of 1,3-dialkylimidazolium rings is one of the major pathways for reactivity of imidazolium species, in particular of imidazolium ILs.[6] Wang et al. made use of this to achieve an equimolar CO_2 capture in 1,3-dialkylimidazolium ILs by addition of a superbase, 1,8-diazabicyclo[5.4.0]undec-7-ene, with formation of the corresponding 1,3-dialkylimidazolium-2-carboxylate.[7] We have recently shown that the C(2) proton can be abstracted to some extent in neat 1,3-dialkylimidazolium ILs if they are paired with a basic enough anion such as acetate even in the absence of any external base.[8] For example, the carbene concentration in 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) and 1-butyl-3-methylimidazolium acetate ([C_4mim][OAc]) is high enough to enable formation of imidazole-2-chalcogenones by the direct addition of elemental chalcogens to these ILs. However, we also realized that complex anion formation (e.g., acetic acid/acetate) resulted in stabilization of the volatile acetic acid thus formed, preventing further decomposition reactions and allowing these ILs to act as stable reservoirs of carbenes for direct carbene-based chemistry. Recently reported quantum chemical calculations[9] support this concept.

Here, we report direct experimental evidence in the form of single-crystal X-ray structures of solid-state products resulting from the reaction of CO_2 with acetate ILs, which confirm both the reaction mechanism and the role of complex anion formation. Since to the best of our knowledge there were no reported crystal structures of 1,3-dialkylimidazolium acetate salts, we first investigated the crystal structure of 1,3-diethylimidazolium acetate ([C_2C_2im][OAc]), an off-white crystalline solid with a melting temperature of 30 °C (Figure 1 and Supporting Information). As expected, the anion is strongly hydrogen-bonded to the C(2)-H proton (O2···H 2.16 Å), resulting in unsymmetrical C−O bond lengths in the anion (C10−O1 1.245(2) Å, C10−O2 1.258(2) Å). In the solid state there is no evidence of carbene, as also might be expected.

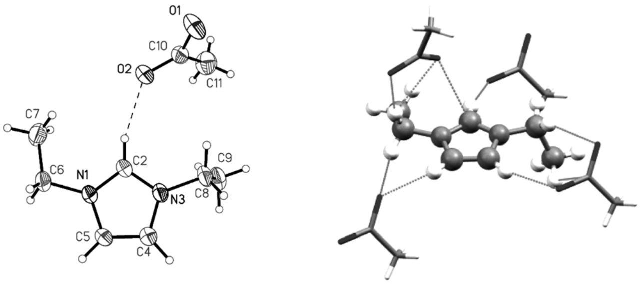

Figure 1. ORTEP diagram and cation environment of [C_2C_2im][OAc].[10] Thermal ellipsoids set at 50% probability.

To explore the reactivity of the acetate ILs with CO_2, we bubbled CO_2 through [C_2mim][OAc], in a glass bubbler at

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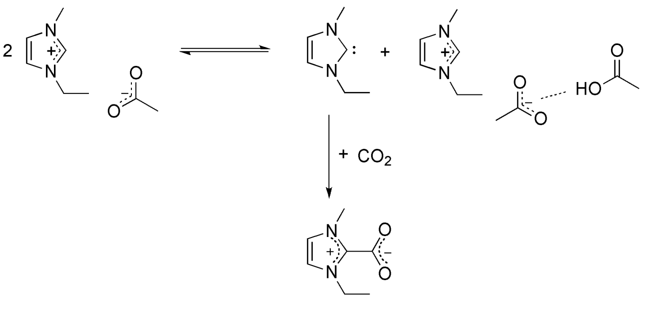
atmospheric pressure and ambient temperature. After 24 h, formation of the corresponding imidazolium carboxylate, namely 1-ethyl-3-methylimidazolium-2-carboxylate ([C_2mim$^+$-COO$^-$]), could be observed by NMR spectroscopy of the clear liquid (Scheme 1). After 36 h, the liquid mixture became turbid, and then solidified. The smell of acetic acid was clearly noticeable after opening the bubbler at the end of the experiment (a total bubbling time of three days). Conducting this reaction in a sealed reactor led to much reduced solid yield. When the reaction was carried out at elevated pressure (20 bar) with purging, solidification was observed within 2 h, however, if water was present (1–15 wt%) the solid yields decreased with increasing water content, in agreement with previous results indicating that water inhibits the interaction of the acetate anion with the C(2)-H proton.[8] The inhibitory effect of water should be considered if a humid CO_2 stream were contacted with the IL, for example in the case of potential applications for CO_2 capture.



Scheme 1. Proposed reaction of CO_2 and [C_2mim][OAc].

We also found analogous reactivity of CO_2 with the 2:1:1 statistical mixture [C_2mim][OAc]:1,3-dimethylimidazolium acetate:[C_2C_2im][OAc] synthesized through a one-pot procedure (see Supporting Information for details).[11] The ratios of the imidazolium carboxylates formed corresponded to the initial ratios of the three different cations in the mixture.

The crystalline solids isolated from these reactions proved to be remarkably hygroscopic, as well as difficult to purify from unreacted IL and acetic acid; however, single crystals of sufficient size and quality for X-ray diffraction analysis could be isolated from all of the above single IL studies. The crystal structure obtained when water is not present (Figure 2 and Supporting Information) clearly demonstrates the formation of the imidazolium carboxylate and the role of acetate in complexing acetic acid. The asymmetric unit consists of the neutral zwitterion ([C_2mim$^+$-COO$^-$]), the [C_2mim]$^+$ cation, and an anion that can best be described as [H(OAc)$_2$]$^-$. The structural features are dominated by a strong interaction between the C(2)-H proton of the cation and the carboxylate portion of the zwitterion, and a strong, symmetric interaction between two acetate anions sharing a single proton. The interpretation of the anion is supported by the corresponding C–O bond lengths which are statistically identical. This close interaction between acetic acid and acetate was observed by Johansson et al.,[12] and identified in our previous work as a key factor enabling the presence of carbene species in equilibrium within stable imidazolium acetate ILs.[8]

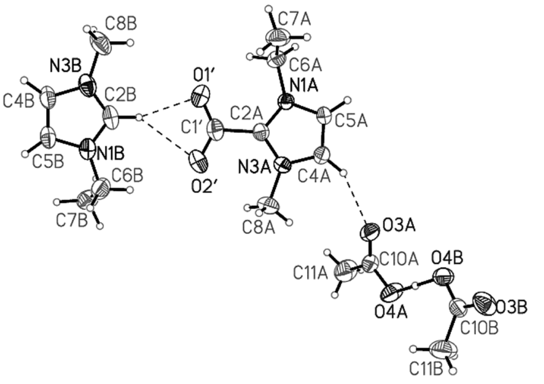


Figure 2. ORTEP diagram of [C_2mim][H(OAc)$_2$][C_2mim$^+$-COO$^-$]. The zwitterion and cation are disordered, modeled with the carboxylate group on C(2A) 75% of the time and on C(2B) 25% of the time.[10] Thermal ellipsoids set at 50% probability.

Fast release of the absorbed CO_2 was observed upon addition of water, with stirring, to the [C_2mim][H(OAc)$_2$]-[C_2mim$^+$-COO$^-$] complex (see videos in the Supporting Information), leading to the formation of [C_2mim][HCO_3], which was also structurally characterized (Figure 3 and Supporting Information). This salt was also isolated in CO_2 reactions conducted in the presence of water. Previous studies have shown the dialkylimidazolium carboxylate zwitterion to react with water and acids in a similar manner; a fact now used to synthesize ILs.[13] Here, one can envision a regeneration process where water or acid can be used to both release and recover the CO_2 while regenerating the IL.

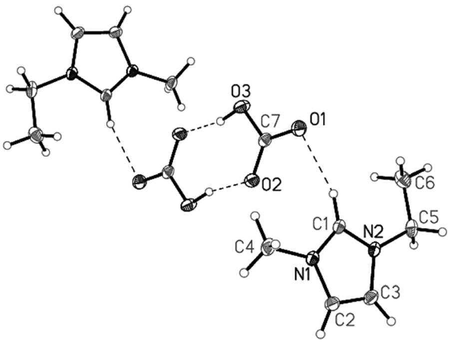


Figure 3. ORTEP diagram of [C_2mim][HCO_3] showing two asymmetric units.[10] Thermal ellipsoids set at 50% probability.

The mechanism demonstrated here is consistent with the experimental data reported to date for the “absorption” of CO_2 in these ILs. Shiflett et al. determined the solubility of CO_2 in [C_4mim][OAc][14] and found a “saturation fraction” of CO_2 in the IL, at atmospheric pressure, of almost 30 mol%, which is not far (especially taking into account that there was a substantial amount of water present in the IL sample used) from the theoretical maximum of 0.33 molar fraction that corresponds to the reaction described in Scheme 1. The authors noted a smell of acetic acid evolving from the mixture of IL and suggested the possibility of a chemical reaction, however, just to a minor extent, giving preference to the hypothesis of formation of a complex. The increased molar fraction of CO_2 absorbed at higher pressures is consistent with physisorption of the gas in the resulting mixture of products. The same research group also explored the combination of CO_2 with [C_2mim][OAc],[5b] observing again that the pressure of the gas became practically zero in the CO_2 molar fraction range up to approximately 0.3, and now clearly opting for the hypothesis of chemisorption.

Almost simultaneously, Carvalho et al. also explored the system CO_2 + [C_4mim][OAc], and its interactions.[5d] Their results also seemed to point to chemisorption up to CO_2 molar fractions of 0.3, and on the basis of NMR results, and corroborated by ab initio calculations, they suggested a preferential interaction of the acid carbon of the CO_2 molecule with the carboxylate group of the acetate anion. Although their NMR spectra are not clearly interpretable from the perspective suggested in the present work, the crystal structure experimentally obtained suggests that there is an "internal" interaction of anion and cation of the IL (as for example shown in Figure 1), which results in the formation of the zwitterionic imidazolium carboxylate species.

In summary, the experimental evidence offered in this work sheds light on the interactions of 1,3-dialkylimidazolium acetate ILs with CO_2, leading to a re-consideration of previous results available in the literature. Since these types of ILs and similar ones are being actively investigated in cutting-edge research fields (for instance in valorization of lignocellulosic renewable sources, production of biofuels, and carbon capture), the results presented here can be critical for a better evaluation of the behavior, possibilities, and limitations of these ILs in such fields. By extension, and taking into account that the most investigated types of ILs to date are those with a 1,3-dialkylimidazolium cation, and that there are many basic anions that can be combined with such cations, this work provides a basis for a general reconsideration of the use of these ILs for different applications. We would further reiterate that the ability of the anion to complex any formed acid, essentially acting as an internal buffer, should be factored into any consideration of the use of these ILs and serve as a reminder that the ions comprising these ILs cannot always be considered independently.

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