

## Equimolar CO<sub>2</sub> Absorption by Anion-Functionalized Ionic Liquids

Burcu E. Gurkan, Juan C. de la Fuente,<sup>†</sup> Elaine M. Mindrup, Lindsay E. Ficke, Brett F. Goodrich, Erica A. Price, William F. Schneider,\* and Joan F. Brennecke\*

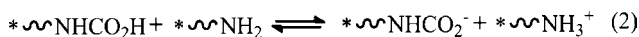
Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556

Received November 2, 2009; E-mail: wschneider@nd.edu; jfb@nd.edu

The discovery of materials that selectively and efficiently absorb CO<sub>2</sub> from flue gases is essential to realizing practical carbon capture and sequestration (CCS). Ionic liquids (ILs) are promising in this regard because of their negligible vapor pressures, high thermal stability, and virtually limitless chemical tunability. Here we show how we can obtain extremely high capacity (up to one mole of CO<sub>2</sub> per mole of IL) of CO<sub>2</sub> in anion-functionalized ILs.

CO<sub>2</sub> has a large physical solubility in many ILs, and this solubility can be enhanced, for instance, by fluorinating the anion or cation components.<sup>1–3</sup> Even with these improvements, however, Henry's law constants are too large for practical CO<sub>2</sub> separations from postcombustion flue gas.

Taking a cue from the chemistry of aqueous organic amines reacting with CO<sub>2</sub>,<sup>4</sup> amine functionalities can be added to ILs to introduce specific and tunable chemical reactivity with CO<sub>2</sub>. The first reported example contained an amine group on an imidazolium cation which reacted with CO<sub>2</sub> in a manner similar to aqueous amines, by forming carbamate and ammonium ions in a stoichiometry of one CO<sub>2</sub> to two amines,<sup>5</sup> as shown in eqs 1 and 2.



While CO<sub>2</sub> uptake of ILs with amine-functionalized cations is much greater than is possible by physical absorption, this 1:2 stoichiometry is atom inefficient. The 1:2 reaction stoichiometry (eqs 1 and 2) effectively arises from amine deprotonation of a carbamic acid intermediate.

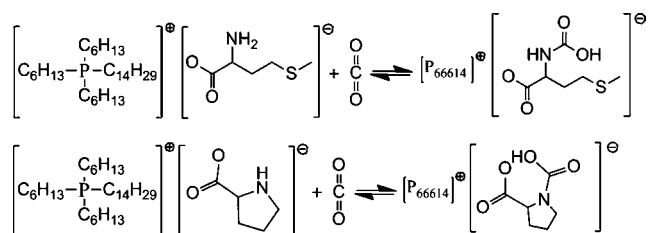
A number of groups have explored other amine-functionalized ILs, including functionalized sulfones,<sup>6</sup> and amino acids anions with imidazolium<sup>7</sup> and phosphonium<sup>8</sup> cations. All systems have been assumed to produce 1:2 stoichiometry, although some of the evidence<sup>6</sup> points to higher capacities and may warrant revisiting in light of the findings presented in this paper. Nonetheless, the question remains whether more favorable stoichiometry than one CO<sub>2</sub> for two amines (1:2) can be achieved.

We report here the synthesis and characterization of amino acid-based ILs, including trihexyl(tetradecyl)phosphonium proline ([P<sub>66614</sub>][Pro]) and methioninate ([P<sub>66614</sub>][Met]), that react with CO<sub>2</sub> in a ratio of one CO<sub>2</sub> per one amine (1:1 stoichiometry).

Termination of the reaction sequence at (reaction 1) would result in a 1:1 stoichiometry and more atom-efficient use of the IL. We used *ab initio* calculations to explore the relationship between the position of the amine functional group and the relative energies of reactions 1 and 2.<sup>9</sup> Calculations showed that tethering the amine to the cation favored the formation of the carbamate (reaction 2), reflecting the electrostatic stability of the zwitterions product, while tethering the amine to the anion favored the carbamic acid (reaction 1), reflecting

the instability of the product dianion. These trends are most pronounced when the charge center and amine are in close proximity.

Following our previous work,<sup>9</sup> we performed electronic structure calculations at the B3LYP/6-311G++(d,p) level on isolated proline and methioninate anions reacting with CO<sub>2</sub> and observed similar trends favoring 1:1 reaction. The net energies to form the proline and methioninate complexes are –71 and –55 kJ·mol<sup>–1</sup>, respectively. This difference reflects the diminishing effect of ring strain on the reactivity of the proline N.



**Figure 1.** Reaction schematics of CO<sub>2</sub> with [P<sub>66614</sub>][Met] (top) and [P<sub>66614</sub>][Pro] (bottom).

[P<sub>66614</sub>][Met] and [P<sub>66614</sub>][Pro] were synthesized from reaction of [P<sub>66614</sub>][OH] with the corresponding amino acids. CO<sub>2</sub> absorption was measured in a custom-built isochoric apparatus, containing an accurately calibrated stirred cell. From the initial and final pressures of CO<sub>2</sub>, the amount of CO<sub>2</sub> absorbed was calculated with the ideal gas equation of state. The total equilibrium CO<sub>2</sub> capacities of [P<sub>66614</sub>][Pro] and [P<sub>66614</sub>][Met] at 22 ± 1 °C are shown in Figure 2. Measurements shown were made in both a stoichiometric uptake apparatus and isochorically in an IR system. The data are in good agreement and the techniques are described in Supporting Information.

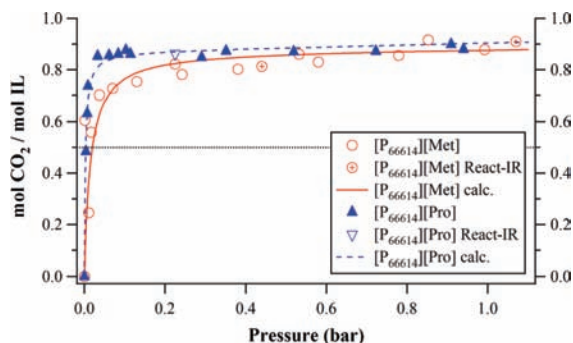
Clearly, the CO<sub>2</sub> capacity is significantly greater than one CO<sub>2</sub> per two ILs and approaches the 1:1 stoichiometry expected from the theoretical arguments. There are two distinct portions of the isotherms: a large uptake at low pressures due to chemical complexation and further increase in capacity at higher pressures due to physical absorption. For both ILs, the vast majority of the uptake is due to chemical complexation, as discussed below. There is clearly a difference in the CO<sub>2</sub> uptake curves for the [P<sub>66614</sub>][Met] and [P<sub>66614</sub>][Pro], with the [P<sub>66614</sub>][Pro] being much steeper at lower pressures, indicative of a higher heat of reaction. This is entirely consistent with the electronic structure results.

Both isotherms evidently saturate at values slightly less than 1:1 stoichiometry. This deviation cannot be explained by residual halide impurities, and we see no evidence of partial carbamate formation (see below). The differences may arise from deactivation of amine groups via some mechanism at high CO<sub>2</sub> loadings; further characterization is necessary to fully elucidate this behavior.

As further evidence of the proposed reaction mechanism, we directly measured the heats of absorption and reaction of CO<sub>2</sub> in [P<sub>66614</sub>][Pro] and [P<sub>66614</sub>][Met] using calorimetry at 25 °C and 2–3 bar. The experimental values are –80 kJ·mol<sup>–1</sup> and –64 kJ·mol<sup>–1</sup>

<sup>†</sup> Present address: Departamento de Ingeniería Química y Ambiental, Universidad Técnica Federico Santa María, Valparaíso, Chile.

of CO<sub>2</sub>, respectively, in surprisingly good agreement with the reaction energies calculated for the gas-phase anions. The enthalpies were determined using a Setaram MicroDSCIII calorimeter, with CO<sub>2</sub> introduced into a calibrated cell containing a known amount of IL. The heat flux needed to maintain the sample isothermally at 25 °C was measured, and knowing the CO<sub>2</sub> capacity (Figure 2), this heat flux was converted to kJ per mol of CO<sub>2</sub>. The estimated experimental uncertainty is  $\pm 5$  kJ·mol<sup>-1</sup> of CO<sub>2</sub>.



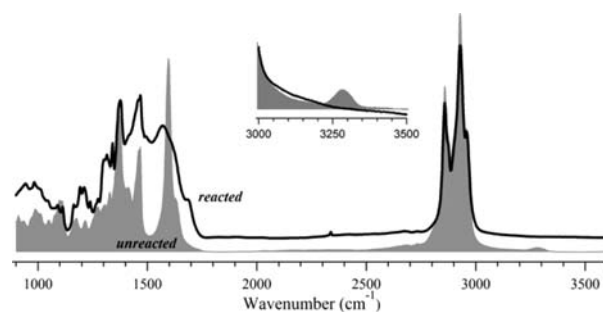
**Figure 2.** CO<sub>2</sub> absorption by [P<sub>66614</sub>][Pro] and [P<sub>66614</sub>][Met] at 22 °C. The lines are Langmuir model fits of the data included to guide the eye.

Furthermore, the 1:1 stoichiometry of the reaction of CO<sub>2</sub> with [P<sub>66614</sub>][Pro] and [P<sub>66614</sub>][Met] has been confirmed by FTIR spectroscopy at 25 °C using a stirred Mettler Toledo model iC10 React-IR system. The FTIR spectrum of [P<sub>66614</sub>][Pro] before and after reaction with CO<sub>2</sub> (at 0.2 bar) is shown in Figure 3. There are three important features in the spectrum. First, the proline N–H stretch observed at 3290 cm<sup>-1</sup> disappears when the CO<sub>2</sub> reacts with the IL (Figure 3, inset). Concomitantly, the N–H bending around 1603 cm<sup>-1</sup>, which overlaps with the carbamate asymmetric stretch, decreases with reaction with CO<sub>2</sub>. Second, there is no evidence for ammonium formation (which would be present for a 1:2 stoichiometry). Specifically, one would expect ammonium bands between 3000 and 2800 cm<sup>-1</sup> and combination bands in the 2800–2000 cm<sup>-1</sup> region, if ammonium ion were present.<sup>10</sup> This is clearly not the case. Third, there is a new band centered at 1689 cm<sup>-1</sup>, which corresponds to the new COOH moiety formed from the reaction of CO<sub>2</sub> with the amine. Assignments are consistent with vibrational spectra obtained from the electronic structure calculations.

The FTIR spectrum of [P<sub>66614</sub>][Met], shown in Supporting Information, shows similar features. The –NH<sub>2</sub> group in the unreacted IL exhibits symmetric and asymmetric stretches centered at 3360 cm<sup>-1</sup> with a shoulder at 3300 cm<sup>-1</sup>. This pair transforms into a single peak with the shoulder as CO<sub>2</sub> reacts. Simultaneously, a new broad peak appears between 1760 and 1660 cm<sup>-1</sup>. Curve fitting applied in this region reveals two distinct C=O stretching environments: (i) 1688 cm<sup>-1</sup> due to the COO<sup>-</sup> asymmetric stretch of the acid of the amino acid anion (symmetric stretch observed at 1469 cm<sup>-1</sup>) and (ii) 1718 cm<sup>-1</sup> of newly formed COOH due to the proton transfer from the amine nitrogen.

In addition, the FTIR spectra allow us to distinguish the fractions of physically dissolved and chemically reacted CO<sub>2</sub>, since the physically dissolved CO<sub>2</sub> appears cleanly between 2370 and 2310 cm<sup>-1</sup>. A calibration plot was developed using tetraglyme (TG), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide as standards with known CO<sub>2</sub> gas solubilities.<sup>3,11,12</sup> At 25 °C, we estimate physical solubility Henry's law constants of 57 bar for [P<sub>66614</sub>][Pro] and 147 bar for [P<sub>66614</sub>][Met]. Thus, at 1 bar pressure of CO<sub>2</sub> the physical uptake of CO<sub>2</sub> at 25 °C by [P<sub>66614</sub>][Met] and [P<sub>66614</sub>][Pro] is less than 1% and 3% of the overall capacity, respectively.

The solid lines in Figure 2 are fits of the data to an isotherm model derived for the reversible 1:1 reaction shown in eq 1, using the physical solubility Henry's law constants. The excellent fits give additional support to the proposed chemistry.



**Figure 3.** IR spectrum of [P<sub>66614</sub>][Pro] before and after reaction with CO<sub>2</sub>. The inset shows disappearance of the N–H stretch.

The CO<sub>2</sub> absorption capacities of a number of tetrabutylphosphonium amino acid ILs supported on high surface area silica gel have been reported,<sup>13</sup> but in all cases any uptake in excess of 0.5 mol CO<sub>2</sub> per mol of IL (i.e., 1:2 stoichiometry) has been attributed to physical absorption. Here, through a combination of theory, spectroscopy, calorimetry, and vapor–liquid absorption measurements, we have clearly shown that neat proline and methionate ILs exhibit significantly higher absorption capacities, approaching 1 mol of CO<sub>2</sub> per mol of IL. B3LYP calculations on glycinate and alaninate support a similar reaction mechanism and reaction energies intermediate between those of the anions studied here.

In conclusion, we have shown that phosphonium-based amino acid ILs can react with CO<sub>2</sub> in a 1:1 stoichiometry, achieving higher molar capacities than cation-functionalized ILs or even aqueous amine absorbents. Moreover, the results demonstrate that the location of functional groups (anion vs cation) in ILs is an additional degree of freedom available in the design of functionalized ILs for specific applications.

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**Supporting Information Available:** Materials, synthesis methods, and other experimental and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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