

Chemisorption of Carbon Dioxide in Carboxylate-Functionalized Ionic Liquids: A Mechanistic Study

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Spectroscopic investigations on the CO₂ chemisorption by tetra-*n*-butylphosphonium formate as an example of carboxylate-functionalized ionic liquids reveal that the formation of hydrogen-bond complexes such as diformate anion supplies the driving force of the chemisorption.

Ionic liquids (ILs) attract growing attention as efficient CO₂ absorbents.^{1–3} The negligibly low vapor pressure of ILs is environmentally preferable and has a potential for an advantage in cost over conventional amine-based CO₂ absorbents such as monoethanolamine. In addition, ILs are designable solvents. This means that we can control the ILs' affinity to various gases by proper choice of cations and anions to attain high selectivity in gas-separation processes. Mechanistic studies on CO₂ absorption are indispensable for successful design of ILs.

ILs absorb CO₂ in two ways; physisorption and/or chemisorption. In hydrophobic ILs whose anion components are fluorinated (e.g., PF₆[−] and NTf₂[−]), absorption is of physical origin ("physisorption") and involves electrostatic and dispersion interactions between dissolved molecular CO₂ and the solvent ions.⁴ On the other hand, chemisorption involves chemical reactions between CO₂ and the solvent at dissolution. Disclosing the reaction mechanism involved is an active research topic.^{5–11}

The chemisorption of CO₂ was first studied in amino-functionalized ILs.⁵ Amino groups can be introduced either on the cations or the anions or both. The amino groups attack CO₂ as a nucleophile and/or a base to form carbamate and/or bicarbonate salts. Later, 1,3-dialkylimidazolium acetates were found to chemisorb CO₂, and the mechanism behind this is attracting significant attention.^{6–11} In contrast to amino-functionality, the carboxylate anions are neither bases nor nucleophiles. The chemisorption mechanism turned out to be rather complex, involving both the cations and the anions. Maginn et al. reported using NMR that the absorbed CO₂ reacts with the imidazolium cations to form zwitterionic species.⁷ A question then arises why only imidazolium acetates can chemisorb CO₂. Rodríguez et al. reasoned that the weak basicity of the carboxylate anions facilitate the formation of carbene, which then can be attacked by CO₂.^{8a} Gurau et al. analyzed the crystal structure of the solid product that is formed after CO₂ chemisorption.^{8b} They identified an anionic complex composed of acetate anion and acetic acid. They pointed out that the stoichiometry for the complex formation explains the observed maximum chemisorption capacity of the imidazolium acetates (ca. 0.5 in mole ratio⁹ to the IL).

In this communication we report CO₂ chemisorption in tetra-*n*-butylphosphonium formate (P₄₄₄₄HCOO), a typical quaternary phosphonium carboxylate IL; in contrast to the imidazolium

acetates the cation in our system is chemically inert. Thus, the role played by the carboxylate anion in CO₂ chemisorption can be highlighted. We demonstrate a new chemisorption mechanism that operates in the presence of water via carbonic acid formation by using in situ NMR and Raman spectroscopy.

P₄₄₄₄HCOO was synthesized as described in ESL.¹² The purity (>99%; H₂O, ca. 0.06%) of P₄₄₄₄HCOO was confirmed by NMR. The ionic liquid was mixed with water at various concentrations. The CO₂ absorption into the IL was performed as follows: 2.00 g of the IL–water solution was loaded into a 10-mL flask. The flask was evacuated for 30 s and then connected via stop valve to a ground-glass 100-mL syringe filled with CO₂ gas. The piston could move freely so that the CO₂ pressure was kept at atmospheric pressure. After the valve was opened, the volume of CO₂ absorbed at each moment was evaluated from the reading of the syringe. It took 10–20 min before absorption reached equilibrium. No solid products were observed. After 2 h, the resultant solution was sampled in a NMR tube under CO₂ atmosphere to measure ¹³C NMR and Raman spectra.¹² For NMR measurements, JEOL ECA-300W equipped with standard TH5 probe was used. Raman measurements were performed at the 90 degree scattering geometry using a green laser (532 nm, Spectra-Physics, EXLSR-532-150). For the detection, a Peltier-cooled CCD camera (Princeton Instrument, Spec-10:400BRXTE) attached to a spectrometer (Jobin Yvon, T64000) was used.¹³

The P₄₄₄₄HCOO–water system absorbs CO₂ mainly through chemisorption when water is added to the IL. This is evidenced by the ¹³C NMR spectra collected after absorption in Figure 1. One finds only a weak signal for molecular CO₂ at 125 ppm and instead a very strong one at 159 ppm. The physisorption contribution is not significant (less than 70 mM in molar concentration) under experimental conditions studied here. Thus, we only discuss the chemisorption part hereafter. The

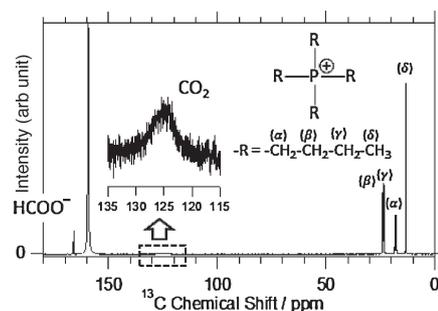


Figure 1. ¹³C NMR spectra of the IL after CO₂ absorption equilibrium is reached at 20 °C and 1 atm. The IL initially contained water at the mole ratio of 1.0 to the IL. ¹³C-labeled CO₂ was employed in this experiment.

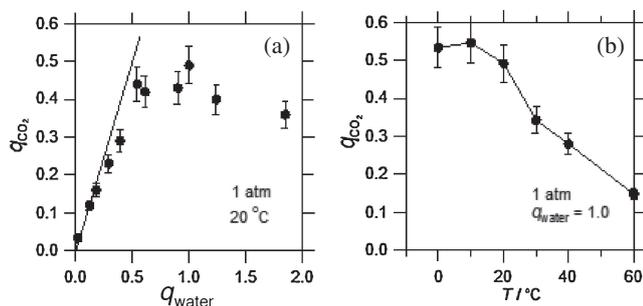


Figure 2. CO₂ absorption capacity of P₄₄₄₄HCOO. The mole ratio of CO₂ (q_{CO_2}) at the absorption equilibrium as a function of (a) the initial mole ratio of water (q_{water}) at the constant temperature of 20 °C and (b) temperature at the constant q_{water} of 1.0. A straight line with a slope of unity is shown for comparison. Errors are estimated to be 10%.¹²

CO₂ absorption capacity (q_{CO_2}) of P₄₄₄₄HCOO is plotted as a function of the initial water mole ratio ($q_{\text{water}} = [\text{H}_2\text{O}]_0/[\text{IL}]$) to the IL at 20 °C and 1 atm in Figure 2a. Here q_{CO_2} is defined as the mole ratio of CO₂ absorbed as obtained from the integral of the peak at 159 ppm in ¹³C NMR spectra.¹⁴ The following aspects are remarkable: (i) The absorption capacity is small at low water concentrations, which is consistent with the previous measurements by Yokozeki et al. under dry conditions,⁹ (ii) the absorption capacity rises linearly by increasing the water mole ratio, and the slope is near unity, and (iii) the capacity reaches saturation at the mole ratio of ca. 0.5 when the water mole ratio reaches ca. 0.5.

We carried out absorption experiments in the temperature range of 0 to 60 °C at a fixed water mole ratio, $q_{\text{water}} = 1.0$ and 1 atm. The CO₂ capacity at each temperature is shown in Figure 2b. As can be seen, lower temperatures resulted in higher CO₂ capacity. This indicates that the chemisorption is an exothermic process. However, the capacity saturated at the level of $q_{\text{CO}_2} \approx 0.5$ even if the temperature is lowered below 20 °C.

The small CO₂ absorption under dry conditions is in contrast to the case of imidazolium acetates; the latter absorbs CO₂ at a mole ratio of 0.38 at 25 °C in the absence of water.⁹ Moreover, Stevanovic et al. reported that the CO₂ absorption capacity *decreases* by the addition of water in imidazolium acetates as opposed to our system.¹⁰ These indicate that the chemisorption mechanisms differ between imidazolium and phosphonium carboxylates.

On the basis of observation (ii), we elucidate that the chemisorption involves 1:1 stoichiometric reaction between H₂O and CO₂, i.e.,



One may question, however, why reaction (1) can proceed nearly quantitatively despite the instability of carbonic acid, H₂CO₃. Moreover, the saturation phenomena in the capacity curve with respect to the water concentration as well as temperature are not expected from reaction (1). Thus, we propose a stepwise chemisorption mechanism as follows:

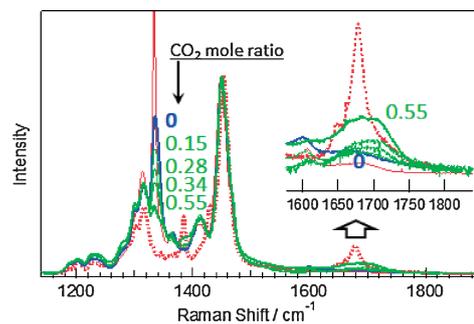
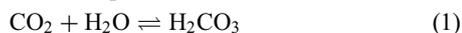
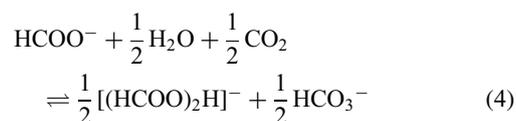


Figure 3. Effect of CO₂ absorption on Raman spectra. CO₂ was absorbed by wet P₄₄₄₄HCOO at the mole ratio of water $q_{\text{water}} = 1.0$. Raman spectra are compared before (blue) and after (green) CO₂ absorption. The absorbed CO₂ mole ratios are 0.15, 0.28, 0.34, and 0.55, with the last one highlighted in bold. For comparison, the spectra for dry P₄₄₄₄HCOO (thin red) and that for the equimolar mixture of P₄₄₄₄HCOO and HCOOH (dotted red) are shown. All the spectra were recorded at 20 °C. Inset shows zoomed spectra.

Here reaction (2) is an acid–base reaction between carbonic acid and formate anion; carbonic acid ($\text{p}K_{\text{a}} = 3.55$) is as strong an acid as formic acid ($\text{p}K_{\text{a}} = 3.75$) in aqueous phase.¹⁵ Reaction (3) proposes a formation of the complex anion between formate anion and formic acid. The complex anion was previously identified in the crystalline potassium diformate (equimolar mixture of HCOOH and HCOOK) from the remarkably short O...H...O bond length.¹⁶ The complex was later theoretically investigated.¹⁷ Moreover, a complex formation of similar type involving acetic acid and acetate ion was proposed by Seddon et al. in ILs.¹⁸ Later Gurau et al. isolated a solid product after CO₂ chemisorption in 1,3-dialkylimidazolium acetates and reported its crystal structure bearing the same complex species.^{8b} Through reactions (1) to (3), we obtain the overall reaction as:



Reaction (4) successfully predicts that the maximum CO₂ absorption capacity is 0.5 in mole ratio and that it is attained when the mole ratio of water (q_{water}) to the IL is larger than 0.5. Moreover, the complex formation proposed by reaction (3) can compensate the positive free energy change in reaction (1).

In attempt to in situ identify the complex species, we applied Raman spectroscopy. In Figure 3, Raman spectra in the finger print region before and after CO₂ absorption are compared. Each spectrum is normalized by the band at 1449 cm⁻¹ due to the cations, since this band appears for P₄₄₄₄Br (not shown). No bands were detected for molecular CO₂, which is consistent with the observation of NMR. The band of 1334 cm⁻¹ is assigned to the symmetric CO₂ stretching vibration of HCOO⁻.¹⁹ It was noticed that this band broadens (blue) by the addition of water to neat P₄₄₄₄HCOO (thin red) in the absence of CO₂. This is probably due to the inhomogeneity induced by hydrogen bonding between water and HCOO⁻. The Raman spectra after CO₂ chemisorption are shown by green curves for various CO₂ loadings but at a fixed water content,

$q_{\text{water}} = 1.0$. By the addition of CO_2 , the band of 1334 cm^{-1} significantly weakened. This is indicative of the gradual disappearance of HCOO^- in a monomeric form and supports the complex formation proposed in reaction (3) with CO_2 chemisorption.

A new band was found around 1700 cm^{-1} after CO_2 absorption as shown in the inset of Figure 3. To characterize this band, we prepared an equimolar mixture of $\text{P}_{4444}\text{HCOO}$ and formic acid (HCOOH); significant heat of mixing was noticed at preparation. The $^1\text{H NMR}$ spectra of this compound evidenced formation of $[\text{H}(\text{HCOO})_2]^-$ anion from unusually large chemical shift of 18 ppm for the OH proton of formic acid. Its Raman spectrum is shown by a dotted red curve. Interestingly, a characteristic band at 1680 cm^{-1} was found near the broad band which evolved with CO_2 absorption (green curves). This coincidence implies that the new band can be related to $[\text{H}(\text{HCOO})_2]^-$ complex. The broad nature of the band, however, suggests that the band may not be assigned to a single chemical species. Formate anion possibly forms hydrogen bonds also with HCO_3^- and/or H_2CO_3 . $^1\text{H NMR}$ spectrum suggested that the hydrogen bonds in the system are relatively short-lived (lifetime $< \text{ca. } 1\text{ s}$). In this regard, reaction (3) should be considered as representative or overly simplified. Further details on molecular interactions in this system are under investigation.

In conclusion, we demonstrated a new CO_2 chemisorption mechanism in tetra-*n*-butylphosphonium formate in the presence of water. In contrast to the imidazolium-based ILs, cations do not take part in the chemisorption. NMR and Raman spectroscopic investigations revealed that the formate anion of the IL forms complex species such as diformate anion ($[\text{H}(\text{HCOO})_2]^-$) after chemisorption. We surmise that this complex formation supplies the driving force for the CO_2 chemisorption, which is otherwise thermodynamically unfavorable. We speculate that the CO_2 chemisorption mechanism proposed here can be operative in a wide range of carboxylate (ca. acetate) ionic liquids (except for the imidazolium-based ILs where the cations directly react with CO_2) because hydrogen bonding of the $\text{O}\cdots\text{H}\cdots\text{O}$ type is expected between the carboxylic acid and its conjugate anion even if the alkyl chain length is different.

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- A chemical exchange can be considered between HCOO^- and HCO_3^- ions through the following mechanism.

$$^{13}\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2^{13}\text{CO}_3 \rightleftharpoons \text{H}^{13}\text{CO}_3^- + \text{H}^+$$

$$\text{H}^{12}\text{COO}^- + ^{13}\text{CO}_2 \rightleftharpoons ^{12}\text{CO}_2 + \text{H}^{13}\text{COO}^- \text{ (hydride transfer)}$$

$$^{12}\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2^{12}\text{CO}_3 \rightleftharpoons \text{H}^{12}\text{CO}_3^- + \text{H}^+$$
 This exchange can be monitored by the increase of the ^{13}C NMR peak integral for HCOO^- (166 ppm) when ^{13}C -labeled CO_2 is used. The exchange was actually noticed at a relatively high temperature ($50\text{ }^\circ\text{C}$) and an elongated reaction time of 3 days but was under detection limit ($< 5\%$ in integral change) within the experimental conditions studied in the present work. Thus, CO_2 absorption capacity was calculated by assuming that such chemical exchange is negligible.
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