

Organic liquid CO₂ capture agents with high gravimetric CO₂ capacity

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We report a new class of CO₂ binding organic liquids that chemically capture and release CO₂ much more efficiently than aqueous alkanolamine systems. Mixtures of organic alcohols and amidine/guanidine bases reversibly bind CO₂ chemically as liquid amidinium/guanidinium alkylcarbonates. The free energy of CO₂ binding in these organic systems is very small and dependent on the choice of base, approximately -9 kJ mol^{-1} for DBU and Barton's base and $+2 \text{ kJ mol}^{-1}$ for 1,1,3,3-tetramethylguanidine. These CO₂ capturing agents do not require an added solvent because they are liquid, and therefore have high CO₂ capacities of up to 19% by weight for neat systems, and slightly less when dissolved in acetonitrile. The rate of CO₂ uptake and release by these organic systems is limited by the rate of dissolution of CO₂ into and out of the liquid phase. Gas absorption is selective for CO₂ in both concentrated and dilute gas streams. These organic systems have been shown to bind and release CO₂ for five cycles without losing activity or selectivity.

Introduction

With global demands for energy from fossil fuels expected to rise, an efficient CO₂ trapping system must be employed to minimize the greenhouse gas emissions from fossil fuel combustion. Chemical CO₂ trapping agents, such as aqueous alkanolamines, rapidly bind CO₂ (forming water-soluble carbamate and bicarbonate salts) and are generally effective in post-combustion systems where the CO₂ concentrations are very low (5–15 vol%). However, the process has serious disadvantages.¹ The concentration of ethanolamine rarely exceeds 30 wt% due to the corrosive nature of the solution,² and this reduces the maximum CO₂ volumetric ($\leq 108 \text{ g L}^{-1}$) and gravimetric capacity ($\leq 7 \text{ wt}\%$) of the CO₂ scrubber.² The $\leq 30 \text{ wt}\%$ loading of ethanolamine also means that a large excess of water must be pumped and heated during CO₂ capture and release, and this greatly increases the energy requirements. One way of lowering the energy requirements and increase the volumetric and gravimetric capacity of CO₂ scrubbers would be to remove the solvent. Herein, we present a novel class of CO₂ binding organic liquids (CO₂BOL) that do not require dilution with a solvent and chemically bind CO₂ with high volumetric and gravimetric CO₂ capacity.

CO₂BOLs are based on Jessop's 'switchable solvents', one version of which is a liquid mixture of an alcohol and an amidine or guanidine base that chemically bind CO₂ to form an amidinium or guanidinium alkylcarbonate salt (Fig. 1).^{3–6} The switchable solvents were based on reactions of CO₂ with amidine

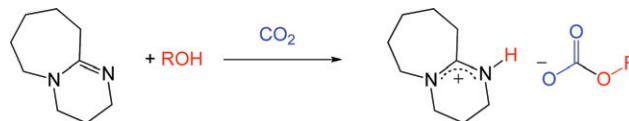


Fig. 1 Reversible binding of CO₂ with an amidine (DBU) and alcohol.

bases such as diazabicyclo[5.4.0]undec-7-ene (DBU) and polymeric amidines.^{7–11} While polymer-bound amidines have been proposed in the literature as CO₂ capturing agents,^{9,12} those studies assumed that amidines are capable of chemically binding CO₂ as a stable zwitterionic adduct. However, there is no direct evidence of the existence of such an adduct of CO₂ with any amidine, and we have shown that the product found by previous researchers from the reaction of CO₂ with amidines is actually a bicarbonate salt and not a zwitterionic adduct.⁷ We therefore conclude that the ability of DBU or polymer-bound DBU to capture CO₂ will be limited to the amount of CO₂ that can physically adsorb or dissolve plus the amount that can be trapped as the bicarbonate by adventitious water. The CO₂BOLs, because they include a stoichiometric amount of alcohol, should be superior because they can chemically bind CO₂ without relying on adventitious water.

Conventional (i.e. non-switchable) ionic liquids functionalized with terminal amines have been shown to be good CO₂ scrubbing agents with moderate weight capacities of CO₂.^{13–15} Davis' group showed their amine tethered imidazolium IL absorbed 0.5 molar equivalents of CO₂ (7.4% CO₂ by weight) as a carbamate salt and took three hours to reach saturation.¹³ CO₂BOLs differ from these ionic liquids because they are only ionic liquids after the CO₂ is chemically bound. Furthermore, CO₂BOLs do not contain CO₂ trapping functional groups tethered to a charged but inert core, and subsequently have the potential for higher weight capacities of CO₂.

In the studies of switchable solvents, CO₂BOLs were shown to reversibly bind CO₂ with a high gravimetric and volumetric capacity. CO₂BOLs are liquids before and after reacting with

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CO₂, eliminating the need for superfluous inert solvents that reduce the weight and volumetric capacity of the trapping agent. Gravimetric measurements showed that DBU:1-hexanol CO₂BOL is capable of capturing 1.3 mol of CO₂ per mol DBU, the additional 0.3 (4 wt%) being presumably due to physical rather than chemical absorption; the total CO₂ absorbed is 19% by weight and 147 g CO₂ L⁻¹ liquid. The combination of chemical and physical adsorption gives CO₂BOLs potentially higher CO₂ gravimetric capacity and volumetric capacity than aqueous ethanolamine systems (7 wt%, 108 g L⁻¹ liquid) for 30% MEA in water. Using lower molecular weight alcohols and bases could increase the gravimetric CO₂ capacities of CO₂BOLs even further.

CO₂ is chemically bound in CO₂BOLs, as an alkylcarbonate salt rather than the bicarbonate or carbamate salts seen in conventional aqueous amine CO₂ scrubbing systems.² Carbamate and bicarbonate salts have strongly bound CO₂ with high hydrogen bonding. CO₂ is bound more weakly in an alkylcarbonate salt, at least partly because of decreased hydrogen bonding, so that less energy is required to thermally strip the CO₂ from the liquid. CO₂ release from some CO₂BOLs has been shown to occur at temperatures as low as room temperature, although the reaction is slow under those conditions.^{3,4}

Physical and chemical properties of CO₂BOLs can be manipulated by changing alcohol/base pairs, as well as by chemically modifying the alcohol/base pairs. Almost any primary or secondary alkanol could be used. Appropriate bases include amidines, guanidines, phosphazines, and possibly some amines; four examples that we have studied are shown in Fig. 2. Due to the potential for dozens of CO₂BOL systems, they can be tailor-made for a specific weight capacity, volumetric capacity, regeneration temperature and physical properties. We present here this novel class of liquid organic, high-capacity CO₂ scrubbing agents.

Experimental

All chemical reagents were purchased from the Aldrich Chemical Company. Bases were distilled over CaH₂ under an inert atmosphere and then dried over 4 Å molecular sieves. Alcohols were distilled over Mg activated with I₂ under an inert atmosphere and stored over 4 Å molecular sieves. All reagents were handled under a N₂ atmosphere in a dry box. CO₂ was purchased from Praxair, SFE grade (99.9995%), and pumped directly into the pressure cell. Water content measurements were performed on a Mettler Toledo DL-37 Karl Fischer Titrator. ¹H NMR and ¹³C NMR spectra were acquired on a Varian 300 MHz and a Bruker 400 MHz spectrometers.

All CO₂ uptake measurements were performed in a Parr 160 mL pressure vessel. The pressure vessel incorporated an Omega

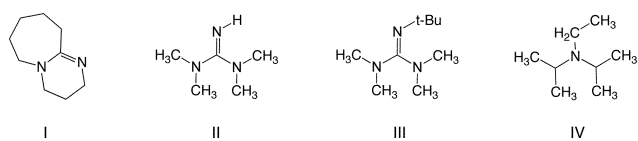


Fig. 2 Bases investigated in this study. I, diazabicyclo[5.4.0]-undec-7-ene (DBU); II, 1,1,3,3-tetramethylguanidine (TMG); III, Barton's base; IV, Hünig's base.

CDCE-90-1 (10–10 000 μS conductivity probe and Omega PX01CO-200 A5T 0–200 psi pressure transducer. CO₂ uptake was measured by changes in conductivity and decrease in pressure. The pressure vessel was retrofitted to contain an internal sampling system to add liquid reagents to the system. The conductivity measurements were started when the base component was transferred into the reaction solution of alcohol in MeCN.

CO₂ evolution experiments were performed in an automated burette system designed in-house.¹⁶ CO₂BOL components were syringed inside an oven-dried round bottom flask and sealed. The reactor flask was attached to the burette system, opened to the burette system, and then plunged, up to its neck, in a preheated oil bath.

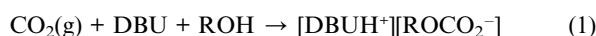
For competitive binding experiments, a 1 : 1 : 1 (by moles) mixture of DBU, MeOH, and another reagent (2-propanol, t-butanol, water or aniline) was prepared in a vial. ¹H and ¹³C NMR spectra of each sample were acquired before and after CO₂ treatment. The CO₂ bubbling was continued until the NMR spectra showed no further change. The integration ratio of the methyl groups of methanol, methylcarbonate, and the unreacted and reacted forms of the other reagent were measured by ¹H NMR spectroscopy (32 scans, delay time of 20 s). Analyses were performed in duplicate. For the experiment with water, quantitative ¹³C NMR spectroscopy was used to determine the concentrations of the bicarbonate and methylcarbonate anions. To obtain reliable integration values, the ¹³C NMR spectra were obtained in inverse-gated mode with a delay time of 50 s, which is 5 times the T₁ relaxation time.

Thermodynamic measurements were performed with 0.1 M solutions of base and alcohol in *d*-MeCN. All liquid reagents were syringed under an N₂ environment at room temperature to an NMR tube. CO₂ was sparged through the solution for 10 min, and then the tube was capped and sealed with teflon tape. Equilibrium constants were calculated from the concentrations of species in solution plus the pressure of CO₂. The CO₂ pressure was 1 atm of CO₂ at 24 °C (the temperature at which the sample was flushed with CO₂) and was assumed to slightly rise at higher temperatures due to the release of CO₂ from the salt. The amount of that pressure rise was calculated from the observed increase in the concentration of free alcohol.

Results and discussion

CO₂ uptake

The rate of CO₂ uptake by CO₂BOLs (eqn (1)) was evaluated by measuring the change in conductivity of a solution of an amidine or guanidine base and an alcohol in acetonitrile as a function of time. As shown in previous studies,^{3–5} solutions of amidine and guanidine bases and alcohols are non-conductive until CO₂ is present and the amidinium alkylcarbonate salt is produced (Fig. 1).



The uptake of CO₂ at 28 °C was complete within 20 seconds regardless of choice of base (DBU or TMG) or the choice of alcohol (ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol). However, the rate was strongly dependent on the stirring rate,

indicating that the reaction was limited by the rate of mass-transfer of CO₂ from the gas phase into solution rather than the reaction of dissolved CO₂ with the base and alcohol. We attempted to increase the rate of mass transfer of CO₂ into solution by exclusively using liquids pre-saturated with CO₂ and by increasing the stir-rate to 500 rpm but the rate remained dependent on the stir-rate. The process is as rapid as current mixing will allow, which is clearly promising for CO₂ capture applications.

Selectivity of CO₂ absorption

In order for a CO₂ scrubbing system to be applicable for post and pre-combustion CO₂ capture, it needs to have high selectivity towards CO₂ in either pressurized (pre-combustion) or atmospheric (post-combustion) gas streams. The selectivity of CO₂BOLs towards CO₂ was demonstrated by reacting DBU and 1-hexanol with CO₂ under a N₂ atmosphere (Fig. 3). A 1 : 1 molar ratio of DBU and 1-hexanol was placed in a pressure vessel, exposed to gases, and monitored for changes in pressure and conductivity. At first, 50 psig of pure N₂ was added; the N₂ pressure did not decrease and there was no change in conductivity, indicating no absorption of N₂. Under constant stirring, one equivalent of CO₂ (50 psig) was added to the reactor vessel, bringing the total pressure to 100 psig. A subsequent pressure drop of 50 psig (Fig. 3) indicated that the CO₂ was absorbed. The conductivity of the solution increased, indicating that [DBUH⁺][ROCO₂⁻] was formed. Thus CO₂BOLs are selective towards capture of CO₂ in a pressurized 50% gas mixture of CO₂ and N₂, suggesting that CO₂BOLs may be useable for pre-combustion CO₂ capture. As shown in previous work, DBU: 1-hexanol are able to selectively capture CO₂ from a mixture of CO₂ and N₂ at 1 atm,¹⁷ demonstrating its applicability towards post-combustion CO₂ capture.

CO₂ release

For measurements of the rate of CO₂ evolution, CO₂ saturated CO₂BOLs were placed in the automatic burette system and plunged into a pre-heated oil bath while being stirred and monitored for CO₂ evolution. On average, decarboxylations from [DBUH⁺][ROCO₂⁻] (R = 1-hexyl, 1-pentyl, 1-butyl) and

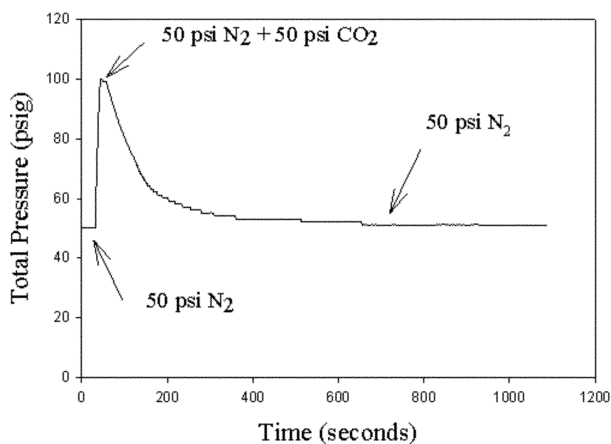
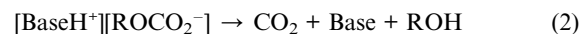


Fig. 3 Selectivity of DBU : 1-hexanol for CO₂ in an N₂-CO₂ mixture.

[TMGH⁺][ROCO₂⁻] (ROH = 1-hexyl, 1-pentyl, 1-butyl) were achieved within 1 min of heating at 90 °C under a static atmosphere at 250 rpm stirring. The rate of CO₂ evolution from the CO₂BOLs (eqn (2)) was first order with respect to the concentration of CO₂BOL salt in solution. Ethanol, 1-propanol, 1-butanol, 1-pentanol and 1-hexanol showed similar rates of CO₂ evolution when paired with DBU and heated at the same temperature and solution stir-rate. Changing the solution stir-rate altered the rate at which CO₂ evolved from the CO₂BOL, suggesting that the rate-limiting step was mass-transfer of CO₂ from solution, rather than chemical release of CO₂ from the alkylcarbonate anion. The E_{act} for the process was determined to be 23–33 kJ mol⁻¹ from an Arrhenius plot of the first order rate constant.



The total amount of released CO₂ detected by the gas burette system was highly dependent on the temperature. CO₂BOLs do not decompose or evolve CO₂ at an appreciable rate at room temperature under a static atmosphere.¹⁷ CO₂ evolution from CO₂BOLs at a reasonable rate requires either mild heating or continuous flushing of an inert gas or air through the liquid.³ In the burette experiments without flushing of a gas through the liquid, the [DBUH⁺][ROCO₂⁻] (R = 1-hexyl, 1-pentyl, 1-butyl) and [TMGH⁺][ROCO₂⁻] (ROH = 1-hexyl, 1-pentyl, 1-butyl) CO₂BOLs, on average 0.25 equivalents of CO₂ are evolved when heated to 50 °C, 0.50 equivalents at 70 °C and up to 0.65 equivalents at 90 °C. This is attributed to the established thermodynamic equilibrium between the gaseous and dissolved CO₂. Elevating the temperature of the CO₂BOL shifts the equilibrium, forcing more CO₂ evolution.

In comparison with currently employed aqueous alkanolamine systems, CO₂BOLs have the potential to be much more energy efficient for CO₂ release. 60% of the energy penalty for CO₂ capture from power plants is attributed to the thermal stripping of CO₂ from solution.² The large inefficiency of MEA systems is caused by the high specific heat of water (4.18 J g⁻¹ deg⁻¹).¹⁸ The specific heat of CO₂BOLs to date have not been measured, however the specific heat of other ionic liquids such as 3-ethyl-1-methyl-imidazolium tetrafluoroborate and 3-butyl-1-methyl-imidazolium tetrafluoroborate have been shown to be 1.28 J g⁻¹ deg⁻¹ and 1.66 J g⁻¹ deg⁻¹, respectively.¹⁹ It is predicted that the specific heat of CO₂BOLs would fall between 1.2–2.0 J g⁻¹ deg⁻¹, analogous to other ionic liquids, and therefore at least 50% less energy would be required to thermally strip CO₂ from CO₂BOLs than from aqueous systems at comparable temperatures.

Another problem with the aqueous ethanolamine system is solvent loss arising from the requirement for heating the liquid above the boiling point of the solvent.² This is less likely to be a problem because the temperature required for CO₂ release from CO₂BOLs is well below the boiling point of the components (159 °C for 1-hexanol and 256 °C for DBU).

Recycling

For industrial applications, a CO₂ capture agent must be recyclable. To assess the ability of CO₂BOLs to be used repeatedly, we performed a series of capture and release cycles with

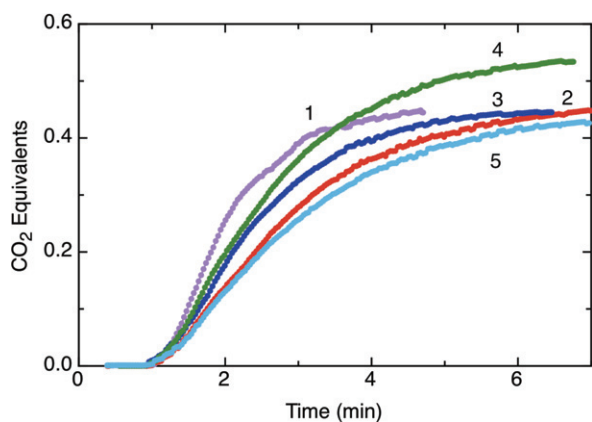


Fig. 4 Lifetime/repeated CO₂ release from DBU and HexOH at 90 °C. Heating begins at one minute.

DBU:1-hexanol using our automated gas burette system. The CO₂BOL was isolated from the burette system and then carboxylated by sparging the solution with CO₂. The CO₂BOL was connected to the burette system and then decarboxylated by plunging the stirred flask into a pre-heated oil bath at 90 °C. For each cycle, the mixture of DBU and 1-hexanol was sparged with CO₂ for five minutes to form the alkylcarbonate salt [Base-H⁺][ROCO₂⁻] and then subsequently plunged into a hot oil bath and measured for CO₂ release (Fig. 4). After CO₂ release, the flask was cooled to room temperature and CO₂ was sparged into the solution for another five minutes, this process was repeated for five cycles. DBU and 1-hexanol were carboxylated and decarboxylated five times with no visible loss of activity. We anticipate that the DBU and 1-hexanol CO₂BOL could be cycled indefinitely as long as the gas stream is anhydrous and the evaporative losses remain low.

If water is present, the system selectively forms the much more thermally stable bicarbonate salt, [DBUH⁺][HCO₃⁻], rather than the CO₂BOL alkylcarbonate [DBUH⁺][ROCO₂⁻]. While gas streams used in this study have very low water content, industrial flue gas streams can have water content as high as 15%,²⁰ so there is a high probability that CO₂BOLs would form significant amounts of the stable bicarbonate salt unless steps are taken to exclude water. While the [DBUH⁺][HCO₃⁻] salt may therefore appear to be problematic, it can be stripped of CO₂ at 121 °C, the same temperature used for MEA systems. The stripping of CO₂ from CO₂BOLs, even with small conversion to [DBUH⁺][HCO₃⁻], will still be more energy efficient than MEA systems because the specific heat of [DBUH⁺][HCO₃⁻] should be lower than that of water and the enthalpy for releasing CO₂ from that salt should not be significantly more than that from MEA.

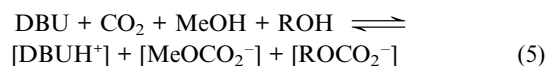
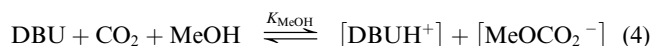
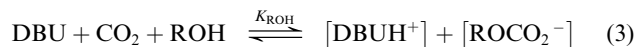
Competitive binding experiments

A series of competitive experiments were performed to determine the preference of DBU for certain alcohols. Methanol was chosen as the standard. The competitive binding experiments were performed by bubbling CO₂ through 1 : 1 : 1 mixtures of DBU, methanol and another reagent ROH (R = n-propyl, isopropyl, *t*-butyl, or H, eqn (3)–(6)). The ratio of equilibrium

Table 1 Relative equilibrium constants for the reaction of DBU and CO₂ with ROH (or aniline) versus methanol

| ROH | $K_{\text{ROH}}/K_{\text{MeOH}}$ |
|-------------------|----------------------------------|
| H ₂ O | 1.43 |
| MeOH | 1.0 |
| PhNH ₂ | 0.97 |
| PrOH | 0.96 |
| <i>iso</i> -PrOH | 0.80 |
| <i>t</i> -BuOH | 0 |

constants $K_{\text{ROH}}/K_{\text{MeOH}}$ was calculated from the NMR integration ratios.



$$\frac{K_{\text{ROH}}}{K_{\text{MeOH}}} = \frac{[\text{MeOH}][\text{ROCO}_2^-]}{[\text{ROH}][\text{MeOCO}_2^-]} \quad (6)$$

The relative equilibrium constants (Table 1) showed that DBU and CO₂ react more favourably with water (forming the bicarbonate salt) than methanol, although the preference for H₂O over alcohols is not strong. This result suggests that any water present in the gas stream would be in direct competition with alcohols, and that the formation of the HCO₃⁻ salt could be mitigated by competition in solution. Using hydrophobic reagents, or ensuring that there is always significantly more alcohol than water could potentially inhibit formation of significant amounts of the CO₂BOL bicarbonate salt. The shortest/most acidic species, water, binds stronger than longer and less acidic species such as methanol and propanol. There was little preference for methanol over a longer primary alcohol (1-propanol), but both of those primary alcohols were preferred over the secondary alcohol *iso*-propanol and very strongly preferred over the tertiary alcohol *t*-butanol. In a competition between methanol and *t*-butanol, there was no detectable conversion of *t*-butanol to *t*-butylcarbonate anion. However, in the absence of methanol, a small amount of *t*-butylcarbonate anion was detectable at 158.0 ppm in the ¹³C NMR spectrum. These experiments show that for optimum binding of CO₂, CO₂BOLs should be made using primary alcohols or aniline, with secondary and especially tertiary alcohols being poorer choices.

Aromatic amines such as aniline can serve the same role as an alcohol in this type of reaction, forming a carbamate salt [DBUH⁺][PhNCO₂⁻] rather than an alkylcarbonate salt. A competitive binding experiment showed that aniline has roughly the same affinity for CO₂ and DBU as methanol. Alkylamines were not tested because, unlike anilines, they can serve as bases and thereby could complicate the competition experiments.

Table 2 Thermodynamics of the capture of CO₂ by select CO₂BOLs in MeCN, estimated by NMR spectroscopic determination of equilibrium constants^a

| Base/alcohol pair | $\Delta H/\text{kJ mol}^{-1a}$ | $\Delta S/\text{J mol}^{-1}\text{K}^b$ | $\Delta G/\text{kJ mol}^{-1c}$ | CO ₂ absorption in MeCN at 25 °C (%) |
|--------------------------------------|--------------------------------|--|--------------------------------|---|
| DBU/HexOH | -140 | -440 | -9.4 | 87 |
| DBU/PentOH | -120 | -390 | -7.5 | 82 |
| DBU/BuOH | -140 | -450 | -9.7 | 88 |
| DBU/ PrOH | -130 | -420 | -7.8 | 83 |
| DBU/ <i>i</i> -PrOH | -140 | -450 | -5.7 | 76 |
| DBU/linear alcohol ^d | -136 | -425 | -8.6 | — |
| TMG/HexOH | -160 | -530 | 1.6 | 42 |
| TMG/PentOH | -210 | -710 | 0.7 | 47 |
| TMG/BuOH | -180 | -590 | 2.4 | 38 |
| TMG/PrOH | -170 | -590 | 2.3 | 39 |
| TMG/ <i>i</i> -PrOH | -160 | -550 | 5.5 | 25 |
| TMG/linear alcohol ^d | -180 | -610 | 1.7 | — |
| Barton's/HexOH | -83 | -250 | -11 | 90 |
| Barton's/PentOH | -52 | -150 | -8.7 | 85 |
| Barton's/BuOH | -60 | -180 | -8.0 | 83 |
| Barton's/PrOH | -53 | -160 | -9.0 | 86 |
| Barton's/ <i>i</i> -PrOH | -76 | -240 | -7.7 | 82 |
| Barton's/linear alcohol ^d | -72 | -210 | -9.2 | — |

^a Data rounded to two significant figures. ^b Calculated at 25 °C from NMR integrations using $\Delta G = -RT \ln K_{\text{eq}}$, $K_{\text{eq}} = [\text{BaseH}^+][\text{ROCO}_2^-]/P_{\text{CO}_2}[\text{Base}][\text{ROH}]$. ^c Calculated at 25 °C using $\Delta G = \Delta H - T\Delta S$. ^d Average of the unrounded values for PrOH, BuOH, PentOH, HexOH.

Thermodynamics

The thermodynamics of binding are critical for designing a system that can efficiently capture CO₂ without requiring too much energy input for the subsequent CO₂ release. Approximate thermodynamic data for select CO₂BOLs were obtained by ¹H NMR spectroscopic measurements of the CO₂ binding equilibrium (eqn (1), Table 2). The experiments were performed in *d*-MeCN to prevent the viscosity of the CO₂BOLs from broadening the ¹H NMR spectrum. The CO₂ absorption has been reported to be slightly lower in solvents²¹ than in neat systems.⁵ The concentrations of all relevant species were determined spectroscopically after flushing of CO₂ through dilute solutions of base and alcohol in deuterated MeCN. The ¹H NMR integrations of the alpha-hydrogen on the bound (RCH₂OCO₂⁻) and free alcohol (RCH₂OH) were measured over a temperature range of 24–60 °C. The reaction enthalpy was determined from the slope of the Van't Hoff plot of the equilibrium data. Such plots are known to exhibit curvature if the temperature range is too large; significant curvature was observed with Barton's base, so a shorter temperature range of 25–50 °C was used for the tests with that base.

While there is significant scatter in the data, there are very clear trends. The ΔH and ΔG values are almost independent of the choice of alcohol, which is not surprising because the linear alcohols have almost identical pK_a values in MeCN. The less favourable ΔG values for *iso*-propanol could be due to the steric bulkiness of the secondary alcohol destabilizing the alkylcarbonate anion. Tertiary alcohols such as *t*-butanol were unable to form [BaseH⁺][ROCO₂⁻] salts in significant quantities.

The reaction energetics depend strongly on the choice of base. Looking at the average values for each base combined with linear alcohols (Table 2), the enthalpy varies in the following order of decreasing exothermicity: TMG > DBU > Barton's base. The weakest base of the three, TMG, (pK_{aH} of the conjugate acid,

meaning the pK_a of the protonated base, in MeCN is 23.3)^{22,23} had the least favourable ΔG of reaction and therefore the weakest ability to capture CO₂. Surprisingly, however, this was not due to reaction enthalpy; CO₂ capture by TMG and alcohol

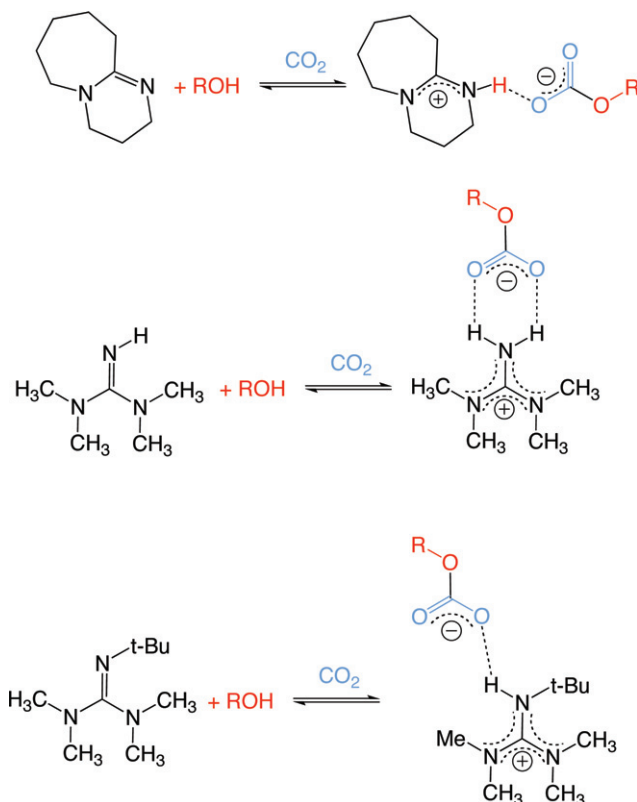


Fig. 5 Proposed hydrogen bonding of cation with anion for salts made from DBU, TMG and Barton's base with ROH and CO₂.

had the most favourable reaction enthalpy, presumably because the salt $[\text{TMGH}^+][\text{ROCO}_2^-]$ is capable of more hydrogen bonding interactions than the corresponding DBU and Barton's salts (see discussion below and Fig. 5). It is the very negative ΔS that is responsible for the positive ΔG and therefore the weak capture of CO_2 by TMG/alcohol mixtures. Extensive hydrogen bonding would be expected to lower the entropy. DBU, the intermediate base ($\text{p}K_{\text{aH}}$ in MeCN is 24.3)^{16,18} and Barton's base, the strongest of the three bases (estimated $\text{p}K_{\text{aH}}$ in MeCN is 25.3)²⁴ had almost identical abilities to bind CO_2 but DBU had a much more favourable reaction enthalpy. Barton's base, on the other hand, has a better reaction entropy ($-390 \text{ J mol}^{-1} \text{ K}^{-1}$ for DBU vs. $-185 \text{ J mol}^{-1} \text{ K}^{-1}$ for Barton's). The enthalpy of Barton's base is also comparable to that for a 30 wt% of MEA solution in water at 40°C ($-80 \text{ kJ mol}^{-1} \text{ CO}_2$).²⁵ The $\text{p}K_{\text{aH}}$ of the base is not a sufficient predictor of the ability of a base to react with CO_2 and an alcohol.

Hydrogen bonding is believed to be important in the stabilization of the salts. The TMG data suggest that too much hydrogen bonding can lower the ΔG of CO_2 binding by negatively impacting the ΔS . Therefore the design of a CO_2 BOL must take into consideration the number of hydrogen bonding interactions in the salt as well as the strength of those interactions. The alkylcarbonate salts of DBU and Barton's base are likely to have fewer hydrogen-bonding interactions than the salt of TMG because $[\text{TMGH}^+]$ has two hydrogen-bond donor sites. Additionally, hydrogen-bonding in the TMG salt is likely to be stronger due to the formation of an entropically-favoured 6-member ring (Fig. 5). Similar 6 member rings of carboxylates and amidines have been reported previously by Kraft *et al.*²⁶ In general, however, the strength of hydrogen-bonding in the alkylcarbonate salts of all three bases is likely weaker than would be expected in salts that lack delocalization in the cation. DBU is reported to be a weak H-bond donor because of its highly delocalized cation.²⁷ Galezowski *et al.* claim that highly delocalized charges make amidines really weak H-bond donors; as guanidines are more delocalized than amidines, they should therefore be poorer H-bond donors. Hydrogen bonding may also be responsible for the preference for DBU and CO_2 to bind water rather than alcohol. Crystallographic structures of $[\text{DBUH}^+][\text{HOCO}_2^-]$ ¹⁰ and $[\text{DBUH}^+][\text{CH}_3\text{OCO}_2^-]$ ⁵ show that the proton on the anion gives the former salt more extensive hydrogen bonding than the latter.

The reaction entropies can also be explained by considering the hydrogen-bonding of the salts. The ΔS term is least negative for Barton's base, perhaps because the bulky *t*-butyl group forces the alkylcarbonate anion farther away from the BartonH⁺ cation. The ΔS value for DBU is more negative due to the decreased steric bulk around the protonated nitrogen. The ΔS value is most negative for TMG, because of the proposed 6-member H-bonding ring being the most ordered and entropically unfavorable. From this data, we can conclude that the ability of a base/alcohol combination to trap CO_2 can not be predicted or explained by the $\text{p}K_{\text{aH}}$ of the protonated base; it is necessary to include hydrogen-bonding arguments and the entropy of reaction.

The thermodynamic results correspond well with the relative equilibrium constants of DBU paired with methanol and other alcohols as discussed previously. The relative thermodynamics

show that alcohol choice ($>\text{C}_2$) plays a minimal role in the binding energies of CO_2 compared to the choice of base. As discussed in previous work,^{3,4} the alcohol chain length does affect physical properties such as melting point and viscosity of the CO_2 BOL. While the alcohol may play a minimal role in thermodynamic properties, alcohols can be chosen to alter the physical properties of the CO_2 BOLs, making them molecularly tunable.

Tertiary amines such as triethylamine and Hünig's base do not form CO_2 BOLs. Whether Hünig's base should be basic enough ($\text{p}K_{\text{aH}}$ s of trialkylamines in MeCN are 18.1–18.8)^{28,29} to accept a proton from the produced alkylcarbonic acid is unclear because the $\text{p}K_{\text{a}}$ s of alkylcarbonic acids are unknown. It is known that applying high pressures of CO_2 over a solution of NEt_3 in methanol causes the production of $[\text{NEt}_3\text{H}^+][\text{CH}_3\text{OCO}_2^-]$, but reducing the pressure to ambient causes the salt to fall apart into the amine, alcohol, and CO_2 .³⁰

The amidine and guanidine bases and alkylcarbonate salts that comprise CO_2 BOLs have charges that are highly delocalized, which weakens the attractions between the ions. We suggest that the delocalization inherent to protonated amidines and guanidines plays a vital role in determining not only the chemical properties (reversibility of CO_2 binding and release) of CO_2 BOLs, but also the physical properties (*e.g.* melting point or viscosity). A more in-depth investigation of CO_2 BOLs is underway in our laboratory to confirm the effect of the highly delocalized charges of the amidine and guanidine bases on the binding and release of CO_2 .

Conclusions

CO_2 BOLs have been shown to repeatedly bind and release CO_2 with a high gravimetric and volumetric CO_2 capacity (19% by weight, 147 g L^{-1} liquid) for neat mixtures because they require no solvent to dissolve the CO_2 carrier. The binding and release of CO_2 from CO_2 BOLs appears to be mass-transfer limited, with the dissolution of CO_2 in and out of the liquid phase being the rate-limiting step. Binding of CO_2 under dilute and concentrated streams was selective, making CO_2 BOLs applicable in post or pre-combustion CO_2 capture. CO_2 BOLs chemically bind CO_2 weakly as alkylcarbonate salts, the binding energies for CO_2 is no more than 10 kJ mol^{-1} , which is lower than CO_2 release from bicarbonate salts observed in aqueous systems. CO_2 BOLs organic composition and lower specific heat mean that far less energy is required for stripping CO_2 from these agents than from conventional MEA aqueous systems, which are constrained by the high specific heat of water as well as the large volumes of water needed to keep the system liquid. CO_2 BOLs can be competitively formed in the presence of water, by dilution in a large excess of alcohol. If water is in significant quantities, undesirable bicarbonate salts will be formed, however they can be broken down more efficiently than in MEA systems due to the anticipated lower specific heat of CO_2 BOLs than water. The alcohol was shown to have a limited role in the energetics of binding CO_2 , while the base showed some influence on ΔH and ΔG . The low energetics of CO_2 binding and release is due to the weak ion-pairs of the CO_2 BOLs and is not a simple function of the $\text{p}K_{\text{a}}$ of the base. Calorimetric measurements of the heat capacity and ΔH of reaction are being pursued. With multiple

alcohols and bases to choose from, CO₂BOLs can be tuned at the molecular level to further enhance their physical and chemical properties. Ultimately, CO₂BOLs have tremendous potential to be energy efficient industrial liquid CO₂ capture agents.

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