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Electrochemical Capture and Release of Carbon Dioxide Using a Disulfide–Thiocarbonate Redox Cycle

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Supporting Information

ABSTRACT: We describe a new electrochemical cycle that enables capture and release of carbon dioxide. The capture agent is benzylthiolate (RS^-), generated electrochemically by reduction of benzyldisulfide (RSSR). Reaction of RS^- with CO_2 produces a terminal, sulfur-bound monothiocarbonate, $RSCO_2^-$, which acts as the CO_2 carrier species, much the same as a carbamate serves as the CO_2 carrier for amine-based capture strategies. Oxidation of the thiocarbonate releases CO_2 and regenerates RSSR. The newly reported *S*-benzylthiocarbonate (IUPAC name benzylsulfanylformate) is characterized by ^1H and ^{13}C NMR, FTIR, and electrochemical analysis. The capture–release cycle is studied in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP TFSI) and dimethylformamide. Quantum chemical calculations give a binding energy of CO_2 to benzyl thiolate of −66.3 kJ mol^{-1}, consistent with the experimental observation of formation of a stable CO_2 adduct. The data described here represent the first report of electrochemical behavior of a sulfur-bound terminal thiocarbonate.

Climate impacts from high atmospheric CO_2 concentrations due to carbon-based fuel combustion continue to drive high levels of research activity in carbon capture and sequestration (CCS).[1] A number of approaches have been described for carbon capture, both at point sources such as power plants (postcombustion CO_2 capture) and directly from the atmosphere (direct air capture). Many of these approaches rely on chemical interaction between an electron-rich nucleophile and CO_2 to form some type of adduct. One of the best known approaches in this vein involves reaction of amines with CO_2 to give carbamates.[2] This chemistry can be carried out in basic aqueous solutions containing amines, with amines immobilized onto various types of solid supports, or with other solid or liquid media containing amine groups, such as ionic liquids.[2] In most such cases the release of CO_2 to recycle the capture agent requires heat. Few other chemistries have been described that enable reversible CO_2 capture. Thus, there is interest in exploring new methods for CO_2 capture. In addition, there is a broader need to more fully explore the chemistry of CO_2, and especially to explore the chemistry of compounds that form adducts with CO_2.

Several research efforts have explored approaches to capture CO_2 using electrochemically generated nucleophiles. Mizen and Wrighton demonstrated that electrochemical reduction of quinones under aprotic conditions produces radical anions capable of CO_2 capture at the quinone oxygen, producing aromatic carbonates.[3] They also showed that the resulting carbonates could be electrochemically oxidized, regenerating the quinone species and releasing CO_2. This stimulated a number of groups to explore CO_2 capture using quinones.[4−6] In a related approach, release of amine ligands from Cu(II) amine complexes by electrochemical reduction to Cu metal can be used to drive CO_2 capture via carbamate formation, connecting the traditional amine capture agent approach with the superior energetics inherent in electrochemical cycling.[7] In a recent report, we examined the reaction between 4,4′-bipyridine radical anion (which can be produced either electrochemically or photochemically) and carbon dioxide, demonstrating formation of a unique N-bound CO_2 adduct species.[8] One electron oxidation of the adduct releases CO_2 and regenerates 4,4′-bipyridine. All of these systems demonstrate chemically reversible electrochemical capture and release of CO_2. Their common theme is that electrochemical reduction of a precursor is employed to either directly generate or cause the release of a potent nucleophile that is capable of attacking the electrophilic carbon atom in CO_2, thereby forming an adduct. A subsequent oxidation process leads to CO_2 release and regeneration of the precursor to the capture agent. For the quinone and bipyridine cases, release is accomplished by oxidation of the adduct itself.

We describe here a new chemistry for electrochemical CO_2 capture and release that employs reduction of organic disulfide precursors to generate thiolate species that are potent nucleophiles toward CO_2. We show that benzylthiolate can bind CO_2 to form a sulfur-bound thiocarbonate and that subsequent oxidation of the thiocarbonate leads to release of CO_2 and regeneration of the disulfide. We are aware of only a few previous reports of S-bound terminal thiocarbonates,[9−11] and no previous reports of their electrochemical properties. In most of this study, the electrochemical capture and release of CO_2 is pursued in ionic liquid (IL) media. A substantial literature exists on capture of CO_2 using ILs containing amines and other nucleophilic functional groups.[12] Their low volatility

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and suitability as electrochemical solvents makes ILs especially useful as supporting electrolytes in the present study. In some experiments we also employ dimethylformamide (DMF) as solvent, demonstrating the broader applicability of this chemistry to more traditional solvents. The reasonable solubilities of benzyldisulfide (BDS) in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP TFSI) and DMF (106 mM and 2 M, respectively) allow for facile electrochemical and synthetic experimentation.

Figure 1 shows a cyclic voltammogram (CV) of the reduction of BDS in BMP TFSI at a concentration of 20

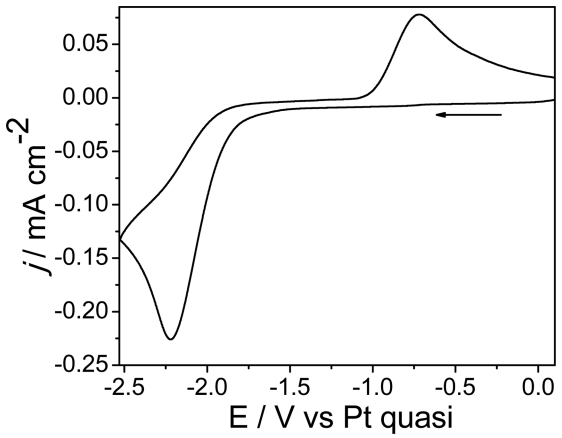

Figure 1. Cyclic voltammetry of 20 mM benzyldisulfide in BMP TFSI ionic liquid. Conditions: working, glassy carbon electrode; reference and counter, Pt electrode; scan rate, 10 mV/s.

mM. Reduction gives a well-formed voltammetric wave with a peak potential near −2.2 V. This overall two-electron reduction process is as expected for reduction of organic disulfides, producing 2 equiv of the corresponding thiolate.[13] Oxidation of the benzylthiolate that is produced is seen on the return scan as an oxidation wave with a peak potential of −0.7 V. The significant difference between the peak currents for disulfide reduction and thiolate oxidation is likely due to significant differences in diffusion coefficients for these two species. A similar phenomenon has been previously reported for the dioxygen/superoxide and ferrocene/ferrocenium redox couples in ILs, and attributed to significantly lower diffusion coefficients for charged species compared to neutrals.[14,15] The large peak separation between disulfide reduction and thiolate oxidation results from the fact that this redox mechanism is not microscopically reversible. We explored the mechanism of this process in some detail previously for a related disulfide/thiolate redox couple.[16] Briefly, reduction initially produces the $RSSR^-$ radical anion. This species dissociates to produce 1 equiv each of RS^- and $RS^\bullet$ (i.e., thiolate and thiyl radical).[17] The rapid electrochemical reduction of $RS^\bullet$ produces a second equivalent of RS^-. On the subsequent positive-going scan, oxidation of the thiolate initially produces $RS^\bullet$, two of which rapidly couple to regenerate the parent disulfide. Subsequent work has confirmed the mechanistic aspects of this redox process, as well as providing more details about the nature of the dissociative electron transfer of the disulfides.[18,19] For the present purposes, a key feature of the disulfide reduction is that it produces thiolates, which are well known as potent nucleophiles and have been previously reported to react with CO_2 to give S-bound thiocarbonates.[9−11]

Figure 2 shows the results of several experiments in 20 mM BDS in BMP TFSI in which the concentration of dissolved

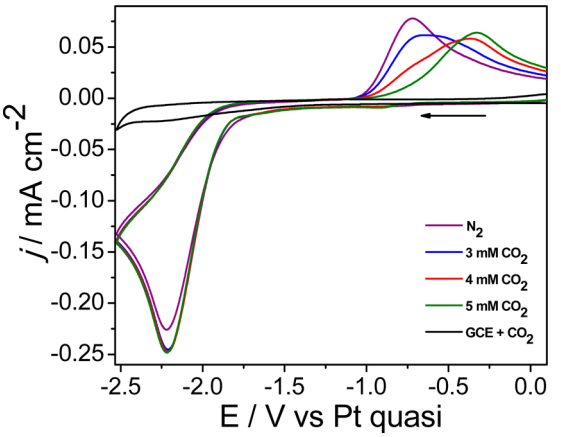

Figure 2. Cyclic voltammetry of 20 mM BDS in BMP TFSI IL with different concentrations of CO_2: N_2 (purple), 3 mM CO_2 (blue), 4 mM CO_2 (red), 5 mM CO_2 (green), 100 mM CO_2 in the absence of BDS in IL (black), Conditions: working, GCE; reference and counter, Pt electrode; scan rate, 10 mV/s.

CO_2 was serially increased by increasing the CO_2 partial pressure in a purging gas stream comprising a mixture of N_2 and CO_2. As $[CO_2]$ is increased, the benzylthiolate oxidation peak at −0.7 V is decreased. At the same time, a new oxidation peak appears at −0.3 V. As will be shown further below, this new oxidation peak corresponds to oxidation of *S*-benzylthiocarbonate, $RSCO_2^-$. This is the first report of electrochemical behavior for a terminal S-bound thiocarbonate species. Figure 2 also shows a background CV at a glassy carbon electrode (GCE) in pure BMP TFSI at 100 mM CO_2 but containing no BDS, demonstrating that CO_2 is electrochemically inactive at glassy carbon over the potential range shown in the CV. For comparison, Figure S7 shows the chemically irreversible reduction of CO_2 at Au over this same range of potentials, demonstrating a large reduction peak for CO_2 at −2.3 V. The lack of CO_2 electroactivity at a GCE over this potential range is likely due to the absence of strong adsorption at this surface. We take advantage of this lack of reactivity to explore the interactions between thiolates and CO_2 without interference by direct CO_2 reduction. The observation that 5 mM CO_2 is sufficient to completely eliminate the oxidation response from 40 mM benzylthiolate (produced by reduction of 20 mM BDS) is attributed to the much faster diffusion of CO_2 than benzylthiolate in the IL, similar to the discussion above regarding dissimilar diffusion coefficients.[14,15] In other words, the rapid diffusive transport of CO_2 to the region near the electrode allows a 5 mM CO_2 solution to provide sufficient CO_2 to completely consume the higher concentration of electrochemically generated thiolate through formation of the thiocarbonate.

The reversibility of the uptake of CO_2 by thiolate and release by thiocarbonate oxidation was also examined. Figures S8 and S9 show that the new thiocarbonate oxidation peak at −0.3 V can be caused to appear or disappear simply by purging a BDS solution in BMP TFSI with a CO_2-rich or N_2-rich gas stream, respectively, prior to a cyclic voltammetric scan over the disulfide reduction wave. This shows that the CO_2 capture-and-release cycle is chemically reversible under the conditions of these experiments. Figure S10 shows the scan rate dependence

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of the capture−release cycle at a concentration of CO_2 sufficiently high to consume all of the thiolate produced during the reduction. The discussion of the figure in the Supporting Information provides the mechanistic details of the adduct formation, revealing that it is not a simple EC type of mechanism due to the complexity of the RSSR reduction pathway.[20]

In order to show that the oxidation peak at −0.3 V is caused by a thiocarbonate species, the voltammograms of authentic samples of benzylthiolate and *S*-benzylthiocarbonate were directly compared. Figure 3 shows the results of cyclic

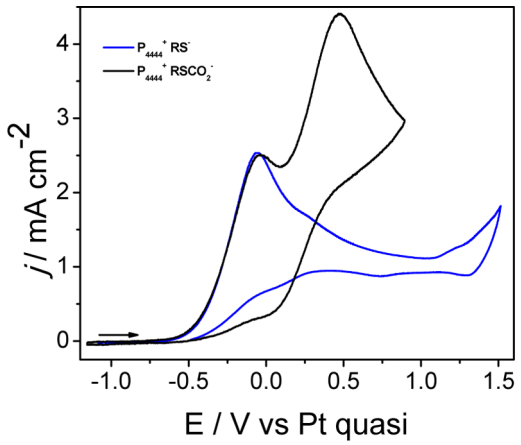

Figure 3. Cyclic voltammetry of 30 mM P_{4444}^+ RS^- (blue) and 30 mM P_{4444}^+ $RSCO_2^-$ (black) in 0.1 M TBAP in DMF. Conditions: working, GCE; reference and counter, Pt electrode; scan rate, 50 mV/s.

voltammetric experiments in which authentic samples of the P_{4444}^+ salts of benzylthiolate and *S*-benzylthiocarbonate were sequentially added to DMF supporting electrolyte in equimolar amounts. Preparation and characterization of these samples are described in the Supporting Information. As can be seen, the two species exhibit different oxidation potentials. The benzylthiolate oxidation peak is observed at −0.1 V. The *S*-benzylthiocarbonate oxidation peak is observed at +0.4 V, shifted in the positive direction by 0.5 V compared to the thiolate oxidation peak. Figure S11 shows the CV for an equimolar solution of the P_{4444}^+ salts of benzylthiolate and *S*-benzylthiocarbonate in P_{4444} TFSI. Again, one can see that the two species are oxidized at different potentials, though the broadness of the peaks in this much higher viscosity IL makes the individual responses less resolvable. The results in Figures 3 and S11 are consistent with the interpretation that the new oxidation observed in Figure 2 when CO_2 is dissolved into the IL solution is due to the appearance of a thiocarbonate species that is more difficult to oxidize than the thiolate.

To further demonstrate uptake and release of CO_2 for this system, we performed bulk electrolysis experiments in which purge gases were swept through the cell to monitor CO_2 uptake and release using a nondispersive CO_2 gas sensor downstream from the cell. In Figure S12 we show the results of a reductive bulk electrolysis of BDS in the presence of a flowing stream of 350 ppm of CO_2 in N_2. The figure shows that CO_2 in the purge gas stream is completely consumed when reductive current is passed in the working electrode chamber, which produces benzylthiolate that subsequently reacts with CO_2. In Figure S13 we show the results of a quantitative oxidative bulk electrolysis of a sample of *S*-benzylthiocarbonate. In this experiment, we monitor the evolution of CO_2 during oxidation by sweeping it from the cell in a stream of pure N_2 and detecting it downstream. The right plot in the figure shows that moles of e^- (from the oxidative charge) and moles of CO_2 released (from integration of the sensor signal) are equal within experimental error. Except for a short lag time due to the transit time to the detector, the CO_2 release is seen to be coincident with the accumulation of oxidative charge. This plot shows clearly that CO_2 release in this experiment is due to oxidation of the thiocarbonate, and that 1 equiv of CO_2 is released for each equivalent of oxidative charge. Taken together, the results confirm that electrochemical generation of benzylthiolate in the presence of CO_2 produces *S*-benzylthiocarbonate. Oxidation of this thiocarbonate releases CO_2 and regenerates the disulfide, which can be observed on the following negative-going scan via its reduction, as evidenced by the continuous scans in Figures S8 and S9. These observations show that oxidation of a terminal S-bound thiocarbonate is similar to the well-known Kolbe oxidation of organic carboxylates, where oxidation results in decarboxylation.[21] Thus, these results are consistent with the electrochemical capture and release of CO_2 as mediated by the disulfide/thiocarbonate redox couple.

Quantum chemical calculations at the B3LYP/aug-cc-pVQZ level were also used to understand the nature of the interaction between the thiolate and CO_2 and the stability of the thiocarbonate. Figure 4 shows the results of such a calculation

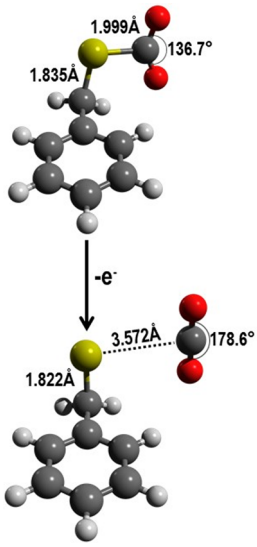

Figure 4. Quantum mechanical calculation of *S*-benzylthiocarbonate done at B3LYP/aug-cc-pVQZ level. Atoms: S (yellow), O (red), H (light gray), C (dark gray).

done at the B3LYP/aug-cc-pVQZ level on *S*-benzylthiocarbonate. Calculations at this level of theory were found to yield good agreement with experimental enthalpies of sulfur-containing compounds.[22] The figure shows the minimized geometry of the thiocarbonate (upper structure). The C−S bond length is 1.999 Å, and the calculated B3LYP/aug-cc-pVDZ enthalpy for the binding of CO_2 to the thiolate is −66.3 kJ/mol. This enthalpy for binding shows formation of a stable S-bound terminal thiocarbonate for this case. These respective quantities are within the range expected for C−S single bonds and for other stable CO_2 adducts.[23−26] The OCO bond angle of 136.7° indicates considerable rehybridization around carbon resulting from strong interaction with the sulfur center. Thus,

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the quantum chemical calculations support the formation of a stable S-bound thiocarbonate from the reaction between benzylthiolate and CO_2.

Figure 4 also shows the minimized geometry of the thiocarbonate after removal of one electron. The S−CO_2 bond length is dramatically elongated, at 3.572 Å, and the O−C−O bond angle is increased to 178.6°. These values confirm that there is essentially no bonding interaction of the CO_2 moiety with the S atom after oxidation, consistent with the release of CO_2 after oxidation. Figure S14 shows the HOMO and HOMO−1 electron density maps for the thiocarbonate. These orbitals are quasi-degenerate,[27,28] and show significant bonding electron density between the S atom and the carboxylate C atom. Thus, one electron oxidation should lead to destabilization of the S−C bond. This is similar to C−C bond cleavage leading to decarboxylation in Kolbe oxidation products, such as $H_3CCO_2^{\bullet}$, the acetyloxyl radical.[29] In summary, these computational studies support the experimental results showing the formation of a stable terminal thiocarbonate from reaction of benzylthiolate and CO_2. They also show that thiocarbonate oxidation results in cleavage of the S-CO_2 bond, producing a benzyl thiyl radical (two of which will then couple to form disulfide) and free CO_2. This is similar to the oxidative dissociation of CO_2 previously reported for the adduct between the 4,4′-bipyridine radical anion and CO_2, where oxidation from the HOMO leads directly to N−C bond scission and release of 4,4′-bipyridine and CO_2.[8] More extensive calculations on a range of benzyl and phenyl thiocarbonate derivatives, to be reported elsewhere, reveal that the energy for binding of CO_2 to the RS^- species depends on the electron density on the sulfur atom in RS^-, implying that the enthalpy of CO_2 binding can be tuned through judicious choice of structural features on RS^-.

We have demonstrated a completely new type of chemically reversible, electrochemical process for capture and release of CO_2 based on an organic disulfide/thiocarbonate redox couple. These data also comprise the first report of the electrochemical behavior for terminal S-bound thiocarbonates. Quantum chemical calculations are consistent with the capture of CO_2 by RS^-, producing a stable thiocarbonate, and release of CO_2 after oxidation of the thiocarbonate. Additional experiments are underway to explore CO_2 separations based on this chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10806.

Experimental details and characterization data, including Figures S1−S14 (PDF)

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Notes

The authors declare no competing financial interest.

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