

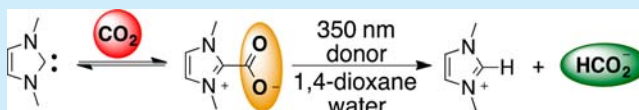
Photochemical Reduction of CO<sub>2</sub> Using 1,3-Dimethylimidazolydene

Derek M. Denning, Matthew D. Thum, and Daniel E. Falvey\*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States

## Supporting Information

**ABSTRACT:** Product analysis along with fluorescence quenching and laser flash photolysis experiments demonstrate that it is possible to effect a net photochemical reduction of CO<sub>2</sub> through photolysis of an excited state donor in the presence of 1,3-dimethylimidazolium-2-carboxylate.

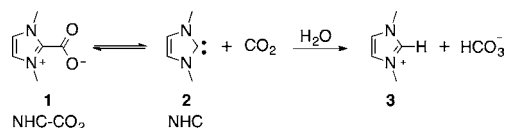


Rising atmospheric levels of carbon dioxide (CO<sub>2</sub>) and the potential climate impacts of this greenhouse gas has driven interest in developing new chemistries that can convert this gas into useful chemicals and/or fuels.<sup>1</sup> While numerous efforts have been made to develop new materials for CO<sub>2</sub> capture and storage/sequestration (CCS), current efforts of interest involve CO<sub>2</sub> capture and utilization (CCU) in which CO<sub>2</sub> could undergo a chemical conversion, making it a renewable C<sub>1</sub> chemical feedstock. Current attempts at utilizing CO<sub>2</sub> include chemical hydrogenation,<sup>2</sup> the synthesis of cyclic carbonates/carbamates,<sup>3</sup> and carboxylation of olefins,<sup>4</sup> as well as the methylation of amines<sup>5</sup> and formation of amides.<sup>6</sup> Additionally, CO<sub>2</sub> can be electrochemically reduced to yield reduction products such as formic acid and carbon monoxide.<sup>7</sup> However, one general problem is that a net reversal of the combustion processes that produce CO<sub>2</sub> requires energy inputs that are independent of combustion. One such input, solar energy, motivates the search for photochemical based methods for CO<sub>2</sub> reduction. Approaches under active investigation include the use of transition metal photocatalysts,<sup>8</sup> semiconducting layered double hydroxide catalysts,<sup>9</sup> and solar driven photoelectrochemical cells.<sup>10</sup> However, the use of organic photochemical and electrochemical catalysts for both capture and reduction is not as readily studied as its transition metal counterpart.<sup>11</sup> Efforts include high-energy radical anion aromatics,<sup>12</sup> tetraalkylammonium,<sup>13</sup> and pyridinium<sup>14</sup> ions.

The thermodynamic and kinetic stability of CO<sub>2</sub> creates challenges in designing reduction reactions ( $E_{\text{red}} = -1.90$  V vs normal hydrogen electrode, NHE).<sup>7a</sup> For example, there is a substantial kinetic barrier associated with the reorganization energy required for the one-electron reduction due to the geometry change from linear CO<sub>2</sub> to bent CO<sub>2</sub><sup>•-</sup>. One strategy is to identify catalysts that facilitate this bending, and in doing so reduce the kinetic barrier to reduction. While numerous species bind to CO<sub>2</sub> in this manner, it is equally important that such binding be weak enough to permit the release of the reduced species. Therefore, we have undertaken a program aimed at identifying organocatalysts that facilitate the photochemical reduction of CO<sub>2</sub>. While the overall goal of any CO<sub>2</sub> reduction program would be a catalytic system with high turnover efficiency, an important initial step is to identify new pathways for CO<sub>2</sub> photoreduction.

Since the discovery of the addition of *N*-heterocyclic carbenes (NHCs) to carbon dioxide to form stable zwitterionic imidazolium-2-carboxylates (NHC-CO<sub>2</sub>),<sup>15</sup> the chemistries associated with these species are quickly gaining attention. Among them, studies have shown the ability to incorporate CO<sub>2</sub> into new products such as carboxylates and carbonates by utilizing these adducts as CO<sub>2</sub> transfer reagents.<sup>16</sup> Additionally, a study by Ying et al. found that these adducts can facilitate the reduction of CO<sub>2</sub> into methanol through the use of silanes.<sup>17</sup> An earlier study from our group showed that NHCs bind to CO<sub>2</sub> in a reversible manner (Scheme 1) and that the equilibrium constant

**Scheme 1. Reversible Binding of CO<sub>2</sub> to a NHC Followed by Irreversible Protonation upon the Addition of Small Amounts of H<sub>2</sub>O to the Imidazolium Cation**



can be modulated by solvent polarity.<sup>18</sup> Polar solvents favor binding while nonpolar solvents favor release. The following study was undertaken to assess the ability of NHCs to serve as photocatalysts for CO<sub>2</sub> reduction. Specifically, it is demonstrated that (1) 1,3-dimethylimidazolium-2-carboxylate **1** can be reduced by excited state photosensitizers and (2) this photo-reduction process generates a formate ion, a product from CO<sub>2</sub> reduction. The current system presented in this study is not catalytic; however, it demonstrates a new photochemical process for CO<sub>2</sub> reduction using a mediator that can reversibly bind to CO<sub>2</sub> and thus offering the possibility of future catalytic development.

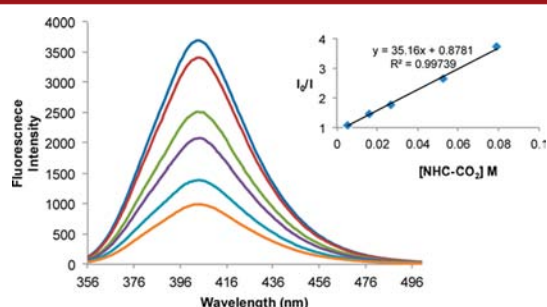
Complex **1** was prepared using previously described methods.<sup>19</sup> As noted before, this species is stable in aqueous media, solvent mixtures containing a high fraction of H<sub>2</sub>O, and in rigorously anhydrous CH<sub>3</sub>CN. However, it was found to decompose rapidly in solvents containing low concentrations of water. High concentrations of water render the medium

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sufficiently polar that decarboxylation is inhibited. Under low polarity conditions, decarboxylation occurs reversibly. However, small amounts of water are sufficient to irreversibly protonate the carbene **2** by forming imidazolium cation **3** (Scheme 1). Thus, an important consideration in this study is identifying solvent systems that (1) stabilize **1**, (2) solubilize all of the reaction components, and (3) promote the release of reduced CO<sub>2</sub>. Therefore, in the following fluorescence and laser studies, where lower concentrations of sensitizer are needed, water ratios of ≥40% were used to ensure stability of **1** over the time it took to conduct the experiments. However, in the preparative photolysis experiments, where higher concentrations of sensitizer were required, water ratios had to be reduced (≤10%) to ensure solubility.

In order to determine if **1** would accept electrons from an excited state reductant, a series of fluorescence quenching experiments were undertaken. As illustrated in Figure 1,



**Figure 1.** Fluorescence quenching analysis of TMB with **1** in 40% H<sub>2</sub>O in 1,4-dioxane with the corresponding Stern–Volmer plot.

increasing concentrations of **1** diminishes the fluorescence intensity of *N,N,N',N'*-tetramethylbenzidine (TMB), an excited state electron donor, showing that there is an interaction of **1** with the excited singlet state of TMB. Stern–Volmer analysis of these data along with the previously determined singlet state lifetime of TMB provides a quenching rate constant ( $k_q$ ) for this reaction of  $3.51 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

$$\Delta G_{\text{ET}} \approx 23.06(E_{\text{ox}} - E_{\text{red}}) - E_{00} - S \quad (1)$$

Table 1 summarizes results from quenching studies using various sensitizers in solvent mixtures of sufficiently high water ratios ensuring that **1** is the active ground state oxidant and not the aforementioned decomposed imidazolium cation **3**. The thermodynamic driving force ( $\Delta G_{\text{ET}}$ , kcal/mol) for the electron

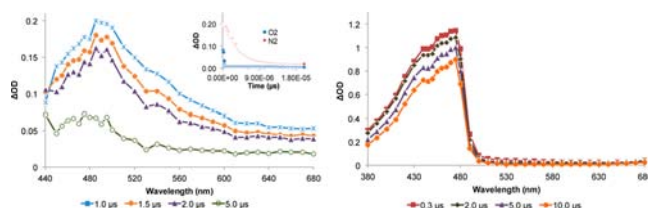
**Table 1.** Fluorescence Quenching Results of Sensitizers and **1** in 1,4-Dioxane/H<sub>2</sub>O Mixtures

sensitizer	$E_{\text{ox}}^*$ (V) <sup>a</sup>	% H <sub>2</sub> O	$k_q$ (M <sup>-1</sup> s <sup>-1</sup> )	$\Delta G_{\text{ET}}$ (kcal/mol)
TMB	-3.17	40.0	$3.51 \times 10^9$	-31.6
TMB	-3.17	50.0	$4.46 \times 10^9$	-31.6
TMB	-3.17	60.0	$3.55 \times 10^9$	-31.6
TMB	-3.17	70.0	$2.74 \times 10^9$	-31.6
<i>N</i> -methylcarbazole	-2.56	50.0	$1.03 \times 10^9$	-17.6
2-aminoanthracene	-2.30	50.0	$5.70 \times 10^8$	-11.4
anthracene	-2.21	50.0	$3.32 \times 10^8$	-9.56
phenanthrene	-2.08	50.0	$1.30 \times 10^7$	-6.40
9,10-dibromoanthracene	-1.78	50.0	<10 <sup>7</sup>	+0.52

<sup>a</sup> $E_{\text{ox}}^* = E_{\text{ox}} - E_{00}$ .

transfer step was derived from eq 1.<sup>20</sup>  $E_{\text{ox}}$  (V) represents the ground state oxidation potential of the donor,  $E_{\text{red}}$  (V) is the ground state reduction potential of the acceptor,  $E_{00}$  (kcal/mol) denotes the excited singlet state energy of the donor, and  $S$  is the solvation parameter which is assumed to be negligible in the polar solvents considered here. Though we were unable to measure the  $E_{\text{red}}$  for **1** electrochemically, similar imidazolium cations have been reported to be reduced around -1.8 V vs the saturated calomel electrode (SCE)<sup>21</sup> and that value was used to calculate the driving force for this electron transfer step.

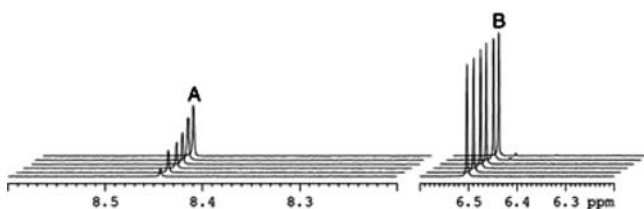
Laser flash photolysis experiments were carried out to determine if the electron transfer lead to cage-escaped radical intermediates capable of generating reduced CO<sub>2</sub>. Figure 2



**Figure 2.** (Left) Transient absorption spectrum of 1.60 mM TMB with no quencher. Oxygen quenching monitored at 480 nm (insert). (Right) Transient absorption spectrum of 1.60 mM TMB with 0.142 M of **1** as a quencher. Both samples were done in 40% H<sub>2</sub>O in 1,4-dioxane.

shows transient absorption spectra resulting from pulsed laser photolysis (355 nm, 7 ns, 10–30 mJ/pulse) solutions of TMB alone (left) and in the presence of **1** (right). Excitation of TMB alone provides a transient spectrum of its excited triplet state ( $\lambda_{\text{max}} = 485 \text{ nm}$ ,  $\tau = 3.68 \mu\text{s}$ ). When **1** is included, the triplet is replaced by a longer-lived species with  $\lambda_{\text{max}} = 470 \text{ nm}$  which is assigned to the TMB cation radical. While the two intermediates have overlapping absorption bands, they are readily distinguished by their kinetic behavior: the triplet is short-lived and rapidly quenched by O<sub>2</sub>; the cation radical is long-lived ( $\tau > 17.7 \mu\text{s}$ ) and its decay is insensitive to O<sub>2</sub>. Both the triplet and radical cation spectrum obtained for TMB are consistent with previous reports.<sup>22</sup> The cation radical for *N*-methylcarbazole was also detected in the presence of **1** (see Supporting Information (SI)).

The photolysis products were determined using <sup>1</sup>H NMR spectroscopy. Specifically, solutions containing **1** and a donor were degassed with N<sub>2</sub> and irradiated under a UV light source with a maximum output at 350 nm for 60 min. The solvent was evaporated, and the product mixture was analyzed using <sup>1</sup>H NMR. Except where noted below, the CO<sub>2</sub> reduction product, formate ion **4**, was detected by its resonance at 8.45 ppm along with imidazolium ion **3** (derived from protonation of the NHC **2**). Due to the thermal instability of **1**, accurate quantification of the byproduct **3** proved difficult. However, its formation as a major product is verified by the resonance at 7.35 ppm, which is observed to increase when authentic **3** is added to the photolysis mixture. Figure 3 illustrates the time course of formate production as measured against fumaric acid, which was added as an internal standard. The colorimetric assay reported by Sleat and Mah<sup>23</sup> was also carried out on selected photoproduct mixtures, and this further verified the photochemical production of formate. Of course the alternative product, oxalate **5**, would not produce a signal by <sup>1</sup>H NMR. Therefore, product mixtures were also analyzed for oxalate using HPLC. Photolysis mixtures of TMB and **1** in 10% H<sub>2</sub>O in MeCN and 1,4-dioxane gave low yields of oxalate (<6%), while increasing the alkalinity of the H<sub>2</sub>O



**Figure 3.** Photolysis time course of formate production (4.39 mM **1**, 10.2 mM TMB in 5.0% H<sub>2</sub>O in 1,4-dioxane at 350 nm). <sup>1</sup>H NMR showing the increase in formate (A) over photolysis time (0, 15, 30, 45, 60, 90 min, front to back) and fumaric acid as the internal standard (B).

component only provided a slight increase in the amount of oxalate that was observed (see SI).

Yields of formate, measured at nearly complete conversions of **1**, are listed in Table 2. The maximum yield of formate obtained

**Table 2. Photolysis Results (60 min) of **1** and Sensitizer (Sens) in Mixtures of an Organic Solvent and H<sub>2</sub>O as Analyzed by <sup>1</sup>H NMR**

sens	[sens] mM	[ <b>1</b> ] mM	organic	% H <sub>2</sub> O	% yield formate <sup>d</sup>
TMB	10.2	5.59	1,4-dioxane	3.0	38.1 ± 4.29
TMB	10.2	5.59	1,4-dioxane	5.0	42.4 ± 4.23
TMB	10.2	5.59	1,4-dioxane	10.0	43.4 ± 2.10
TMB	0.00	5.59	1,4-dioxane	5.0	18.8 ± 2.84
TMB	20.2	5.59	1,4-dioxane	5.0	42.5 ± 3.33
TMB <sup>a</sup>	7.60	0.00	1,4-dioxane	5.4	< 10.0
TMB <sup>b</sup>	9.45	0.00	1,4-dioxane	5.0	< 10.0
TMB <sup>c</sup>	9.45	5.59	1,4-dioxane	5.0	47.3 ± 5.89
TMB	10.1	4.39	MeCN	1.0	13.4 ± 2.56
TMB	10.1	4.39	MeCN	5.0	15.9 ± 3.10
ANT	10.1	5.59	1,4-dioxane	5.0	41.4 ± 5.02
9,10-DBA	9.83	5.59	1,4-dioxane	5.0	29.8 ± 0.93

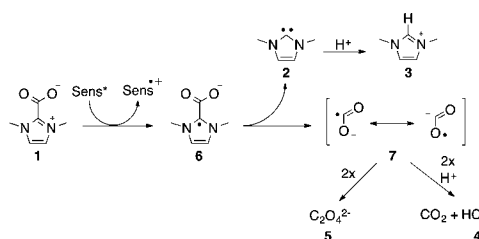
<sup>a</sup>24.2 mM 1,3-dimethylimidazolium tetrafluoroborate solution saturated with CO<sub>2</sub> (90 min photolysis). <sup>b</sup>Solution saturated with CO<sub>2</sub>. <sup>c</sup>10% v/v 1,4-cyclohexadiene (average of 2 samples). <sup>d</sup>Yields presented represent high conversion of **1**.

under the conditions described herein was *ca.* 47%. Increasing the TMB concentration from 10 to 20 mM, changing the aqueous component of the cosolvent from 3% to 10%, or adding a strong H atom donor (1,4-cyclohexadiene, 10%) had insignificant effects on the production of formate. However, moderately lower yields (<30%) were observed when the organic component of the solvent mixture is changed to CH<sub>3</sub>CN, or when 9,10-dibromoanthracene (9,10-DBA) is used as the donor. The latter is a much weaker excited state donor, and the quenching studies show that it is less reactive. In the absence of sensitizer, low yields of the product are observed. This is attributed to overlap of the low wavelength tail of the lamp output with the high wavelength tail of the absorption of **1**. The mechanism of this direct process was not examined in detail. Additionally, there is *ca.* 15% production of formate in the nonirradiated background sample for each of the entries listed in Table 2. We attribute this background production to our workup procedure in which thermal electron transfer could help explain the results observed, though we did not examine this process in detail either (see SI for background formate production). The importance of complex **1** in the photochemical generation of formate was verified by three control experiments. First, a solution of TMB that was saturated with CO<sub>2</sub> in the absence of **1**

and, second, a solution of TMB and 1,3-dimethylimidazolium tetrafluoroborate that was saturated with CO<sub>2</sub> in the absence of **1** were photolyzed. Neither direct reduction of CO<sub>2</sub> from excited state TMB nor a mediated CO<sub>2</sub> reduction by way of a reduced imidazolium cation, which has been reported for 1,3-dialkylimidazolium ionic liquids,<sup>24</sup> resulted in any measurable amount of formate. Finally, fluorescence quenching experiments were conducted to see if excited state TMB could be quenched by HCO<sub>3</sub><sup>-</sup> (a product arising from the thermal decomposition of **1**). No significant quenching was observed under concentration levels of bicarbonate that well exceed what would be produced under the previously mentioned photolysis experiments. Thus, the importance of complex **1** for the photochemical reduction of CO<sub>2</sub> is apparent.

The mechanism shown in Scheme 2 is consistent with the results of this study. Electron transfer from the excited singlet

**Scheme 2. Proposed Mechanism for the Photochemical Generation of Formate Ion**



state of TMB (Sens\*) provides the anion radical **6**. Heterolytic dissociation of the latter would provide CO<sub>2</sub> anion radical **7** along with NHC **2**. It is assumed that (at least) 1 equiv of TMB is consumed in each photochemical reaction. However, the large excess of TMB used and the diversity of stable products expected from its cation radical<sup>25</sup> made quantitation of its consumption impractical. Conversion of CO<sub>2</sub>•<sup>-</sup> to the observed formate product requires a second reduction or H atom transfer step. In principle, H atom transfer from the sensitizers, solvent, or additives could account for the second reduction step. Two observations suggest that such reactions do not contribute in a major way.

First, adding a strong H atom donor (1.06 M, 1,4-cyclohexadiene) had only a negligible effect on the yield. H atom transfer could also occur from the *N*-methyl groups on TMB<sup>+•</sup>. Such reactions are known to produce the corresponding iminium ion,<sup>26</sup> which would hydrolyze to form *N,N,N'*-trimethylbenzidine. In fact, trace amounts of this byproduct are seen in the mass spectrum of the photoproduct mixtures (*m/z* = 227 ESI(+)-MS, SI). However, replacing TMB with anthracene (ANT) has only a negligible effect on formate production, suggesting that H atom transfer from the sensitizer is, at best, only a minor contributor to the overall production of formate. The C–H bond dissociation energy for 1,4-dioxane is 96.0 kcal/mol, only slightly lower than the C–H bond dissociation energy for formic acid (96.6 kcal/mol),<sup>27</sup> implying that while H atom transfer from the solvent to CO<sub>2</sub>•<sup>-</sup> is possible, it is likely to be fairly slow.

These considerations suggest that the most likely source of additional reducing equivalents is disproportionation of CO<sub>2</sub>•<sup>-</sup> and/or its conjugate acid, HOCO•. While the electrochemical reduction of CO<sub>2</sub> in neat aprotic organic solvents has been reported to yield oxalate as a major product, pulse radiolysis experiments of Flyunt et al. have shown that CO<sub>2</sub>•<sup>-</sup> decays with a

bimolecular rate constant that is near the diffusion limit in aqueous solution.<sup>28</sup> The products of this process are an oxalate dianion, formed from dimerization, or CO<sub>2</sub> and HCO<sub>2</sub><sup>-</sup> formed from a net disproportionation. Dimerization predominates at high pH, but at low pH, where HOCO• can form, disproportionation is favored. Presumably, the predominantly organic, and thus less polar, solvent conditions employed here also favor formation of HOCO• and thus disproportionation to formate and CO<sub>2</sub>.

In summary, it is demonstrated here that one-electron reduction of imidazolium-2-carboxylates can be effected with excited state donors. It is further shown that such reductions ultimately produce the formate ion, presumably through heterolytic dissociation of the reduced complex followed by disproportionation of the resulting radical species. The latter process limits the theoretical yield of formate to <50% under single turnover conditions. Therefore, current efforts are directed toward exploiting the reversible binding of CO<sub>2</sub> to N-heterocyclic carbenes in order create a truly photocatalytic system.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS publication Web site. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01891.

All synthesis and characterization data as well as detection of formate, fluorescence quenching, laser studies, and HPLC results (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: falvey@umd.edu.

### Notes

The authors declare no competing financial interest.

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