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The Effect of Solvent Identity and Hydride-Donor on the Reduction of CO₂ into Useful Fuels

by

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**Introduction**

The dramatic increase of carbon dioxide in the atmosphere due to the burning of fossil fuels is the leading cause of climate change. With the increase in electricity use over time, more fossil fuels are burned now than ever before, leading to dramatic CO₂ emissions\(^7\text{-}^9\). As of 2011, fossil fuels were responsible for 82\% of the energy supply\(^8\). With the harmful effects of fossil fuel usage, there must be a way to remove the CO₂ from the atmosphere. One option is to look to nature as the solution. Plants use carbon dioxide in photosynthesis to create glucose as fuel. As carbon dioxide is released into the atmosphere, plants capture what is available for use in photosynthesis. Until the early 1900s, the amount of CO₂ released was similar to the amount of CO₂ consumed by plants in photosynthesis. However, with the drastic increase in fossil fuel usage and deforestation, plants can no longer keep up with the amount of CO₂ found in the atmosphere. In the mid-1900s a dramatic increase in the concentration of atmospheric CO₂ can be seen (Figure 1), leading to dramatic changes to the global climate.

![Global atmospheric carbon dioxide compared to annual emissions (1751-2022)](image-url)
Figure 1. Annual CO₂ emission and overall atmospheric CO₂ each year from
1751-2022. An increase over time can be noted in both CO₂ emission and
atmospheric CO₂, with a sharp increase after 1930¹.

One of the main attempts to solve this problem is the use of renewable energy to replace
fossil fuels¹⁰. Though the efforts to develop renewable energy options are important and should
be continued, there is little evidence renewable energy will ever replace fossil fuels completely.
Renewable energy depends greatly on weather and other variable factors, so it tends to give
inconsistent amounts of energy. In addition, renewable energy can only limit the amount of CO₂
released into the atmosphere rather than using what is already in the atmosphere. Therefore,
another option in addition to renewable energy is needed to reverse climate change rather than
just slowing the progress. CO₂ reduction, in contrast to most renewable energy efforts, takes CO₂
out of the atmosphere and also reconverts it into a fuel that can be reused to give energy.

For this reason, there are efforts to capture CO₂ in the atmosphere and reconvert it into
useful fuels, such as methanol. The balanced equation is the equivalent of a reverse combustion
reaction (Equation 1). About 1.2V of energy are required to complete this process, which is less
than that of a AAA battery. What makes this reaction complicated to complete is the number of
products CO₂ and H₂O can form (Figure 2). CO only requires two electrons to be transferred,
making it the kinetically favored product. In contrast, methanol requires the transfer of six
electrons and six protons per molecule, causing it to require specific catalysts and conditions to
allow for the creation of methanol.

\[
2CO_2 + 4H_2O + Energy \rightarrow 2CH_3OH + 3O_2 \quad (1)
\]

¹ Taken from the National Oceanic and Atmospheric Association
Some examples of the different products a reduction of $\text{CO}_2$ can form.

Formate ($\text{HCOO}^-$) and carbon monoxide (CO) are the most likely products, because they only require the transfer of two electrons per molecule.

There are many examples of previous research that have successfully reduced $\text{CO}_2$ to CO. The majority of research has focused on heterogeneous catalysts to perform the reduction. Ag, Au, Zn, Cd, Cu, and Pd are the most common metals used to catalyze $\text{CO}_2$ into CO, with Au being the most effective because it does not bind too strongly nor too weakly to the molecule. Because Au is so expensive Ag is also often used in its place, though it still is not a very economic option. Pd is a catalyst that can also be manipulated to produce formate. However, it is also very expensive, so it isn’t promising on a commercial scale.

Transition metals have shown some promise as a low-cost option for the reduction of $\text{CO}_2$ into CO. Jiao et al created nanostructured Zn dendrite catalysts by electrodeposition, which exhibited a faradaic efficiency of 80% for the reduction of $\text{CO}_2$ into CO, in comparison to around 20-30% for zinc foil. There are also ways to manipulate the catalysts to get a higher efficiency, and this particular catalyst could serve as an economic option to reduce $\text{CO}_2$. Therefore, there is an opportunity to also try out other transition metals to test their $\text{CO}_2$ reducing properties.
However, with the heterogeneous metal catalysts the mechanism by which \( \text{CO}_2 \) is reduced can be challenging to study\(^3\).

Because of the mechanistic challenges of using metals for \( \text{CO}_2 \) reduction, there is also current research on the use of molecular catalysts to form a homogeneous solution to reduce \( \text{CO}_2 \). For example, a cobalt molecular catalyst (Figure 3) was synthesized, which has a faradaic efficiency for CO of almost 100\(^{\text{a}}\). Other molecular catalysts from metals such as ruthenium, copper, and iron have also been synthesized in order to reduce \( \text{CO}_2 \) to \( \text{CO} \)^{10-13}.

![Figure 3. A cobalt catalyst synthesized by Curtis P. Berlinguette, and Marc Robert. This catalyst forms a homogeneous solution, which makes mechanistic studies easier to perform.](image)

One of the competing reactions, making the reduction of \( \text{CO}_2 \) less efficient is the hydrogen evolution reaction. It is difficult to avoid this reaction when in the presence of bicarbonate electrolyte, which are often found in the \( \text{CO}_2 \) reduction experiments. Because bicarbonate is a weak buffer, it develops diffusional gradients of the \( \text{CO}_2 \). This is caused by the interfacial reactions occurring at the electrode and the slow acid-base equilibrium reached with bicarbonate as a buffer. The diffusional gradient affects the kinetics of the \( \text{CO}_2 \) reduction reaction in comparison to the hydrogen evolution reaction. Enhanced mass transport can help prevent the gradients from occurring, so experiments must be altered to limit the hydrogen evolution and cause it to favor the reduction of \( \text{CO}_2 \)^{16}. 
Because CO is not a useful molecule, the end goal of CO formation is to turn it later into methanol (CH$_3$OH) or methane (CH$_4$). To reach one of these products, a concerted proton-electron transfer must be performed, which requires an additional four steps to add protons and electrons to the molecule until methanol is formed. This process has been performed and is possible to do, but it adds complications to the reduction of CO$_2$. Fe, Ni, Pt, and Cu are some common catalysts used in these steps. Because each step requires the addition of catalysts, it is unlikely that this will ever reach a commercial scale. In order for the reduction of CO$_2$ to have an environmental impact, the process must be economic and scalable$^5$.

Because of the challenges of converting CO into methanol, it would be more effective to form methanol directly. Because of the kinetic barrier in the production of methanol directly from CO$_2$ instead of forming CO first, it can be complicated to do so. Multiple electrons would have to be transferred at once. In order for this to work, hydride donors are used. A hydride donor acts as a reductant, donating a H$, which can simplify the reaction, making it more favorable. Because the hydrogen and the electron are added at once, the reduction to methanol can be completed with only three hydrides and three protons, instead of six electrons and six protons which it would need if it were performed directly without the use of a hydride donor (Equations 2-5). Therefore, hydride donors allow for the possibility of adding more electrons in a reaction, making a product requiring more electrons possible.

Reaction without a hydride donor:

1. \[ \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \]  \hspace{1cm} (2)
2. \[ \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O} \]  \hspace{1cm} (3)
3. \[ \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH} \]  \hspace{1cm} (4)

Reaction with hydride donor:
\[ \text{CO}_2 + 3\text{H}^+ + 3\text{H}^+ \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \tag{5} \]

**Results and Discussion**

One area of research in the reduction of \( \text{CO}_2 \) is in the area of catalysis. In order to select methanol from the reduction of \( \text{CO}_2 \), various catalysts and hydride donors were synthesized. They were adapted from previous literature which lay out the synthesis of catalysts or hydride donors that have been shown to reduce \( \text{CO}_2 \) previously. Also, cyclic voltammetry was performed on each compound synthesized to analyze its \( \text{CO}_2 \) reducing capabilities. Finally, NMR was used to capture and characterize the products. Experiments were performed by NMR to analyze the products formed, because cyclic voltammetry does not allow for the capture of products. However, ideally a hydride donor is found that can reduce \( \text{CO}_2 \) electrochemically.

Commercially-available hydride-donors have been successfully used to reduce \( \text{CO}_2 \). For example, pinacolborane combined with an alkyne containing a carbon-capturing group and solvent have reduced \( \text{CO}_2 \) in NMR experiments (Figure 4). In the case of pinacolborane, when DMSO was the solvent, \( \text{CO}_2 \) was reduced to formate within a few hours (Schemes 1 and 3). However, even after heating no additional products were observed. When the reduction was performed in acetonitrile as the solvent, the major product was the 6 electron reduction to methoxyborane (Scheme 2), which can be easily converted into methanol through a protonation. Pinacolborane is not a hydride donor that would work on a commercial scale due to the cost and the lack of electrochemical reducing capability; however, these results show that hydride donors work as a \( \text{CO}_2 \) reducing pathway.
Scheme 1. Synthesis of formate from pinacolborane and an alkyne with a known carbon-capturing functional group in DMSO (NMR A).

Scheme 2. Synthesis of the methoxy group using pinacolborane and an alkyne with a known carbon-capturing functional group in acetonitrile (NMR B).
Scheme 3. Synthesis of formate from pinacolborane and an alkyne (NMR C).

NMR A:
NMR B:

NMR C:
Figure 4. $^{13}$C NMR spectra of pinacolborane and two different alkynes, chosen for their carbon-capturing functional group (schemes 1-3 respectively). The reactions in DMSO formed formate, but the reaction in acetonitrile went to the methoxy group.

It is difficult to reduce gaseous CO$_2$, because it may not interact with the catalyst. Therefore, there are also efforts to look at functional groups that could interact with CO$_2$ to potentially capture it and make it more available for a reduction. Therefore, carbon-capturing functional groups on alkynes show promise in assisting the reduction of CO$_2$, because they grab onto the CO$_2$ molecule to make it easier to reach and reduce. Several alkynes with known carbon-capturing functional groups were tested electrochemically. The alkyne with an acid anhydride functional group in particular showed potential for the reduction of CO$_2$ electrochemically (Figure 5). Performing cyclic voltammetry in acetonitrile under CO$_2$ it showed a large reduction as opposed to argon. Electrochemistry does not allow for the analysis of a product formed, but it demonstrated that this functional group could be used as a part of a molecule to capture and reduce CO$_2$. However, this indicates that this functional group could be used in the synthesis of hydride donors to assist in the reduction of CO$_2$. 
Figure 5. CVs of an alkyne with an acid anhydride functional group in acetonitrile at 25 mV/s under argon and carbon dioxide. A large irreversible reduction is shown under CO₂ in contrast to under argon, indicating that the CO₂ was successfully reduced.

This is shown by NMR (Figure 6). Several derivations of the literature were also synthesized, using different alkynes with different carbon-capturing functional groups and variations of the starting material. Most of the attempts to create the compound were unsuccessful due to low yields and impure product. However, it was found that the product could be washed in dichloromethane to remove starting material and then dissolved in ethyl acetate to give a pure product (Figure 7).
Other alkynes used in synthesis:

Other starting material used (starts in second step of reaction):

Figure 6. The reaction scheme from the procedure from Choudhury et al\textsuperscript{6} to create a hydride donor along with other starting material and alkynes tested in the procedure.
Figure 7. The NMR in DMSO shows the clean product before the final (reduction) step.

Cyclic voltammetry was also performed on the synthesized hydride donor before the reduction to test the possibility of a reduction under CO$_2$. In acetonitrile as the solvent, it showed a small irreversible reduction under CO$_2$, which indicates that the CO$_2$ was reduced. As electrons are added, they reduce the hydride donor, which then goes on to reduce the CO$_2$, rather than returning the added electrons to the electrode (Figure 7). In electrochemistry, the products cannot be captured, so it is unknown what compound was created from the reduced CO$_2$. For that reason NMR experiments would need to be performed on the hydride donor to capture the product and determine what was formed.
Figure 7. Cyclic voltammetry experiments at 25 mV/s in acetonitrile were performed on the unreduced product from the literature procedure. A reduction was noticed under CO₂ in comparison to argon.

Another area of work in order to successfully reduce CO₂ into methanol is the use of amines to capture the CO₂ so that it can be reduced. Amines are already used at a large scale to capture carbon dioxide out of the atmosphere\textsuperscript{15}, so they pose a good option for the reduction of that CO₂ as well. One possibility is to bubble CO₂ into liquid amines, which then form a white powder with a carbamate ion (Figure 8). These carbamates could be dissolved in a solvent with the addition of a hydride donor to perform CO₂ reduction on an already captured CO₂ molecule. It was found that primary or secondary amines were able to capture CO₂, but tertiary amines were not able to appreciably drive the equilibrium towards products.
Figure 8. Three different carbamate ions that were successfully formed by bubbling CO₂ into amine. These capture the CO₂ making it easier to reduce.

Conclusions

Hydride donors can be used to assist in the reduction of CO₂ into a useful fuel such as methanol because they simplify the reduction, making it possible to add the necessary protons and electrons. Therefore there is an opportunity to continue to create different hydride donors to find one that can be synthesized economically with a high yield and pure product. Hydride donors should reduce CO₂ electrochemically, because it is possible to use renewable energy. This makes it so that the energy gained from the burning of the methanol can be used for other purposes. Also, there is the opportunity to try different combinations of hydride-donor, amine, carbamate ions, solvents, or other additions to find a combination that favors the production of methanol. After mixing together captured CO₂ with a hydride donor in a solvent, NMR
experiments must be performed to determine the product. Photochemistry, electrochemistry, and heat can also be used to assist in the reduction if it does not reduce on its own. Finally, reverse micelles can also be used as a part of the solution to create a more controlled environment, instead of or in addition to other carbon-capturing techniques. Reverse micelles can also be used to create a film on an electrode to perform the reduction electrochemically.

**Experimental**

**Materials and Methods.** The NADPH analogue was synthesized from a previously published procedure. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was purchased from Oakwood Chemicals and was recrystallized three times from absolute ethanol before use in electrochemistry. Deuterated NMR solvents were purchased from Cambridge Isotopes. All other reagents were ACS grade and purchased from Millipore Sigma. Electrochemical measurements and analyses were performed on either a CH Instruments model 600E or 660E potentiostat/galvanostat. A 3 mm glassy carbon disk was used as the working electrode and Ag/AgNO₃ was used as the reference electrode in all experiments. Experiments were conducted in 0.1 M TBAPF₆ acetonitrile solutions. ¹H and ¹³C NMR spectra were collected on Bruker AV-400 and AV-500 NMR spectrometers at ambient temperature.

**1H-phenanthro[9,10-d] imidazole.** The synthesis was adapted from the procedure by Choudhury et al. Phenanthrene-9,10-dione (2.0g, 9.6mmol), formaldehyde (1.6mL, 37wt%), and ammonium acetate (1.53, 19.8mmol) were combined with glacial acetic acid (38mL) in a flask. The reaction mixture was refluxed at 120°C 6 hours. After cooling, the reaction was poured into 50mL H₂O. It was neutralized to pH 8 with ammonium hydroxide (28-30wt%) and cooled in the
freezer. The precipitate was filtered and rinsed with H₂O, acetone, and ether, leaving a brown powder.

**Yield** = 1.889g, 90.6%

**¹H NMR** (500MHz, DMSO-d6) δ 13.41 (s, 1H), 8.84 (dd, J = 18.6, 8.1 Hz, 2H), 8.52 (d, J = 7.8 Hz, 1H), 8.35 (d, J = 7.8 Hz, 1H), 8.31 (s, 1H), 7.71 (q, J = 7.2 Hz, 2H), 7.62 (q, J = 8.1 Hz, 2H).

2,6-bis-(benz)imidazoyl pyridine. The 1H-phenanthro[9,10-d] imidazole (1.889g, 8.7mmol), 2,6-dibromopyridine (1.03g, 4.3mmol), and cesium carbonate (2.83g, 8.7mmol) were combined in a flask and heated at 190°C 24 hours. After cooling to room temperature, it was extracted with dichloromethane and H₂O. The organic solution was dried over magnesium and isolated in the rotary evaporator, leaving a brown powder.

**Yield** = 1.126g, 50.6%

**¹H NMR** (500 MHz, DMSO-d6) δ 8.92 (d, J = 8.4 Hz, 2H), 8.87 (d, J = 8.3 Hz, 2H), 8.66 (s, 3H), 8.61 (dd, J = 8.0, 1.5 Hz, 2H), 8.27 (d, J = 7.9 Hz, 2H), 7.76 (t, J = 7.5 Hz, 2H), 7.68 (m, 4H), 7.60 (ddd, J = 8.3, 7.0, 1.3 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H).

c-Pybim1-cPybim2. 2,6-bis-(benz)imidazoyl pyridine (1.126g, 2.2mmol) was methylated with iodomethane (1.37mL, 2.2mmol) in 3mL dry DMF and heated at 100°C for 24 hours. After cooling to room temperature, 10mL THF was added, and the precipitate was filtered. The solid left was washed in THF, ether, and dichloromethane leaving a powder.

**Yield** = 0.290g, 20.2%
NADP⁺ Analogue. cPybim1-cPybim2 (0.1g, 0.153mmol) was combined with sodium acetate (0.063g, 0.765mmol), pentamethycyclopentadienyl rhodium dichloride dimer (0.005g, 0.00765mmol), silver trifluoride sulfonate (0.197g, 0.765mmol), and diphenylacetylene (0.058g, 0.327mmol) were combined in a flask with 5mL dichloroethane. The reaction mixture was stirred at 90°C for 24 hours and cooled to room temperature. Dichloromethane was added, and the reaction mixture was filtered through a celite plug and washed through with dichloromethane. The dichloromethane mixture was set aside, and the plug was washed through with ethyl acetate, which was evaporated in the rotary evaporator.

Yield = 0.178g, 97.6%

NADPH Analogue. The reduction was performed on the NADP⁺ analogue (0.794g, 0.67mmol) by dissolving it in dichloromethane and adding sodium borohydride (0.050g, 1.0mmol) and stirring for 15 minutes at room temperature. Water was added and an extraction was performed. It was dried over magnesium sulfate and evaporated in the rotary evaporator, leaving a fluorescent pink oil.

Carbamate Ions. Dry ice was used to bubble CO₂ into about 3mL of a liquid primary or secondary amine (isopropyl amine, diisopropyl amine, or diethanolamine), forming a white solid. The solid was captured by vacuum filtration, leaving a white powder.
References


(3) Electrodeposited Zn Dendrites with Enhanced CO Selectivity for Electrocatalytic CO2 Reduction, Jonathan Rosen, Gregory S. Hutchings, Qi Lu, Robert V. Forest, Alex Moore, and Feng Jiao, ACS Catalysis 2015 5 (8), 4586-4591


(6) Bis-Imidazolium-Embedded Heterohelicene: A Regenerable NADP⁺ Cofactor Analogue for Electrocatalytic CO2 Reduction, Pirudhan Karak, Sanajit Kumar Mandal, and Joyanta Choudhury, Journal of the American Chemical Society 2023 145 (13), 7230-7241. DOI: 10.1021/jacs.2c12883


(12) Factors Influencing the Performance of Copper-Bearing Catalysts in the CO2 Reduction System Zhiyi Sun, Yaning Hu, Danni Zhou, Mengru Sun, Shuo Wang, and Wenxing Chen ACS Energy Letters 2021 6 (11), 3992-4022 DOI: 10.1021/acsenergylett.1c01965

(14) Aysegul Yagmur Goren, Dogan Erdemir, Ibrahim Dincer,


(16) Competition between CO2 Reduction and Hydrogen Evolution on a Gold Electrode under Well-Defined Mass Transport Conditions
Akansha Goyal, Giulia Marcandalli, Vladislav A. Mints, and Marc T. M. Koper
Journal of the American Chemical Society 2020 142 (9), 4154-4161
DOI: 10.1021/jacs.9b1006