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# **Producing Fuel from Carbon Dioxide Using Zinc**

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## Abstract

Carbon dioxide,  $CO_2$ , is a molecule produced industrially by burning hydrocarbons used as fuel, and biochemically, by exhaling to allow our bodies to maintain homeostasis. Carbon dioxide is a very stable, low energy molecule; furthermore, the physical property of most concern is atmospheric carbon dioxide's ability to trap infrared radiation, heat, produced from sunlight that hits the earth's surface. This phenomenon is known as the greenhouse effect. The Earth has ways of using or storing carbon dioxide: photosynthetic organisms use  $CO_2$  to make sugars, and  $CO_2$  dissolves into the oceans. However, man's production of  $CO_2$  is overtly becoming beyond the capacity of naturally occurring processes. We have found evidence that zinc can react with  $CO_2$ , which after a series of chemical steps will produce the gas, methane. Among these steps, we propose a mechanism process in which formaldehyde,  $CH_2O$ , is produced and can then be reacted with zinc to produce methane by a well-established mechanism called the Clemmensen reduction. In a Clemmensen reduction, Zn is known to produce hydrocarbons from aldehydes, such as formaldehyde, which represent plausible chemical substances as intermediates along our path in this mechanistic exploration. Here, we will focus on explaining the path in which zinc, a relatively inexpensive and abundant metal, captures  $CO_2$  and allows us to turn it into a combustible gas.

Keywords: Fuel, Zinc, Carbon Dioxide

#### **1. Introduction**

For more than a century, hydrocarbons have driven the world to amazing progress by persisting as its main energy source. In light of this fact, the abundance of carbon dioxide, one of the products of hydrocarbon combustion, has led to the increased interest of harnessing the potential energy in this renewable feedstock for fuels. Carbon dioxide reduction has been studied in many different facets including metal catalysts and electrochemical reduction. The most desirable products for carbon dioxide reduction are methanol and methane, which are produced by 6-electron and 8-electron reductions, respectively, shown below.

$$CO_2 + 6e^- + 6H^+ \longrightarrow CH_3OH + H_2O \quad (E^\circ = -0.38 \text{ V})$$
(1)

$$CO_2 + 8e^- + 8H^+ \longrightarrow CH_4 + 2H_2O \quad (E^\circ = -0.24 \text{ V})$$
 (2)

Carbon dioxide can be reduced to a variety of products including CO, formaldehyde and methane by transition metals such as rhenium, rhodium, and ruthenium.<sup>1-3</sup> However, these metals are limited by their scarcity and access to multiple oxidation states, which complicates results by lowering selectivity. In addition to these expensive metals, electrochemical reduction of carbon dioxide has been studied with various metal electrodes.<sup>4,5</sup> Zinc electrodes are known to reduce CO<sub>2</sub> to carbon monoxide, formic acid, and even methane.<sup>6</sup> Because zinc is abundant and non-toxic, it is a plausible alternative reductant for CO<sub>2</sub> reduction. Along the path of carbon dioxide reduction, several products can be formed; in fact, one minor product in many reactions is formaldehyde. Logically, further reduction of formaldehyde can lead to highly reduced products such as methane. Zinc is used to reduce aldehydes, to alkanes via the Clemmensen reduction shown below.

2 Zn + 
$$R \longrightarrow O$$
 + 2H<sup>+</sup>  $ZnO$  + Zn<sup>2+</sup> + Alkane (3)  
R= alkyl, H

We decided to focus on the unique ability of zinc to reduce both carbon dioxide and carbonyl compounds to alkanes. Since the mechanism of electrochemical  $CO_2$  reduction is still unknown, we propose formaldehyde is a plausible intermediate that can undergo reduction all the way to methane by a Clemmensen mechanism.

#### 2. Methodology

In this study we have combined modeling using Density Functional Theory to predict key plausible intermediates of the path shown below catalyzed by zinc. A few preliminary experimental results are presented.

$$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \end{array} \xrightarrow{2H^{+}/2e^{-}} H \xrightarrow{0} H \xrightarrow{2H^{+}/2e^{-}} H \xrightarrow{0} H \xrightarrow{2H^{+}/2e^{-}} H \xrightarrow{0} H \xrightarrow{2H^{+}/2e^{-}} H \xrightarrow{H \xrightarrow{1} H \xrightarrow{1} H \xrightarrow{2H^{+}/2e^{-}} H \xrightarrow{1} H \xrightarrow{1}$$

## 2.1 Computational Details

All calculations were carried out using density functional theory as implemented in the ab initio quantum chemistry package ORCA.<sup>7</sup> Geometry optimizations were performed with B3LYP<sup>8-11</sup> and a contracted Gaussian split-valence basis set (SV(P)).<sup>12</sup> The energies of the optimized structures were re-evaluated by additional single-point calculations using Ahlrichs contracted Gaussian triple-z basis set augmented by polarization functions (TZVP).<sup>13,14</sup> The nature of stationary points located on the potential energy surface has been checked by harmonic frequency calculations, and all molecules considered in this work possess no imaginary frequencies.

## 2.2 Experimental

All reagents and solvents were used as obtained from the manufacturer without further purification. NMR solvents were obtained from Cambridge Isotope Laboratories and were not purified further. NMR spectra were obtained using a 400 MHz Varian Unity Inova NMR Spectrometer. IR spectra were obtained using an ATR IR Spectrometer. Inert atmospheres were produced using ultra high purity nitrogen gas.

## a) Reaction of Zn and paraformaldehyde in the presence of 2,2'-Bipyridine

Zn dust (0.419 g, 6.4 mmol) was placed in a three-neck round-bottom flask and suspended in 200 mL of methanol. This mixture was combined with 2,2'-Bipyridine (1g, 6.4 mmol) and paraformaldehyde (0.576 g, 6.4 mmol). The mixture was stirred at room temperature under a blanket of  $N_2$  for 24 h. The mixture did not show any changes and the temperature was increased to reflux (65 °C). The mixture was stirred at this temperature for an additional 72 h. After this time, the grey solid (Zn) had been consumed, the mixture changed to a pale yellow and the heat was removed. The solvent was evaporated under vacuum. NMR and IR analysis of the residue showed changes of the signals of the free bipyridine.

<sup>1</sup>H NMR, CD3OD δ 3.5, m; 7.73, s (broad); 8.27, s (broad); 8.60, s (broad). FT-IR (ATR, cm<sup>-1</sup>) 1594, 1575.

#### **3. Results**

In order to gain a better understanding of the likelihood of our hypotheses, we created and tested theoretical models via computational analysis. In the models below, 2,2'-Bipyridine has been added with the idea of providing a scenario that can be easily replicated experimentally. A ligand like bipyridine can stabilize an oxidized metal ion.

$$Zn + bpy + CO_2 + H_3O^+ \longrightarrow N Zn O^+ + H_2O$$

$$\Delta E = -80.74 \text{ kcal/mol}$$
(5)

In equation 5, above, it became evident that an acidic medium facilitates  $CO_2$  activation giving rise to a carbonyl complex. Given the small number of Zn carbonyl compounds, an expected side-reaction is CO loss. This means that the acidic medium can favor CO coordination because protonation of the cis hydroxide may be preferred.

$$Zn + bpy + H_3O^+ \longrightarrow Xn - H + H_2O$$

$$\Delta E = -97.07 \text{ kcal/mol}$$
(6)

Equation 6 shows the thermodynamics of the possibility of proton reduction as a competing reaction. This reaction, however, can lead to formate formation.<sup>15</sup> From a formate intermediate under acidic conditions and excess reducing agent, a gem-diol can be generated that can decompose into formaldehyde.

$$Zn + bpy + HCHO$$
  $\longrightarrow$   $N$   $Zn$   $H$   $\Delta E = -5.22 \text{ kcal/mol}$  (7)

Equation 7, represents the reduction of formaldehyde on zinc to produce a formyl intermediate. The driving force of this reaction is considerably lower than the reaction using a proton source.

# 3.1 Spectroscopic Analysis Of Attempted Stoichiometric Reactions

Attempts to react zinc with  $CO_2$  have not produced any tractable results. We decided to pursue the reduction of formaldehyde by zinc in the presence of a ligand that may stabilize zinc and can allow us to capture an intermediate relevant to a Clemmensen reduction of formaldehyde. Reaction of zinc dust with paraformaldehyde in methanol in the presence of 2,2'-Bipyridine at room temperature did not proceed. When the mixture was refluxed for 72 hours, however, the color of the mixture changed from gray to orange as seen below.



Figure 1. Solution of Zn reaction with paraformaldehyde after 3 days of reflux in methanol (right)

<sup>1</sup>H NMR and IR analysis of the product mixture showed the peaks corresponding to bipyridine had shifted and broadened compared to the signals of the free ligand. This shift may be indicative of coordination to Zn, possibly  $Zn^{2+}$ , which would mean oxidation of the metal has occurred. The reaction is reproducible; however, crystallization of the product remains challenging. Stretching frequencies of the ligand seem to have also been affected and a slight increase in the C=C region may also be indicative of an inductive effect of a Lewis-acidic ion such as  $Zn^{2+}$ .





Figure 2. a. Comparison of <sup>1</sup>H NMR signals of 2,2'-Bipyridine ligand in CD<sub>3</sub>OD, as free ligand (blue); after refluxing mixture for 72 h in the presence of Zn and paraformaldehyde (red); reaction mixture in a mixture of CD<sub>3</sub>OD and CDCl<sub>3</sub> (green). b. IR signals in the C=C stretching region in free ligand (blue) and in reaction mixture (pink).

# 4. Conclusion and Future Work

We have presented several plausible intermediates of Zn-catalyzed reduction products. It is possible to link these intermediates to both  $CO_2$  reduction and the Clemmensen reduction. Indication of a reaction between Zn and formaldehyde is presented in the absence of acid, which may allow the formation and isolation of an intermediate that may be relevant to both reductions. We are presently conducting reactions at a lower pH to compare with our present results, as well as pursuing structural characterization of the product from the reaction shown here. Modeling of all possible routes including formate and carbon–carbon bond formation is also underway. We plan to evaluate the use of a terdentate ligand, e.g. 2,2':6,2"-Terpyridine, to compare with 2,2'-Bipyridine. We envision that the elimination of a coordination site may enhance a bond-forming event. Because Clemmensen reductions that produce alkanes operate in acidic media, we plan to change the conditions increasing the pH for our reactions to be able to trap organometallic intermediates.

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