Photochemical carbon dioxide reduction with metal complexes: Differences between cobalt and nickel macrocycles

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1. INTRODUCTION

Problems related to increases of green house gases in the atmosphere and the depletion of fossil fuels have made the conversion of CO₂ into useful chemicals and fuels an important area of research. However, CO₂ reduction poses many scientific challenges. Despite intense interest in photochemical and electrochemical CO₂ reduction, the kinetics and mechanism of the reduction remain unclear in many systems.

A number of 14-membered tetraazamacrocyclic complexes serve as catalysts for photochemical and electrochemical CO₂ reduction. [CoHMD(H₂O)](ClO₄)₂ (HMD = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradeca-4,11-diene) and Ni(cyclam)Cl₂ (cyclam = 1,4,8,11-tetraazacyclotetradecane) have been used as electrocatalysts for the reduction of CO₂ in H₂O or aqueous CH₃CN. The ratio for CO/H₂ production is ~1 for [CoHMD(H₂O)](ClO₄)₂ and >100 for Ni(cyclam)Cl₂. Metal(I) complexes, metal(II) hydride complexes, and metallocarboxylates such as [Ni(III)(cyclam)(CO₂⁻)]⁺ are postulated as intermediates in the electro- and photo-chemical CO₂ reduction.

Our research focuses on mechanistic and kinetic studies of photochemical and electrochemical CO₂ reduction that involves metal complexes as catalysts. This work makes use of UV-vis, NMR, and FTIR spectroscopy, flash photolysis, pulse radiolysis, X-ray diffraction, XANES (X-ray absorption near-edge spectroscopy) and EXAFS (extended X-ray absorption fine structure). Here we summarize our research on photochemical carbon dioxide reduction with metal macrocycles.

2. NATURE OF Co-CO₂ ADDUCTS

We and others have characterized the interaction of low-spin d⁸ CoHMD⁺ with CO₂ in CH₃CN⁵-⁹ and in H₂O⁰¹¹ Schmidt et al.¹² have characterized the binding thermodynamics as a function of organic solvent. The chiral N-H centers of the macrocycle give rise to two diastereomers, N-rac and N-meso. The CoL complexes are shown below.
The equilibration between the N-rac- and N-meso cobalt(II) isomers is slow in acidic aqueous and organic media, but equilibration of the two cobalt(I) isomers is relatively rapid (>2 x 10^{-3} s^{-1}) in CH₃CN.

The CO₂ binding constants of the corresponding [CoHMD]⁺ isomers are quite different: N-rac-[CoHMD]⁺, (1.2 ± 0.5) x 10^4 M^{-1}; N-meso-[CoHMD]⁺, 165 ± 15 M^{-1}. While hydrogen bonding interactions between the bound CO₂ and amine protons of the macrocycle will tend to stabilize both adducts, the N-meso adduct is destabilized by the steric repulsion by the macrocyclic methyl group.

Although the N-rac-[CoHMD(CO₂)]⁺ adduct decomposes to N-rac-[CoHMD]²⁺ and CO in wet CH₃CN, it is stable enough to handle in dry CH₃CN under a CO₂ atmosphere. The complex is thermochromic, being purple at room temperature and yellow at low temperature (-100 °C) as shown in Figure 1. The equilibrium between five-coordinate [CoHMD(CO₂)]⁺ (purple) and six-coordinate [CoHMD(CO₂)(CH₃CN)]⁺ (yellow) has been studied by UV-vis, ¹H NMR, FT-IR, XANES and EXAFS in CH₃CN.

\[
[\text{CoHMD}]^+ + \text{CO}_2 \rightleftharpoons [\text{CoHMD}($\text{CO}_2$)]^+ \tag{1}
\]

\[
[\text{CoHMD}(\text{CO}_2)]^+ + \text{CH}_3\text{CN} \rightleftharpoons [\text{CoHMD}(\text{CO}_2)(\text{CH}_3\text{CN})]^+ \tag{2}
\]

\[
K_s = \frac{[\text{CoHMD}(\text{CO}_2)(\text{CH}_3\text{CN})]^+}{[\text{CoHMD}(\text{CO}_2)]^+} \tag{3}
\]

The singular value decomposition (SVD) spectral analysis of the temperature-dependent UV-vis data between 26 and -40 °C is consistent with the presence of two species in CH₃CN. The fit gives ΔH° = -7.0 kcal mol⁻¹ and ΔS° = -27 cal K⁻¹ mol⁻¹ for eq. 2. The equilibration is rapid on the NMR time scale. The pressure dependence of the equilibrium constant shows that increasing pressure shifts the equilibrium toward the six-coordinate species with an overall reaction volume of ΔV° = -17.7 ± 1.0 mL mol⁻¹ at 15 °C in CH₃CN. The FT-IR spectra measured over the range 25 to -75 °C in CD₃CN and in a CD₃CN/THF mixture indicates the existence of four CO₂ adducts with and without intramolecular hydrogen bonds between the bound CO₂ and the amine hydrogens of the ligand: a five-coordinate, non-hydrogen-bonded form (νC=O = 1710 cm⁻¹, νNH = 3208 cm⁻¹), a five-coordinate hydrogen-bonded form (νC=O = 1626 cm⁻¹), a six-coordinate non-hydrogen bonded form (νC=O = 1609 cm⁻¹, νNH = 3224 cm⁻¹), and a six-coordinate hydrogen-bonded form (νC=O = 1544 cm⁻¹, νNH = 3145 cm⁻¹).
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X-ray absorption spectroscopy is an attractive tool for the characterization of metal complexes in solution. The metal coordination number, geometry, and electronic properties can be studied using XANES and the metal-ligand bond distances are obtained through analysis of EXAFS. Previous work\textsuperscript{17-19} has also shown that the edge energy correlates with the oxidation state of the metal. The XANES spectra (Figure 2) for a series of CoHMD complexes\textsuperscript{9} indicate that the edge positions ($E_0$) are sensitive to the oxidation state of the metal.
The edge energy, relative to [CoIIHMD]2+, decreases 1 eV upon reduction and increases 2 eV upon oxidation. As seen from Figure 2A, the $E_0$ for five-coordinate [CoHMD(CO$_2$)]$^+$ at room temperature is similar to that of [CoIIHMD]$^{2+}$. This is consistent with theoretical predictions$^{20,21}$ that the bound CO$_2$ receives 0.71 electrons mainly from the Co d$_{z^2}$ orbital. The six-coordinate [CoHMD(CO$_2$)(CH$_3$CN)]$^+$ species shows a 1.2 eV shift towards Co(III) and is interpreted as a Co(III)-CO$_2^{2-}$ carboxylate complex. Although the Co(III) carboxylates have been postulated as intermediates in CO$_2$ reduction and water-gas shift reactions, the XANES results provide the first unambiguous evidence that active metal catalysts, such as [CoIHM]$^+$, can promote two-electron transfer to the bound CO$_2$ and thereby facilitate its reduction.

3. PHOTOCHEMICAL CO$_2$ REDUCTION WITH COBALT MACROCYCLES: MECHANISTIC AND KINETIC STUDIES

Our previous studies indicated that cobalt macrocycles mediate the photoreduction of CO$_2$ to CO with p-terphenyl (TP) as a photosensitizer and a tertiary amine as a sacrificial electron donor in a 5:1 acetonitrile/methanol mixture.$^{22}$ The system enhances the activity of the TP by suppressing the formation of dihydroterphenyl derivatives and produces CO and formate efficiently with only small amounts of H$_2$. The total quantum yield of CO and formate is 25% at 313 nm in the presence of triethanolamine (TEOA) and Co(cyclam)$^{3+}$.

Transient absorption measurements provide evidence for the sequential formation of the p-terphenyl radical anion (TP$^-$), the CoHMD$^+$ complex, the [CoHMD-CO$_2$]$^+$ complex and the [S-CoHMD(CO$_2$)]$^+$ complex ($S$ = solvent) in the catalytic system containing triethylamine (TEA).$^{23}$ The electron-transfer rate constant ($k_6$) for the reaction of TP$^-$ with CoIIHMD$^{2+}$ is $1.1 \times 10^{10}$ M$^{-1}$ s$^{-1}$ and is probably diffusion controlled because of the large driving force ($\sim 1.1$ V). Flash photolysis studies yield a rate constant ($k_7$) of $1.7 \times 10^8$ M$^{-1}$ s$^{-1}$ and an equilibrium constant of $1.1 \times 10^4$ M$^{-1}$ for the binding of CO$_2$ to CoHMD$^+$. These values are consistent with those previously obtained by conventional methods in CH$_3$CN.$^5$

$$
\begin{align*}
TP^+ + TEA & \xrightleftharpoons{k_4} TP^- + TEA^+ \\
TP^- + CO_2 & \xrightleftharpoons{k_5} TP + CO_2^- \\
TP^- + Co^{II}HMD^{2+} & \xrightarrow{k_6} TP + Co^{I}HMD^+ \\
Co^{I}HMD^+ + CO_2 & \rightleftharpoons{k_7} Co^{I}HMD(CO_2)^+ \\
Co^{I}HMD(CO_2)^+ + S & \rightleftharpoons{k_8} [SCo^{III}HMD(CO_2)^{2+}] 
\end{align*}
$$

(4) (5) (6) (7) (8)
The dependence of the decay rate of TP" on [CO₂] in the absence of the cobalt macrocycle (eq 5) is not linear. We estimate a rate constant k₅ < 10⁶ M⁻¹ s⁻¹ for electron transfer between TP" and [CO₂]. This rate constant is consistent with the large reorganization energy of the CO₂/CO₂" couple (associated the geometry change from a linear to a bent molecule) and small driving force for the reaction (0.3 V). Under our photocatalytic conditions the cobalt reacts with the TP" > 20 times faster than does the CO₂. Thus the direct reduction of CO₂ by TP" plays a negligible role here and all of the photochemically generated reducing equivalents are captured by the cobalt macrocycle.

The production of CO from CoL(CO₂)⁺ requires a second reducing equivalent. The source of this equivalent is of interest. Under flash photolysis conditions the TP" has completely reacted before the CoL(CO₂)⁺ is formed. On the other hand, under continuous photolysis TP" can react with the CoII(²) or the CoL(CO₂)⁺ complexes. In the flash photolysis, where only Et₂NCHCH₃ and/or CoL⁺ may act as the electron donor, the decomposition of CoLCO₂⁺ is slow owing to the low concentrations of these two species. In fact, since CoLCO₂⁺ decomposes faster with low [CO₂] (i.e. higher [CoL⁺]), CoL⁺ is the likely electron donor under flash photolysis conditions. We suggest that reactions 10-12 are responsible for the production of CO in the photolysis. The slow step is likely to be the C–O bond breakage of the bound carboxylic acid with either Et₂NC'HCH₃, or CoL⁺ acting as electron donor. Unfortunately the UV-vis transient spectrum of [S-CoIIIHMD(CO₂²⁻)]⁺ is too weak to study the proton dependence of its disappearance.

4. PHOTOCHEMICAL CO₂ REDUCTION WITH NICKEL MACROCYCLES

4.1 Photochemical CO₂ reduction

In contrast to the cobalt-based system, small amounts of H₂ and no CO are produced when nickel cyclam or other saturated 14-membered tetraazamacrocycles (L) in Figure 3 are used to replace the cobalt complex in the above system. Flash photolysis studies indicate that the electron-transfer rate constant (k₁₃) for the reaction of the p-terphenyl radical anion with NiII(cyclam)²⁺ is 4.3 × 10⁹ M⁻¹ s⁻¹. However, when CO₂ is added to the solution, the
decay of the TP anion becomes slower! Flash photolysis studies of the acetonitrile solutions suggest the existence of a minor pathway for $M^{1+}$ formation that does not involve TP. When TEA (or TEOA) is used with UV excitation (<320 nm), a minor pathway is observed that can be suppressed by the addition of methanol in the case of CoHMD$^{2+}$, but not Ni(cyclam)$^{2+}$.

$$TP^- + Ni^{II}\text{cyclam}^{2+} \xrightarrow{k_{13}} TP + Ni^{I}\text{cyclam}^+$$  \hspace{1cm} (13)

$$Ni^{I}\text{cyclam}^+ + CO_2 \xrightarrow{k_{14}} Ni^{I}\text{cyclam}(CO_2)^+$$ \hspace{1cm} (14)

Both $Ni^{I}L^+$ and $NiL(CO_2)^+$ species are formed under CO$_2$ atmosphere by irradiation at 313 nm in acetonitrile solutions containing TEA and NiL$^2+$. In order to understand the interesting behavior of these nickel-based systems we have studied the nature of the ground-state complexes, electrochemical CO$_2$ reduction, and the differences in CO$_2$ binding between cobalt and nickel macrocycles.

Figure 3. Structures and geometries of metal macrocycles
4.2 Electrochemical CO₂ reduction with nickel macrocycles

The electrocatalytic activity of various nickel macrocycles in aqueous solution were studied. Cyclic voltammograms indicate that RRSS-NiHTIM2⁺, NiMTC2⁺ and NiDMC2⁺ are better catalysts than Ni(cyclam)2⁺ in terms of more positive potentials and/or their larger catalytic currents. Bulk electrolyses with 0.5 mM Ni complexes confirm that these complexes are excellent catalysts for the selective and efficient CO₂ reduction to CO. The macrocycles with equatorial substituents showed increased catalytic activity over those with axial substituents. These structural factors may be important in determining their electrode adsorption and CO₂ binding properties.

4.3 Properties of Ni[IL]2⁺ complexes

Ni(cyclam)2⁺ is oxidized at 0.98 V and reduced at -1.45 V vs SCE in CH₃CN under argon. Under a CO₂ atmosphere the reduction wave shifts about 10-20 mV more positive, indicating a very small binding constant in CH₃CN. When TEA is added to the solution under argon, the reduction remains at -1.45 V as shown in Figure 4. The oxidation potential is not observed due to the oxidation of TEA. The CV under a CO₂ atmosphere shows a reversible oxidation at 0.31 V. The reduction becomes irreversible and occurs at a very negative potential, -1.8 V in TEA-containing CH₃CN (Figure 4). This indicates that the [Ni(TEA)(CO₂)]²⁺ adduct is unstable. This also explains the slower decay of TP⁻ under CO₂ atmosphere, since the driving force for electron transfer from the TP⁻ to [Ni(II)(cyclam)]²⁺ becomes smaller upon addition of CO₂.

![Figure 4: CV for 1 mM Ni(cyclam)²⁺ with TEA under Ar (solid) and CO₂ (dot) in CH₃CN.](image-url)
The reaction of Ni\textsuperscript{II}(cyclam)\textsuperscript{2+} with TEA/CO\textsubscript{2} was monitored by UV-vis and FT-IR. The d-d absorption intensity of Ni\textsuperscript{II}(cyclam)\textsuperscript{2+} decreases with TEA binding in CH\textsubscript{3}CN and shifts to lower energy with CO\textsubscript{2} binding in a TEA-containing CH\textsubscript{3}CN solution as shown in Figure 5. Both TEA and CO\textsubscript{2} binding are reversible. The IR spectrum of the [Ni(cyclam)(TEA)(CO\textsubscript{2})]\textsuperscript{2+} adduct indicates two kinds of CO stretching bands at 1615 and 1653 cm\textsuperscript{-1} due to two isomers (trans I and III in Figure 3). With RRSS-Ni\textsuperscript{II}HTIM\textsuperscript{2+}, a single isomer, we observed only one CO stretching band at 1630 cm\textsuperscript{-1}. We have determined CO\textsubscript{2} binding constants for both Ni(I) and Ni(II) in CH\textsubscript{3}CN. The CO\textsubscript{2} binding constant to Ni(II) cyclam is 1000 M\textsuperscript{-1}, much larger than that of Ni(I). (See below.)

![Figure 5](image)

**Figure 5.** A: Spectral change of Ni\textsuperscript{II}(cyclam)\textsuperscript{2+} by the addition of two equivalent of TEA in CH\textsubscript{3}CN. B: Spectral change of [Ni\textsuperscript{II}(cyclam)(TEA)\textsubscript{2}]\textsuperscript{2+} by the addition of CO\textsubscript{2} in a TEA containing CH\textsubscript{3}CN.

<table>
<thead>
<tr>
<th></th>
<th>rac-CoHMD\textsuperscript{+}</th>
<th>Ni(cyclam)\textsuperscript{2+}</th>
<th>RRSS-NiHTIM\textsuperscript{2+}</th>
<th>NiTM\textsuperscript{3+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>K\textsubscript{CO\textsubscript{2}} in CH\textsubscript{3}CN (M\textsuperscript{-1})</td>
<td>1.2 × 10\textsuperscript{4}</td>
<td>4</td>
<td>4</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>K\textsubscript{CO\textsubscript{2}} in H\textsubscript{2}O (M\textsuperscript{-1})</td>
<td>4.5 × 10\textsuperscript{8a}</td>
<td>11, 16\textsuperscript{b}</td>
<td>6.0</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>k\textsubscript{CO\textsubscript{2}} in CH\textsubscript{3}CN (M\textsuperscript{-1}s\textsuperscript{-1})</td>
<td>1.7 × 10\textsuperscript{8}</td>
<td>≤ 10\textsuperscript{7}</td>
<td>≤ 10\textsuperscript{7}</td>
<td>---</td>
</tr>
<tr>
<td>k\textsubscript{CO\textsubscript{2}} in H\textsubscript{2}O (M\textsuperscript{-1}s\textsuperscript{-1})</td>
<td>1.7 × 10\textsuperscript{8a}</td>
<td>3.3 × 10\textsuperscript{7b}</td>
<td>3 × 10\textsuperscript{7}</td>
<td>---</td>
</tr>
<tr>
<td>pK\textsubscript{a} of hydride in H\textsubscript{2}O</td>
<td>11.4\textsuperscript{a}</td>
<td>1.8\textsuperscript{b}</td>
<td>1.9</td>
<td>&lt; 0.5</td>
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\(\textsuperscript{a}\text{ ref. 11, } \textsuperscript{b}\text{ ref. 28}\)
This behavior was not observed when H₂O was used instead of CH₃CN. [NiII(cyclam)]²⁺ reacts with both TEA (or OH⁻) and CO₂ in H₂O to form a carbonate-bridged dimer, ([Ni(cyclam)]₂(CO₃)]²⁺ (UV-vis: 352, 548 and 900 nm; νCO₂: 1517, 1460, 1374 cm⁻¹). The structure was confirmed by an X-ray diffraction study.²⁶

CO₂ binding constants of Co(I) and Ni(I), and the pKₐ of ML(H⁻)²⁺ are shown in Table 1. As can be seen, the CO₂ binding constant for CoHMD⁺ is much larger than those for the Ni macrocycles. In H₂O, the binding constants are larger than the corresponding values in CH₃CN. CO₂ binding constants for Ni macrocycles are very small, however we see some effect due to ligands. Complexes with axial methyl groups, such as NiTM, show almost no binding of CO₂. The trend of the binding constants does not parallel the electrocatalytic activities which is RRSS-NiHTIM²⁺ > Ni(cyclam)²⁺ > NiTM²⁺.²⁷ The rate constants for CO₂ binding by CoHMD²⁺ are also about 10 times larger than those by Ni macrocycles. The pKₐ of cobalt hydride is 11.4, but the corresponding pKₐ values for the nickel macrocycles are less than 2.

5. CONCLUDING REMARKS

CoHMD²⁺ and Co(cyclam)²⁺ are good catalysts for photochemical CO₂ reduction because of the small CoII/L²⁺/CoI/L⁺ reorganization energy, the fast CO₂ binding to CoI/L⁺ (1.7 × 10⁸ M⁻¹ s⁻¹) and the large KCO₂. Our XANES results clearly indicate that active metal catalysts, such as [CoI/HMD]⁺, can promote two-electron transfer to the bound CO₂ (reduce CO₂ to CO₂⁻) and thereby facilitate reduction of CO₂. However since CoI/L⁺ reacts with H⁺ in CO₂ saturated water (pH ~4) the selectivity of CO₂ reduction in water is not high.

NiL²⁺ (L = cyclam and its derivatives without axial groups) are excellent electrocatalysts for CO₂ reduction. It is known that adsorbed NiI/L⁺ is the active species, however the CO₂ binding constants are not known. We find high selectivity for CO₂ reduction due to the low pKₐ of the hydride. Ni(cyclam)²⁺ may not be a good photocatalyst because of the large NiII/L²⁺/NiI/L⁺ reorganization energy, small CO₂ binding constant to NiL⁺ and instability of the trivalent state. We note that TEA is not an innocent electron donor. It can bind to the nickel center and make the energetics unfavorable for CO₂ reduction. The Ni(I) species is formed by irradiation of the solution containing [Ni(cyclam)(TEA)₂]²⁺ species at 313 nm probably due to the intramolecular electron transfer from TEA to Ni.

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