Organic molecules as mediators and catalysts for photocatalytic and electrocatalytic CO₂ reduction†

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Reduction of CO₂ by electrochemical and photoelectrochemical methods to produce carbon-rich fuels is a heavily pursued research theme. Most of the current efforts are focused on the development of transition-metal-based catalysts. In this tutorial review, we present an overview of the development of organic molecules as mediators and catalysts for CO₂ reduction. Four classes of organic molecules are discussed: tetraalkylammonium salts, aromatic esters and nitriles, ionic liquids, and pyridinium derivatives. It is shown that reactions mediated or catalyzed by these organic molecules can be competitive compared to their metal-catalyzed counterparts, both in terms of product selectivity and energy efficiency.

1. Introduction

Considering the Earth's abundance of fossil fuels, particularly coal, the world's energy problem is essentially related to the problem of carbon dioxide (CO₂).¹,² The excessive anthropogenic emission of CO₂ resulting from the combustion of fossil fuels has caused and will continue to cause climate change. The idea that CO₂ might be reduced to chemical fuels using renewable energies sounds like chemists' perfect revenge to the CO₂ problem.³ Selective and energy-efficient reduction of CO₂, however, is a chemical challenge that remains unsolved.

The development of electrochemical and photochemical CO₂ reduction catalysts is a recurring research theme. The majority of work has been focused on the catalytic properties of metal electrodes and transition metal complexes. Several excellent reviews are available on this topic.⁴⁻⁸ As pointed out in

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these reviews, a principal difficulty in CO₂ reduction is the kinetic inertness of CO₂. The one-electron reduction of CO₂ to CO₂⁻ has an $E^0$ of −1.90 V vs. NHE (normal hydrogen electrode) at pH = 7 (eqn (1)). Thus, even though multiple proton-coupled electron transfers to CO₂ are thermodynamically facile (eqn (2)–(6)), these reactions require large overpotentials to take place even with the help of catalysts. A second major difficulty in CO₂ reduction is the selectivity. Reduction of CO₂ may lead to CO, HCOOH, HCHO, CH₄OH, CH₄, or higher hydrocarbons. Furthermore, in protic solvents, hydrogen evolution (eqn (7)) is often favored over CO₂ reduction.

$$\text{CO}_2 + e^- \rightarrow \text{CO}_2^- , \ E^0 = -1.90 \text{ V}$$ (1)

$$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O}, \ E^0 = -0.53 \text{ V}$$ (2)

$$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCO}_2\text{H}, \ E^0 = -0.61 \text{ V}$$ (3)

$$\text{CO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{HCHO} + \text{H}_2\text{O}, \ E^0 = -0.48 \text{ V}$$ (4)

$$\text{CO}_2 + 6\text{H}^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}, \ E^0 = -0.38 \text{ V}$$ (5)

$$\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}, \ E^0 = -0.24 \text{ V}$$ (6)

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2, \ E^0 = -0.42 \text{ V} \text{ (pH} = 7)$$ (7)

This review presents the studies of organic molecules as mediators and catalysts for electrochemical and photochemical CO₂ reduction. Four classes of organic molecules are discussed: tetraalkylammonium salts, aromatic esters and nitriles, ionic liquids, and pyridinium derivatives. While the development of metal-free catalysts and cocatalysts is not yet in the main-stream of current research in CO₂ reduction, we believe that this alternative approach might lead to interesting discoveries and creative ideas in catalyst design.

2. Tetraalkylammonium salts as mediators

In 1983, Bockris and co-workers discovered the important role of electrolyte in electrochemical reduction of CO₂ at a p-type CdTe photocathode. In a 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in DMF containing 0.1% to 10% water, CO₂ could be reduced starting at $E = -1$ V vs. SCE under 600 nm illumination. Electrolysis at −1.6 V vs. SCE gave CO as the main reduction product in a 70% current efficiency. The quantum efficiency was close to unity. The results from two different supporting electrolytes, TBAP and lithium perchlorate (LiClO₄), were then compared. The photocurrent for CO₂ reduction when LiClO₄ was used as the supporting electrolyte was unstable and was less than 1/10 of the current observed with TBAP. It was proposed that tetrabutylammonium (TBA) ions provided a more hydrophobic environment at the electrode, which was beneficial for CO formation. Because there was a small change in the onset potential for CO₂ reduction when the water content was changed from 0.2–10%, two reactions were considered to occur (eqn (2) and eqn (8)). Without water, CO₂ reduction was not observed at the same potential. It was soon found that several other tetraalkylammonium perchlorates (C₂–C₈, i.e., tetraethyl to tetractyl) and even NH₄ClO₄ also promoted the photoelectrochemical CO₂ reduction. The particular photoelectrochemical behavior in the presence of NH₄ClO₄ led to the consideration that NH₄⁺ might serve as a redox mediator according to eqn (9).

$$2\text{CO}_2 + 2e^- \rightarrow \text{CO} + \text{CO}_3^{2-}$$ (8)

$$\text{NH}_4^+ + e^- \rightarrow \text{NH}_4^*$$ (9)

In 1989, Bockris and Wass studied the efficiency, kinetics, and mechanism of the photoelectrochemical reduction of CO₂ in DMF (5% water) solutions containing tetraethylammonium perchlorate (TEAP) as the electrolyte. This was a 700 mV improvement over the best metal electrode (In) at that time. The limiting photocurrent was 2.7 mA cm⁻² at −1.5 V vs. NHE. The Faradaic yield for CO production was about 90%, while small amounts of formaldehyde and formic acid were also detected. Based on the kinetic data, the following mechanism was proposed, showing the catalytic role of tetraalkylammonium cations (NR₄⁺) (eqn (10)–(13)).

$$\text{NR}_4^+ + e^- \rightarrow \text{NR}_4^*$$ (10)

$$\text{NR}_4^* + \text{CO}_2 \rightarrow \text{NR}_4^+ + \text{CO}_2^{2-}$$ (11)

$$\text{CO}_2^{2-} + \text{H}^+ + e^- \rightarrow \text{CO} + \text{OH}^-$$ (12)

$$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$$ (13)

An ammonium cation is first reduced by one-electron to form a radical (eqn (10)). The radical reacts with CO₂ to give the CO₂⁻ anion and to regenerate the ammonium cation (eqn (11)). The CO₂⁻ anion reacts further with a proton and an electron to give CO (eqn (12)). The reactions were proposed to occur on two reactive sites which have different adsorption energies for NR⁺ (Fig. 1). NR⁺ is adsorbed at site A, but not at site B. At site A, reactions (10) and (11) occur, and these reactions are light-insensitive. At site B, CO₂⁻ is reduced to CO, and this step requires light energy. The catalytic effect of tetraalkylammonium cations is to provide CO₂⁻ which is further reduced photoelectrochemically.

The photocatalytic activity of this system could be further enhanced using additives, and crown ethers were found to be the best additives. The photocurrents were positively shifted in the presence of crown ethers. The maximum promotional effect was observed when the size of the ring of the crown ether matched with the size of the NR⁺ ion (Fig. 2). Thus, when TEAP was used as the mediator and the electrolyte, the effect of crown ethers increased in the order of 24-crown-8 < 15-crown-5 < 18-crown-6. With 18-crown-6, a positive shift of 410 mV was
achieved, equivalent to $10^3$–$10^4$ times increase in rate constant. The crown ethers were proposed to be adsorbed on the electrode surface. In the absence of crown ethers, the $\text{NR}_4^+$ cation is adsorbed on the outer Helmholtz plane ($d \approx 8 \text{ Å}$). In the presence of crown ethers, $\text{NR}_4^+$ is brought onto the inner Helmholtz plane ($d \approx 3 \text{ Å}$). The electron transfer to $\text{NR}_4^+$ is then significantly faster. It was also proposed that in the presence of crown ethers, the reactions at sites A and B were coupled. It is interesting to note that methanol was produced in about 10% Faradaic efficiency when 18-crown-6 and 15-crown-5 were used as additives. No explanation was given for their formation.

In 1995, the group of Fujishima also reported the influence of supporting electrolytes in the selectivity of CO$_2$ reduction at a Cu electrode in a methanol + CO$_2$ system. CO was the main product when TBA salts were used as the supporting electrolytes. However, methyl formate (the electrolysis gave HCOOH as the CO$_2$ reduction product, and under the reaction conditions, HCOOH reacted with the CH$_2$OH solvent to give methyl formate), was the major product of CO$_2$ reduction when lithium salts were used as the electrolytes (Table 1). At the same time, hydrogen production became significant. Anions such as BF$_4^-$ or ClO$_4^-$ had little influence on the product distribution. The results were consistent with the notion that the hydrophobic environment at the electrode provided by TBA$^+$ ions was important for the selective reduction of CO$_2$ to CO. A more hydrophilic environment provided by the Li$^+$ ions would give rise to more other products such as CH$_3$COOH and H$_2$. Besides poorer selectivity, Li$^+$ ions also caused a larger overpotential for CO$_2$ reduction.

These studies suggest that tetraalkylammonium ions can promote CO$_2$ reduction in two ways: (1) the ions can create a hydrophobic micro environment at the electrode, which will lead to a more selective reduction to CO; (2) the ions can mediate the reduction through 1e reduced radical intermediates. Strictly speaking, these ions are not catalysts because they are in excess with regard to the quantity of the substrate (CO$_2$). It will be interesting to design systems in which the tetraalkylammonium ions are used in catalytic amounts.

### 3. Aromatic nitriles and esters as catalysts

The groups of Saveant and Vianello had studied the catalytic properties of radical anions for CO$_2$ reduction in an aprotic medium such as DMF. They observed a marked difference in the product distribution between direct electrolysis on Hg and electrolysis catalyzed by radical anions. Various mixtures of CO and oxalate were produced in direct electrolysis. In contrast, oxalate was the sole product if the reduction was catalyzed by radical anions of aromatic esters and nitriles (Fig. 3).

The mechanism of direct electrolysis at an inert electrode, such as mercury, was proposed to be a sequence of eqn (14)–(19).

\[
\text{CO}_2 + e^- \rightarrow \text{CO}_2^* \quad (14)
\]

\[
2 \text{CO}_2^* \rightarrow \quad (15)
\]

**Table 1  Effect of the supporting electrolytes on the products in the electrochemical reduction of CO$_2$ in a CO$_2$ + methanol medium (ref. 12)**

<table>
<thead>
<tr>
<th>Salt</th>
<th>Current density (mA cm$^{-2}$)</th>
<th>Potential (V vs. Ag QRE)</th>
<th>H$_2$</th>
<th>CO</th>
<th>CH$_4$</th>
<th>C$_2$H$_4$</th>
<th>CH$_3$COOH</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRABF$_4$</td>
<td>200$^a$</td>
<td>–2.1</td>
<td>3.5</td>
<td>76.0</td>
<td>2.6</td>
<td>1.1</td>
<td>23.4</td>
<td>106.6</td>
</tr>
<tr>
<td></td>
<td>333$^b$</td>
<td>–2.3</td>
<td>5.4</td>
<td>86.6</td>
<td>Not detected</td>
<td>Not detected</td>
<td>9.0</td>
<td>101.0</td>
</tr>
<tr>
<td>TBACIO$_4$</td>
<td>200$^a$</td>
<td>Not measured</td>
<td>9.7</td>
<td>48.1</td>
<td>7.6</td>
<td>5.2</td>
<td>25.4</td>
<td>96.0</td>
</tr>
<tr>
<td>LiBF$_4$</td>
<td>200$^a$</td>
<td>–3.8</td>
<td>33.3</td>
<td>8.6</td>
<td>7.2</td>
<td>0.0</td>
<td>54.5</td>
<td>103.6</td>
</tr>
<tr>
<td>LiClO$_4$</td>
<td>333$^b$</td>
<td>–4.1</td>
<td>58.9</td>
<td>5.9</td>
<td>6.7</td>
<td>Not detected</td>
<td>46.7</td>
<td>118.2</td>
</tr>
<tr>
<td>NH$_4$ClO$_4$</td>
<td>200$^a$</td>
<td>Not measured</td>
<td>84.6</td>
<td>7.9</td>
<td>5.3</td>
<td>0.4</td>
<td>Trace</td>
<td>98.3</td>
</tr>
</tbody>
</table>

$^a$ Electrolyses were performed at 40 atm at 20 ºC. $^b$ Electrolyses were performed at 40 atm at 25 ºC.
CO₂ is first reduced at the electrode to form a CO₂⁻⁻ anion (eqn (14)). Then two CO₂⁻⁻ anion radicals recombine to form oxalate (eqn (15)). But the CO₂⁻⁻ anion can also react with CO₂ to form an adduct (eqn (16)). Reduction of this adduct gives CO and carbonate (eqn (17)). Alternatively, reaction of this adduct with another molecule of CO₂⁻⁻ anion also leads to the formation of CO and carbonate (eqn (17')). If water is present in the reaction medium, the CO₂⁻⁻ anion can be protonated to form HCO₂⁻⁻ (eqn (18)), which after an additional electron transfer step (eqn (19) or (19')), produces formate. The effect of CO₂ concentration and temperature was also investigated. It was shown that the yields of CO increased not only when the concentrations of CO₂ increased, but also when the temperature decreased.

In the reactions catalyzed by aromatic ester and nitrile compounds, the first step is the reduction of ester or nitrile to an aromatic radical anion (eqn (20)). The radical anion then transfers the electron to CO₂ to form a CO₂⁺⁺ anion (eqn (21)), which dimerizes to give oxalate (eqn (22)). The path to the formation of CO (eqn (16) and (23)) is not favorable compared to the path to oxalate under these homogeneously catalyzed conditions.

\[
\begin{align*}
\text{CO}_2^- + \text{CO}_2 & \rightarrow \text{CO} + \text{CO}_2^- + \text{CO}_2^- \\
\text{CO}_2^- + \text{CO}_2^- & \rightarrow \text{CO} + \text{CO}_2^- + \text{CO}_2^- \\
\text{CO}_2^- + \text{H}_2\text{O} & \rightarrow \text{HCO}_2^- + \text{OH}^- \\
\text{HCO}_2^- + e^- & \rightarrow \text{CO}_2^- \\
\text{HCO}_2^- + \text{e}^- & \rightarrow \text{CO}_2^- \\
\text{2 CO}_2^- & \rightarrow \text{CO}_2 + \text{CO}_2^- \\
\text{A} + \text{e}^- & \rightarrow \text{A}^- \\
\text{CO}_2 + \text{A}^- & \rightarrow \text{CO}_2^+ + \text{A} \\
\text{CO}_2^- & \rightarrow \text{CO}_2 + \text{CO}_2^- \\
\end{align*}
\]

In addition to esters and nitriles, chrysene and picene were also employed as catalysts for electrochemical CO₂ reduction. The products derived from CO₂ were not identified. A small extent of photocatalytic CO₂ reduction was reported to occur with anthracene, pyrene, and oligo (p-phenylene). The main product was formate, and the proton likely came from the C–H bond of the sacrificial electron donor (amine).

The aromatic nitriles and esters can be considered as real electro-catalysts in these reactions because they are regenerated after transferring electrons to CO₂. A major drawback of these catalysts is the very negative potential that is required for their reduction. As a result, the overpotential is large. The high selectivity for oxalate formation is however attractive. It remains to be seen if CO₂ reduction might be mediated by more easily accessible aromatic radicals.

### 4. Ionic liquids as mediators

Electrochemical fixation and reduction of CO₂ in ionic liquids have drawn some attention recently. Ionic liquids are organic salts that exist in the liquid state at near room temperature. They are considered as green reaction media thanks to several characteristics, including high thermal and chemical stability, high viscosity, extremely low vapor pressure, and good solvating ability for organic and inorganic compounds. Moreover, ionic liquids exhibit high intrinsic conductivity and wide electrochemical potential windows. A number of reports show the electrochemically assisted reaction of CO₂ with amine to form carbamate in ionic liquid. While this reaction is strictly speaking not a net reduction of CO₂, it occurs via a one-electron reduction of CO₂ at first. Therefore these reports are described here as possible precedents that ionic liquids are used as redox mediators for CO₂ reduction. There are also examples where net reduction of CO₂ is conducted in ionic liquids on metal electrodes. The structures and notation of some representative ionic liquids are given in Fig. 4.

The electrochemistry in CO₂-containing ionic liquids needs to be treated with caution because CO₂ can influence the electrochemical potential window, viscosity, and conductivity of ionic liquids. In this sense, CO₂ might be treated as a non-innocent solute like water or halide ions. For example, it was previously shown that water decreases and halide ions increase the viscosity of ionic liquids. In 2009, Compton and co-workers studied the effect of CO₂ on the redox couple ferrocene/ferroacenium (Fe/Fe⁺) in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethane-sulfonfyl)imide (C₂MIM-NTf₂). In CO₂-saturated C₂MIM-NTf₂, significant increases in both the limiting current...
and the diffusion coefficient of Fe were observed. This work shows the non-innocent character of CO2 in electrochemistry in ionic liquids even if the apparent redox chemistry does not involve CO2. Very often, the physical parameters in ionic liquids are not independent of solutes like CO2, therefore skilled and precise sample preparation is important when working with ionic liquids.

In 2007, the groups of Feroci and Inesi reported an electrochemical method for the synthesis of carbamates from amines and carbon dioxide in a CO2-saturated solution of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (C4MIM-BF4), with ethyl iodide as the alkylating reagent (eqn (24)). 29

\[
\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^-
\]

The cathodic reduction of CO2 to CO2− was the first step in this reaction. The CO2− anion was proposed to yield carbonate anions (CO3^{2−}) in the ionic liquid, and the carbonate anion could react with amine to give carbamate anions, which further reacted with EtI to give ethyl carbamate as the final product (Fig. 5). The reactions were efficient with Pt and Cu as cathodes, at \(E = -2.4 \text{ V vs. Ag electrode, } P(\text{CO}_2) = 1.0 \text{ atm, and } T = 55 \text{ ºC. It was proposed that in C4MIM-BF4, the interaction of carbamate anions with C4MIM cations was weak, leading to an increased nucleophility of the oxygen of the carbamate anion. Consequently, } O\text{-alkylation was favored against N-alkylation.}

The same groups studied the same reactions, but in O2/CO2 saturated ionic liquids. 28 O2 was first reduced to superoxide (O2^-), which reacted with CO2 to give the peroxodicarbonate ion C2O6^{2−}. The latter then reacted with amine and alkyl halide to give carbamates (Fig. 6). Because O2^- can be generated in ionic liquids at a less negative potential (−1.4 V vs. Ag) than that of direct reduction of CO2 (~2.4 V vs. Ag) at a Pt or Cu electrode, this system appears advantageous than the O2-free system.

In 2008, Chu and coworkers studied the electrocatalytic reduction of CO2 on a nanostructured TiO2 film electrode to give low-density polyethylene (LDPE) (eqn (25)). 32

\[
2\text{CO}_2 + 6e^- + 4\text{H}^+ \rightarrow (\text{CH}_2=\text{CH}_2)_n + 2\text{H}_2\text{O}
\]

The reaction was conducted in a mixture of ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (C2MIM-BF4) and H2O (1:1 v/v). The current efficiency of LDPE was about 8–14% at ~1.30 V vs. SCE, but the turnover number was not reported. The overall reaction was proposed as shown in Fig. 7. First, Ti(II) species were produced by reduction of Ti(IV) at the TiO2 electrode. The Ti(II) species then reacted with CO2 to CO2− radical anions which were adsorbed on the surface. The CO2− anion then reacted with a proton and an electron to give surface-adsorbed CO, which was proposed to take 4 protons and 4 electrons to give surface-adsorbed CH2 species. Polymerization of CH2 species then gave polyethylene. There was however no direct evidence for the proposed surface-adsorbed species. It was also proposed that the role of the ionic liquid was to provide a high concentration of CO2 at the electrode surface. Thus, the ionic liquid was not recognized as a redox mediator in this study.
Barrosse-Antle and Compton reported the electrochemical reduction of CO$_2$ in 1-butyl-3-methylimidazolium acetate (C$_4$MIM-Ac) at a Pt electrode. They chose C$_4$MIM-Ac because it could interact with CO$_2$ chemically, which was different from other ionic liquids which absorbed gaseous CO$_2$ physically. The solubility of CO$_2$ in C$_4$MIM-Ac at 25 °C is as high as 1520 ± 50 mM, and the chemical adsorption of CO$_2$ was nearly irreversible. It was found that CO$_2$ could be reduced at ca. −1.3 V vs. cobaltocenium/cobaltocene couple, or −1.8 V vs. Ag wire in this ionic liquid. The diffusion coefficient of CO$_2$ in C$_4$MIM-Ac was also determined electrochemically. A very low value of 2.6 × 10$^{-12}$ m$^2$ s$^{-1}$ was found. Nevertheless, the reduction of CO$_2$ was found to be sustainable for 15 minutes, although the products were not determined.

Compton and Martindale then showed that formic acid could be produced by electrochemical reduction of CO$_2$ in a protic medium at a pre-anodised platinum electrode in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_2$mim]$_2$N$^+$-N$_3^-$). A strong acid, H[NTf$_2$]$_2$, was used as the proton source. In the absence of CO$_2$, hydrogen evolution started at −1.3 V vs. Pt wire. When CO$_2$ was introduced to the reaction medium, an additional reduction feature corresponding to CO$_2$ reduction was observed at −3.3 V vs. Pt wire. Formic acid was identified as one product by electrochemistry. The following reactions were proposed to occur on Pt: (eqn (26)–(30))

H$^+$ + e$^-$ → H$^*$ (26)

2H$^*$ → H$_2$ (27)

CO$_2$ + e$^-$ → CO$_2^*$ (28)

CO$_2^*$ + H$^*$ → H$^-$ + HCO$_2$H (29)

In 2011, Yu and coworkers synthesized an ionic liquid 1-ethyl-3-methylimidazolium chlorotrifluoroborate (C$_2$MIM-BF$_3$Cl) which can be used as an electrolyte, a solvent, and at the same time, a catalyst for electrochemical reduction of CO$_2$. The ionic conductivity of dry C$_2$MIM-BF$_3$Cl was 19.0 mS cm$^{-1}$ at room temperature, and the CO$_2$ solubility was 0.52 ± 0.25 mass% at 1 atm and room temperature. It was suggested that the anion of C$_2$MIM-BF$_3$Cl might catalyze CO$_2$ reduction through an interaction with CO$_2$ as shown in Fig. 8. The B–Cl bond (1.73 Å) is longer and weaker than the B–F bond (1.30 Å). The dissociation of BF$_3^-$ yields BF$_3$, which is an oxophilic Lewis acid. BF$_3$ can form a BF$_3$–CO$_2$ adduct through an oxygen atom of CO$_2$. In BF$_3$–CO$_2$, the C=O bond was proposed to be 1.18 Å, slightly longer than that in CO$_2$ gas (1.16 Å). The interaction of CO$_2$ with BF$_3$ makes it possible to reduce CO$_2$ at a less negative potential. Indeed, CO$_2$ reduction on Pt in this ionic liquid has a current density of 5.7 mA cm$^{-2}$ at −1.8 V vs. Ag wire. No significant CO$_2$ reduction was observed at this potential in other ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF$_4$) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM-N$^+$T$_2$F$_2$). A potential drawback of the system is the low thermal stability of the BF$_3$Cl anion, which decomposes at around 200 °C. Normally ionic liquids are thermally stable until 300 °C.

In 2011, Masel and coworkers reported an important progress in the reduction of CO$_2$ in ionic liquids. The one electron reduction of CO$_2$ to CO$_2^*$ has a very negative equilibrium potential in almost all solvents, leading to a high overpotential. They thought ionic liquid C$_2$MIM-BF$_4$ could complex CO$_2$ in a way that the formation of CO$_2^*$ was also facilitated (Fig. 9). A silver cathode was used as the catalyst for the reduction of CO$_2$ to CO, but C$_2$MIM-BF$_4$ was an indispensable mediator (a small amount of water was also present). The equilibrium potential for the reaction is 1.33 V.

CO$_2$ → CO + $\frac{1}{2}$ O$_2$ (31)

In this Ag-C$_2$MIM-BF$_3$ system, CO was produced at an applied voltage of 1.5 V, which indicated that the overpotential was only about 0.17 V. The Faradaic efficiency of CO production was greater than 96%, and only less than 3% of H$_2$ was formed. Without C$_2$MIM-BF$_4$, CO was not produced until a potential of 2.1 V was applied. The turnover frequency (with respect to Ag) varied from 0.8 to 1.4 s$^{-1}$ when the cell potential was changed from 1.5 to 2.5 V. Thus, the system does not exhibit an ideal Tafel behavior. In an electrolysis experiment, the cell was run at 2.5 V for 7 hours, and 26 000 turnovers were achieved. The system therefore appeared to be robust. Several improvements are still needed before this system can become commercially competitive. The rate of catalysis is still too slow, the electrode surface area is too small, and expensive catalysts (Pt and Ag) and membranes are still required. Nevertheless, this work...
represents a breakthrough for electrochemical CO₂ reduction in terms of energy and Faradaic efficiency.

In summary, ionic liquids have started to be used as solvents and mediators for electrochemical CO₂ reduction. Much emphasis is on the "green solvent" and high CO₂ solubility aspects of ionic liquids, but the stabilization of radical species including the CO₂⁺ radical is being recognized. In the latter aspect, the ionic liquids play a catalytic role. The origin of the stabilization is not fully understood and may become an interesting research topic.

5. Pyridinium derivatives as catalysts

The group of Bocarsly has developed an interesting system for electrocatalytic and photoelectrocatalytic CO₂ reduction using pyridinium as a homogeneous catalyst. Initially they found that CO₂ could be reduced to methanol electrochemically at a hydrogenated Pd electrode in a pH = 5.4 solution, with a Faradaic yield of 30% (eqn (32)).

\[ \text{CO}_2 + 6e + 6H^+ \xrightarrow{\text{Pd, pH=5.4}} \text{CH}_3\text{OH} + \text{H}_2\text{O} \]  

(32)

While hydrogen production was a major side reaction, CO₂ reduction could be sustained for 19 h with a current density of 40 µA cm⁻² at an overpotential of 200 mV. The pH of the reaction mixture was important. No CO₂ reduction was observed if the pH > 7. This indicated that protonated pyridine, or pyridinium, was the active catalyst. For this reason, the reactions were normally conducted at pH ≈ 5 (pKₐ of pyridinium = 5.2). If the pyridinium cation was replaced by the N-methyl pyridinium cation, the reduction of CO₂ could not be observed, further confirming the essential role of pyridinium. Because the efficiency of methanol production increased when the Pd electrode was pre-loaded with hydrogen, there was a possibility that Pd catalyzed the transfer of adsorbed hydrogen to CO₂ and the pyridinium cation served as a selective surface poison. This was deemed to be unlikely because earlier experiments showed that at the hydrogenated Pd electrode, CO₂ was reduced to HCOOH or CO, but not to CH₂OH.

It was later found that Pt could also be used as an electrode, and formic acid and formaldehyde were identified as intermediate products. In Galvanostatic electrolysis experiments at 40 µA cm⁻² (potential not reported), the Faradaic yields for HCOOH and CH₂OH formation were 11% and 22%, respectively. Because Pd and Pt are very active electrodes for hydrogen evolution, hydrogen evolution always outcompeted CO₂ reduction in the electrocatalysis. On the other hand, no detectable CO₂ reduction was observed when a more inert electrode such as glassy carbon was used. This indicates that the surface-adsorbed hydrogen atom plays an important role. It was also shown that the species being reduced is CO₂(sol), but not bicarbonate.

The selectivity for pyridinium-catalyzed methanol production increased significantly under photoelectrocatalytic conditions. Bocarsly and coworkers showed that at an illuminated p-GaP electrode, methanol was produced in a nearly 100% Faradaic yield at a potential of −0.22 V vs. SCE, that is, 300 mV more positive than the dark thermodynamic potential of −0.52 V for this system at pH = 5.2 (eqn (33)). The quantum efficiencies for CH₂OH formation under 365 nm illumination were 11% to 44% at E = −0.20 to −0.50 V vs. SCE. The efficiencies diminished to 1.3% to 2.6% at E = −0.20 to −0.50 V vs. SCE under 465 nm illumination. While solar-to-fuel efficiency is still too low for immediate commercial applications due to the poor overlap between the solar spectrum and the absorption spectrum of p-GaP, this chemistry appears to be the most efficient method for photoelectrochemical methanol formation. It was thought that the higher Faradaic yield for CO₂ reduction was due to the lower activity of p-GaP for hydrogen evolution.

\[ \text{CO}_2 + 6e + 6H^+ \xrightarrow{\text{p-GaP+hn}} \text{CH}_3\text{OH} + \text{H}_2\text{O} \]  

(33)

The CO₂ reduction at the p-GaP photoelectrode involves complex photoelectrochemistry at the semiconductor–liquid interface. Therefore, the mechanism of CO₂ reduction was studied under electrocatalytic conditions at a Pt electrode. In the absence of CO₂, a reduction peak was observed at −0.58 V vs. SCE at pH = 5.2. This peak was attributed to the reduction of pyridinium, formed by protonation of pyridine. Based on date from a thorough electrochemical and computational study, Bocarsly and coworkers proposed the following mechanism (Fig. 10). Under the experimental conditions, pyridine (1) accepts a proton to form pyridinium (2). 2 is then reduced to form pyridinyl radical (3), which reacts with CO₂ to form the key carbamate radical intermediate (4). This is the rate determining step of the catalysis. Further reaction of 4 leads to a surface-adsorbed hydroxymethyl radical (5), possibly with formic acid as an intermediate. The hydroxyformyl radical reacts with surface-bound hydrogen to give a formyl radical (6), which reacts with the pyridinyl anion to give formaldehyde and eventually methanol. For CO₂ reduction at the illuminated p-GaP electrode, because there are no surface-bound hydrogen atoms, the reaction shall proceed through formic acid. Consecutive reduction of formic acid with the pyridinyl radical leads to the formation of methanol (Fig. 10B).

A key intermediate in the mechanism proposed by Bocarsly and coworkers is the pyridinyl radical. While a reduction peak at −0.58 V vs. SCE was attributed to the electrochemical formation of this species under the catalytic conditions, computational studies suggested that the reduction potential of pyridinium was much more negative. For example, Tossell used CBS-QB3 calculation in combination with the CPCM solvation model to calculate the redox potentials and free energies of pyridine, pyridinium, and carbamate radical.

The redox potential of pyridinium was calculated to be −1.44 V vs. SCE, nearly 1 V more negative than the experimentally assigned value. This discrepancy prompted Keith and Carter to investigate further the acidities and redox potential of various proposed intermediate species computationally. The calculations were based on DFT-B3LYP/aug-cc-pVdz, and the solvation calculations (CPCM) omitted non electrostatic energy contributions, used one explicit water in a cluster-continuum approach, and
applied empirical values for the free energies of the proton gas phase and aqueous phase solvation. An extensive benchmarking was conducted to show that the predicted $pK_a$ values had a mean unsigned error of 0.9 $pK_a$ unit and a maximum error of 2.1 $pK_a$ unit. The calculated redox potentials for many substituted pyridinium species were within 0.2 V of the experimentally determined values. The calculations predicted a redox potential of 1.45 V vs. SCE for pyridinium, very close to the value predicted by Tossell$^{44}$ despite the different computational approach. The proton-coupled electron transfer redox potential for pyridine was predicted to occur at 1.47 V vs. SCE at pH = 5.3. The large difference between the redox potential of pyridinium and the observed reduction potential suggests that the pyridinyl radical does not play an important role in the catalysis as previously thought. Furthermore, the calculated $pK_a$ of the pyridinyl radical was as high as 27, suggesting that pyridinyl and similar $N$-protonated pyridinyl species are inactive. These computational results have changed the mechanistic view of pyridinium-catalyzed photoelectrochemical CO$_2$ reduction. However, it remains unclear what the reduction peak at 0.58 V vs. SCE is due to, and what is the active species in the system.

Despite the mechanistic uncertainty, pyridine or pyridinium is clearly a remarkable catalyst in the electrochemical and photoelectrochemical reduction of CO$_2$ to methanol. Substituted pyridines could also be used as precatalysts, but with lower efficiencies than pyridine.$^{41}$ The understanding of the role of the surface in this catalytic system will greatly promote the development of ever better catalysts.

6. Conclusions

Simple organic molecules such as tetraalkylammonium salts, aromatic esters and nitriles, ionic liquids, and pyridinium derivatives have been shown as competent mediators and catalysts for photoelectrochemical and electrochemical CO$_2$ reduction. The products can be CO, oxalate, formic acid, and methanol. It is interesting to note that the product selectivity in these reactions is often high, for example, CO, oxalate, and methanol have been produced exclusively in several systems. Another surprising finding is that CO$_2$ reduction can take place at low overpotentials using organic mediators and catalysts. For example, with C$_2$MIM-BF$_4$ as the mediator, CO is produced at an Ag electrode at an overpotential of less than 170 mV. Likewise, with the pyridinium cation as the catalyst, methanol is produced at a Pt electrode at an overpotential of less than 200 mV. Most of the CO$_2$ reduction reactions described here seem to involve one-electron charge-transfer mediators or catalysts, and the CO$_2^-$ radical appears to be an intermediate. The results prove that single-electron-transfer catalysists can be efficient for multiple-electron-transfer reactions. While current research in CO$_2$ reduction is centered on the development of transition-metal-based catalysts, we believe that redox-active organic catalysts should not be overlooked given their diversity and demonstrated efficiency. Furthermore, the combinations of metal-based and organic catalysts might result in superior bifunctional catalysts that would lead to an eventual practical process for the reduction of CO$_2$ into liquid fuels using renewable energies.

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Notes and references
