Is the Imidazolium Cation a Unique Promoter for Electrocatalytic Reduction of Carbon Dioxide?

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Abstract

There has been considerable recent interest in the use of the imidazolium cation as a promoter in the heterogeneous and homogeneous electrocatalysis of CO$_2$ reduction. However, despite its widespread use for this purpose, the mechanism by which imidazolium operates is not yet fully established. The present work reveals that enhanced catalytic activity is achieved by addition of many cations other than imidazolium. Under cyclic voltammetric conditions at a Ag electrode in acetonitrile solutions (0.1 M $n$-Bu$_4$NPF$_6$), 2.0 mM concentrations of imidazolium, pyrrolidium, ammonium, phosphonium and (trimethylamine)-(dimethylethylamine)-dihydroborate cations can all enhance the kinetics of catalytic CO$_2$ reduction with imidazolium and pyrrolidium being the most active. Analysis of the voltammetric data suggests that imidazolium cations achieve their impact by directly acting as co-catalysts with Ag whereas the other cations affect the reaction rate by modifying the electrochemical double layer. The results also confirm that the active form of the co-catalyst is the reduced imidazolium radical which forms a complex with CO$_2$ before being further reduced to CO or other products at Ag and not an imidazolium carboxylate formed between an imidazolium carbene and CO$_2$. In fact, imidazolium is deactivated during CO$_2$ reduction by the latter reaction. Addition of water inhibits this deactivation pathway allowing the imidazolium cation to act as in a long term for CO$_2$ reduction. In contrast, the pyrrolidium cation, where enhanced catalysis is attributed to an electrochemical double layer effect, retains its catalytic activity for very long periods of time regardless of the presence or absence of water.
1. Introduction

An efficient electrochemical route for the transformation of CO$_2$ into valuable chemicals and fuels is a much sought after goal in chemical processing. If coupled with renewable energy sources, the electrochemical transformation of CO$_2$ will not only translate a currently intractable waste material into a valuable chemical feedstock, but could help to address the persistent problem of energy storage from intermittent renewable energy sources. Unfortunately, CO$_2$ is chemically inert. The first one-electron reduction process to form CO$_2^-$ is kinetically slow and occurs at very negative potentials. Consequently, many potential catalysts including heterogeneous (such as metals$^{1-2}$, metal oxides$^2$ and non-metals,$^3-5$) and homogeneous ones (such as metal complexes$^6$) have been tested to see whether they lower the overpotential for CO$_2$ reduction in protic and aprotic media.

To improve the energy efficiency of the electrocatalytic reduction process, imidazolium-based ionic liquids (ILs) also have been introduced as promoters$^7-8$. They are promising for two reasons: they lower the reduction overpotential and they also suppress the competing H$_2$ evolution reaction.$^9-20$ Masel and co-workers$^{20}$ reported that 18 mol% of 1-ethyl-3-methylimidazolium tetrafluoroborate ([C$_2$mim][BF$_4$]) lowers the overpotential for CO formation on a silver (Ag) electrode in aqueous solutions by about 600 mV. Studies with in situ sum frequency generation spectroscopy indicate that a layer of [C$_2$mim]$^+$ adsorbed on the electrode surface promotes CO$_2$ conversion to CO on Ag and platinum (Pt) electrodes$^{14,17}$. The mechanism proposed (Scheme 1A) involves the formation of an adsorbed C$_2$mim-CO$_2$ complex — a key intermediate that lowers the overpotential for the reduction$^{17}$. In this context, imidazolium cations can be said to effectively promote the formation of CO. Rosenthal and co-workers$^9, 11, 16$ also found that imidazolium facilitates for reduction of CO$_2$ to CO on inexpensive and easily prepared post-transition metal electrodes in dry MeCN. A mechanism proposed in dry MeCN containing an imidazolium-based IL as an electrolyte implies that the
C-2 hydrogen on the imidazolium cation is an available source of protons and facilitates a thermodynamically more favourable proton coupled electron transfer reaction to form CO (Scheme 1B). The enhanced acidity of the C-2 hydrogen under a CO$_2$ atmosphere was also reported in studies of the electroreduction of acetophenone. However, in all these studies, the concentration of the imidazolium-based ionic liquids was at least 0.1 M. Under these conditions, a significant proton concentration is available for CO formation, making it difficult to verify the role of imidazolium as a promoter during CO$_2$ reduction. Furthermore, the presence of a high concentration of ionic liquid could enhance the solubility of CO$_2$ in the molecule solvent and hence influence the mechanism for CO$_2$ reduction.

Scheme 1. Mechanisms proposed in references$^{17, 21}$ for electrochemical reduction of CO$_2$ in aqueous (A) and dry MeCN (B) solutions containing imidazolium-based ionic liquids as electrolytes.

The lack of consensus concerning the mechanism by which imidazolium-based ionic liquids act during CO$_2$ reduction poses several questions: (1) What is the role of the imidazolium cation other than a proton source? (2) Do substituents on the imidazolium cation affect its catalytic activity and stability? (3) Does the electrolyte anion influence the CO$_2$ reduction reaction? (4) Is the catalytic effect specific to imidazolium cations? This work attempts to answer these questions. In order to test whether or not imidazolium cations do act
as co-catalysts by the mechanism described in Scheme 1A, only small concentrations (2.0 mM) were added to the aprotic solvent MeCN containing 0.1 M tetrabutylammonium hexafluorophosphate ($n$-Bu$_4$NPF$_6$) as the supporting electrolyte. The small concentration of additive means that (1) the available proton concentration from the imidazolium cation is negligible compared with the amount of CO$_2$ (0.27 M at 1 atm$^{24}$) and (2) the presence of the additive will not modify the CO$_2$ solubility appreciably, which is also confirmed by the fact that the CO$_2$ reduction peak current remains essentially unchanged upon addition of the additives (Figure 3, vide infra). Ag was chosen as the electrode material since it catalyses the formation of CO from CO$_2$ with high faradaic efficiency.$^1$ To systematically investigate the potential role that imidazolium cations play as co-catalysts or promoters in this reaction, the catalytic activity of 20 compounds, including ionic liquids from several commonly-used classes as well as alkylammonium salts, was investigated. The structures of their constituent ions are shown in Scheme 2.
2. Experimental section

2.1 Chemicals

The ionic liquids [C₄mim][BF₄], [C₁₀mim][BF₄], [C₁₀mim][TFSI], [C₁₆mim][BF₄],
[C₄mpyrld][BF₄], [C₄mpyrld][TFSI] and [C₃mPy][TFSI] were purchased from IOLITEC
(Germany). [N₁₁₄][TFSI], [S₂₂₂][TFSI], [C₁mim-CO₂] (≥ 80%), CTAB, Me₄NCl, n-Hex₄NBr,
n-Bu₄NTfO, n-Bu₄NBF₄, n-Bu₄NBr and ferrocene (Fc) (≥ 98%) were purchased from Sigma
Aldrich. [P₂₂₂₅][TFSI] was purchased from KANTO (Japan). MeCN and dimethyl sulfoxide-
d₆ (DMSO-d₆) were purchased from Merck (Germany). The ionic liquids were dried over
basic alumina for at least 24 h, then placed under vacuum at 80 °C for 24 h prior to use.
[C₆DABCO][TFSI] and [NHHB][TFSI] were synthesized by Dr. Thomas Ruether (CSIRO).
n-Bu₄NPF₆ (GFS Chemicals, Inc, 98%) was recrystallised twice from ethanol prior to use.
Other reagents were analytical grade and used as supplied by the manufacturer.

2.2 Voltammetric measurements

Voltammetric measurements were undertaken at 20 ± 2 °C using a CHI 700
electrochemical workstation (CH Instruments, Texas, USA) and a standard three-electrode cell.
For transient cyclic voltammetric measurements, a 3.0 mm diameter Ag disk electrode or a 1.0
mm diameter glassy carbon (GC) electrode were used as the working electrodes. A Pt wire was
used as a counter electrode. A Pt wire mounted into a capillary sealed with a sintered glass disk
served as a quasi-reference electrode. The solution used in the reference compartment was
MeCN (0.1 M n-Bu₄NPF₆). To convert the quasi-reference potential scale to a known scale,
0.5 mM Fc was added to each experiment and the voltammetric limits were extended to record
the reversible Fc/Fc⁺ process. Analysis of the data allows potentials to be converted to the
Fc/Fc⁺ scale. The working electrode was polished with an aqueous suspension of 0.3 µm
alumina on a polishing cloth (Buehler), sonicated in deionized water, rinsed sequentially with
deionized water and acetone, and dried under a flow of nitrogen (N₂) before use.
2.3 Bulk electrolysis

After the solution was saturated with CO$_2$, controlled potential bulk electrolysis experiments were undertaken at room temperature (20 ± 2 °C), under a CO$_2$ atmosphere in a gas-tight two-compartment divided cell with a Ag wire as the cathode and Pt wire as the anode. The volume for each compartment was 29 mL. The reference electrode was the same as that used in the voltammetric measurements. Both compartments were filled with 10 mL MeCN solution (0.1 M $n$-Bu$_4$NPF$_6$) containing 2.0 mM of the chosen ionic liquid and a constant stream of CO$_2$ was passed through the cell to achieve a saturated solution before the electrolysis.

During electrolysis, the solutions in both compartments were stirred. The volatile reduction products were identified by withdrawing 200 µL samples from the head space of the cathode compartment using a gas-tight syringe and injecting these samples into a gas chromatograph (Agilent 7820A) equipped with an Agilent HP-5 column. Helium was used as the carrier gas for CO detection and N$_2$ as the carrier gas for H$_2$ detection. The liquid phase reduction products were quantified using $^1$H and $^{13}$C NMR (400 MHz, Bruker) spectroscopy. Following bulk electrolyses, 400 µl of the condensed solution was withdrawn and 50 µl $p$-xylene was added as an internal standard. 400 µl DMSO-d$_6$ was also added to provide a deuterated solvent. $^1$H NMR spectra were used to quantify the concentrations of formate and imidazolium-based species, whereas $^{13}$C NMR spectra were used to quantify the oxalate concentration.

3. Results and discussion

3.1 Voltammetric measurements

Voltammetric studies were undertaken to investigate the influence of the ions listed in Scheme 2 on the electrocatalytic reduction of CO$_2$ at a Ag electrode. When needed, control experiments were undertaken using a GC electrode.
3.1.1 Catalysis with $[\text{C}_{10}\text{mim}]^+$

**Figure 1.** Cyclic voltammograms obtained with a 3.0 mm diameter Ag electrode at a scan rate of 0.1 V s$^{-1}$ in the absence and presence of 2.0 mM $[\text{C}_{10}\text{mim}][\text{BF}_4]$ under N$_2$ and CO$_2$ atmospheres in MeCN (0.1 M $n$-Bu$_4$NPF$_6$).

In initial studies, $[\text{C}_{10}\text{mim}][\text{BF}_4]$ was chosen to investigate the effect of the imidazolium cation on CO$_2$ reduction at a Ag electrode in MeCN (0.1 M $n$-Bu$_4$NPF$_6$). Voltammograms obtained under a N$_2$ atmosphere in the presence of 2.0 mM $[\text{C}_{10}\text{mim}][\text{BF}_4]$ display two irreversible reduction processes prior to the cathodic potential limit with peak potentials ($E_{p1,N2}$ and $E_{p2,N2}$) of -2.60 V and -2.85 V vs. Fe/Fe$^+$ (blue trace, Figure 1). These observations are consistent with other reports on the reduction of the $[\text{C}_4\text{mim}]^+$ cation which was shown to undergo a series of one electron reduction and dimerization processes to form a range of products including N-heterocyclic carbene, through a mechanism described in Scheme 3$^{25-28}$.
Scheme 3. Electrochemical reduction of [C₄mim][BF₄] at a Pt electrode²⁵-²⁷.

Under a CO₂ atmosphere, the voltammogram is significantly different to that under N₂ with only one irreversible reduction process being evident. The a peak potential ($E_{p,CO₂}$) value of -2.30 V vs. Fc/Fc⁺ (green trace, Figure 1) is about 0.3 V more positive than $E_{p1,N₂}$ detected under a N₂ atmosphere. As this reduction process is not observed in the absence of [C₁₀mim][BF₄], it is attributed to the reduction of either [C₁₀mim]⁺ or CO₂ followed by the formation of a reduced imidazolium-CO₂ complex, which according to a previous study,¹⁰ is influenced by the mass-transport associated with imidazolium. Since the reduction peak current ($I_{p,CO₂}$) magnitude is about five times that observed for the first reduction process under a N₂ atmosphere ($I_{p1,N₂}$), the enhancement cannot result solely from an increase in the number of electron transferred (e.g. 2 e⁻ vs. 1 e⁻ process). Moreover, the onset potential for CO₂ reduction ($E_{onset,CO₂}$) in the presence of [C₁₀mim][BF₄] is also significantly more positive (-1.95 vs. -2.27 vs. Fc/Fc⁺). This onset potential is derived from the intercept of a linear extrapolation of the low current flat and steep large current regions of the voltammogram. A similar positive shift was also observed in the electrochemical reduction of CO₂ at a Bi-modified electrode in the presence of 20 mM [C₂mim][BF₄]¹⁶. These observations suggest a different reduction mechanism occurs in the presence of CO₂ than under N₂ and this is most probably the catalytic
process reported by Wang et. al. in which a reduced imidazolium-CO$_2$ complex is further reduced to regenerate reduced imidazolium$^{29}$ (Scheme 4). As will be confirmed later, the reaction ultimately leads to the reduction of CO$_2$, so from now on this reduction process is referred to as “CO$_2$ reduction”.

![Scheme 4](image)

**Scheme 4** Mechanism proposed by Wang et. al.$^{29}$ for electrochemical activation of CO$_2$ by ionic liquid [C$_2$mim][BF$_4$].

As highlighted in the Introduction, much higher concentrations of imidazolium-based ionic liquids (typically 0.1 M) have been used as supporting electrolytes in previous studies on the electrochemical reduction of CO$_2$$^9$, $^{11}$, $^{16}$, $^{20}$, $^{30}$. Therefore, voltammetric experiments were also undertaken to establish the influence of the concentration of [C$_{10}$mim][BF$_4$] (Figure S1). The key parameters extracted from the voltammetric data are summarized in Table 1. The onset potentials ($E_{\text{onset,N2}}$ or $E_{\text{onset,CO2}}$) are almost independent of the concentration of [C$_{10}$mim][BF$_4$] ($C_{\text{IL}}$). The negative shift in $E_{p,CO2}$ as the concentration of [C$_{10}$mim][BF$_4$] increases can be attributed to an increase $IR_u$ drop ($R_u$ is typically 250 $\Omega$), associated with the concentration dependent increase in the peak current ($I_{p,CO2}$). Importantly, when the concentration of [C$_{10}$mim][BF$_4$] is doubled from 2.0 to 4.0 mM the $I_{p,CO2}/I_{p1,N2}$ ratio almost remains unchanged, implying the reaction occurs under pseudo first order conditions associated with a large
concentration excess of CO\(_2\). However, when the IL concentration is increased to 50.0 and 100.0 mM the ratio decreases due to the mass transport limitation associated with partial depletion of CO\(_2\). These data are consistent with theoretical predictions for a reaction catalysed by a dissolved electron transfer mediator.

### Table 1. Key parameters extracted from the voltammetric data obtained at a scan rate of 0.1 V s\(^{-1}\) under N\(_2\) or CO\(_2\) atmospheres in the presence and absence of [C\(_{10}\)mim][BF\(_4\)].

<table>
<thead>
<tr>
<th>C(_{IL})/mM</th>
<th>(E_{p,\text{N2}})/V</th>
<th>(E_{\text{onset, N2}})/V</th>
<th>(E_{p,\text{CO2}})/V</th>
<th>(E_{\text{onset, CO2}})/V</th>
<th>(I_{p,\text{CO2}}/I_{p,\text{N2}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>-2.60</td>
<td>-2.28</td>
<td>-2.30</td>
<td>-1.95</td>
<td>5.25</td>
</tr>
<tr>
<td>4.0</td>
<td>-2.62</td>
<td>-2.28</td>
<td>-2.34</td>
<td>-1.93</td>
<td>5.69</td>
</tr>
<tr>
<td>50.0</td>
<td>-2.85</td>
<td>-2.22</td>
<td>-2.74</td>
<td>-1.87</td>
<td>2.15</td>
</tr>
<tr>
<td>100.0</td>
<td>-2.96</td>
<td>-2.30</td>
<td>-2.84</td>
<td>-1.87</td>
<td>1.92</td>
</tr>
</tbody>
</table>

#### 3.1.2 The influence of other imidazolium-based ionic liquids

The imidazolium ionic liquids, [C\(_4\)mim][BF\(_4\)] and [C\(_{16}\)mim][BF\(_4\)] were chosen to ascertain if the alkyl chain length of the substituents on the imidazolium affects the catalytic activity for CO\(_2\) reduction at a Ag electrode. Cyclic voltammetric measurements were again undertaken under either N\(_2\) or CO\(_2\) atmospheres and in the absence and presence of 2.0 mM ionic liquid. With the exception of the magnitude of \(I_{p,\text{CO2}}\), the voltammetry was almost independent of the identity of the ionic liquid, as shown in Figure S2. Under a N\(_2\) atmosphere, two reduction processes were observed. The \(E_{p,\text{N2}}\) values are about -2.60 V vs. Fc/Fc\(^+\) in all ionic liquids and \(I_{p,\text{CO2}}/I_{p,\text{N2}}\) ratios are in the range 4.0–5.5 when a scan rate of 0.1 V s\(^{-1}\) is used. Under a CO\(_2\) atmosphere, both ionic liquids significantly promote the rate of CO\(_2\) reduction, as was the case with [C\(_{10}\)mim][BF\(_4\)]. As shown by inspection of data summarized in Table 2, the onset potential (\(E_{\text{onset, N2}}\) or \(E_{\text{onset, CO2}}\)) for reduction of CO\(_2\) is not strongly dependent on the identity of the added ionic liquid. The \(I_{p,\text{CO2}}:I_{p,\text{N2}}\) ratio increases with chain length on the alkyl substituent when comparing C\(_4\) and C\(_{10}\) data, but the value for C\(_{10}\) and C\(_{16}\) are similar. Increasing the alkyl chain length increases the bulkiness of the imidazolium cation which diminishes the likelihood that the reduced imidazolium intermediate will dimerize (see Scheme 3). Since the [C\(_{10}\)mim]\(^+\) and
[C_{16}mim]^{+} cations are more active in catalysing CO_{2} reduction, it is plausible that the monomers rather than dimers are the active forms of the co-catalysts or promoters. This hypothesis is consistent with that of Wang et al.\textsuperscript{29} who proposed in Scheme 4 by quantum chemistry that a reduced monomeric form of the imidazolium cation containing a C2-hydrogen is the key intermediate in CO\textsubscript{2} reduction.

**Table 2.** Key parameters extracted from the voltammetric data obtained at a Ag electrode with a scan rate of 0.1 V s\textsuperscript{-1} in the presence of 2.0 mM [C\textsubscript{4}mim]\textsuperscript{+}, [C\textsubscript{10}mim]\textsuperscript{+} and [C\textsubscript{16}mim]\textsuperscript{+}-based ionic liquids under N\textsubscript{2} and CO\textsubscript{2} atmospheres.

<table>
<thead>
<tr>
<th>IL</th>
<th>E_{p1,N2}/V</th>
<th>E_{onset,N2}/V</th>
<th>E_{p,CO2}/V</th>
<th>E_{onset,CO2}/V</th>
<th>I_{p,CO2}/I_{p1,N2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C\textsubscript{4}mim][BF\textsubscript{4}]</td>
<td>-2.65</td>
<td>-2.38</td>
<td>-2.30</td>
<td>-2.03</td>
<td>4.19</td>
</tr>
<tr>
<td>[C\textsubscript{10}mim][BF\textsubscript{4}]</td>
<td>-2.60</td>
<td>-2.28</td>
<td>-2.30</td>
<td>-1.95</td>
<td>5.25</td>
</tr>
<tr>
<td>[C\textsubscript{16}mim][BF\textsubscript{4}]</td>
<td>-2.60</td>
<td>-2.31</td>
<td>-2.32</td>
<td>-1.99</td>
<td>5.53</td>
</tr>
</tbody>
</table>

The influence of the anion on the catalytic activity of imidazolium-based ionic liquids for CO\textsubscript{2} reduction also has been investigated. In this case, 0.1 M of either [C\textsubscript{10}mim][TFSI] or [C\textsubscript{10}mim][BF\textsubscript{4}] was used as both the supporting electrolytes and co-catalysts with n-Bu\textsubscript{4}NPF\textsubscript{6} being absent. Cyclic voltammetric results obtained under N\textsubscript{2} and CO\textsubscript{2} atmospheres reveal that catalytic activity of [C\textsubscript{10}mim]\textsuperscript{+} is almost independent of either anion, as judged from the similarity of the onset potentials (Figure S3).

### 3.1.3 Electrochemical reduction of [C\textsubscript{10}mim]\textsuperscript{+} at a glassy carbon electrode

The results presented above confirm that imidazolium cations accelerate the rate of CO\textsubscript{2} reduction at a Ag electrode. However, to establish whether the cations act as the catalysts or co-catalyst with Ag, 2.0 mM [C\textsubscript{10}mim][BF\textsubscript{4}] in MeCN solutions were electrochemically reduced at a 1.0 mm diameter GC electrode under both N\textsubscript{2} and CO\textsubscript{2} atmospheres (GC has a low activity for CO\textsubscript{2} reduction\textsuperscript{22}). As shown in Figure 2, under a N\textsubscript{2} atmosphere, two reduction processes are observed at -2.81 V and -3.05 V vs. Fc/Fc\textsuperscript{+}, which is more negative than found at a Ag electrode (see Figures S1 and S2). Under a CO\textsubscript{2} atmosphere, two reduction processes were again seen at -2.65 V and -2.78 V on the first negative potential sweep, but only one
reduction process at -2.86 V on repetitive cycling of the potential. Presumably, reduction products generated on the first negative-going scan are irreversibly adsorbed onto the GC electrode and inhibit subsequent reduction reactions. Importantly, the positive shift in $E_{\text{onset,CO}_2}$ and enhancement of $I_{p,\text{CO}_2}$ is much less pronounced on GC leading to the conclusion that imidazolium cations act as a co-catalyst along with Ag for CO$_2$ reduction at a Ag electrode. In addition to those reduction processes, an oxidation process was observed at -1.0 V. This process is attributed to the oxidation of an adduct of CO$_2^-$ and [C$_{10}$mim] radicals generated during co-reduction of both CO$_2$ and [C$_{10}$mim]$^+$ according to a study by Hanc-Scherer et al..$^{31}$

![Figure 2. Cyclic voltammograms of 2.0 mM [C$_{10}$mim][BF$_4$] obtained at a 1.0 mm diameter GC electrode with a scan rate of 0.1 V s$^{-1}$ in MeCN (0.1 M $n$-Bu$_4$NPF$_6$) under N$_2$ (─) and CO$_2$ (─) atmospheres.](image)

3.1.4 Catalysis with [C$_4$mipyrd]$^+$ and [C$_4$mim]$^+$

Our data and other studies with imidazolium-based ionic liquids$^{10}$, raise two important questions.
Are other ionic liquid cations also capable of catalysing CO$_2$ reduction?

Does the C2-hydrogen of imidazolium play a critical role in CO$_2$ reduction?

To answer these questions, voltammetric studies were also undertaken using the pyrrolidinium ionic liquids [C$_4$mpyrdr][BF$_4$] and [C$_4$mpyrdr][TFSI], and [C$_4$mmim][BF$_4$] as additives; these ionic liquids do not contain a reactive C2-hydrogen in the cation. Pyrrolidinium ionic liquids are well-known for their high electrochemical stability and low proton availability.$^{32-33}$

Under a N$_2$ atmosphere (black and blue curves, Figure 3), no significant reduction current associated with the presence of 2.0 mM [C$_4$mpyrdr]$^+$ was detected within the potential window available in MeCN (0.1 M n-Bu$_4$NPF$_6$). Under a CO$_2$ atmosphere, the onset potential for CO$_2$ reduction shifted positively by 290 mV in the presence of 2.0 mM [C$_4$mpyrdr][BF$_4$] or [C$_4$mpyrdr][TFSI], a similar magnitude to that observed with 2.0 mM imidazolium-based ionic liquids (320 mV). The catalytic activity of [C$_4$mpyrdr]$^+$ for CO$_2$ reduction is also independent of the BF$_4^-$ or TFSI$^-$ these anions, as judged by the similarity of the $E_{\text{onset}, CO_2}$. Even if mechanistic details differ, the degrees by which imidazolium and pyrrolidinium cations promote CO$_2$ reduction are comparable and hence catalysis of CO$_2$ reduction is not unique to imidazolium-based ionic liquids.
Figure 3. Cyclic voltammograms obtained with a 3.0 mm diameter Ag electrode in MeCN (0.1 M \(n\)-Bu\(_4\)NPF\(_6\)) at a scan rate of 0.1 V s\(^{-1}\) with 2.0 mM [C\(_4\)mpyr][BF\(_4\)] or [C\(_4\)mpyr][TFSI] and under either N\(_2\) or CO\(_2\) atmospheres. Cyclic voltammograms of CO\(_2\) in the absence and presence of 2.0 mM [C\(_{10}\)mim][BF\(_4\)] recorded under the same conditions were shown for comparison.

When the concentration of [C\(_4\)mpyr]\(^+\) is increased up to 100.0 mM, \(E_{\text{onset,CO}_2}\) shifts positively (Figure S4), which differs from results with [C\(_{10}\)mim]\(^+\) where \(E_{\text{onset,CO}_2}\) is almost independent of its concentration. Furthermore, the magnitude of \(I_{p,CO_2}\) is minimally dependent on [C\(_4\)mpyr]\(^+\) concentration, which suggests that CO\(_2\) reduction in the presence of this cation is mass transport limited, whereas it is kinetically limited in the presence of imidazolium. It is highly unlikely that [C\(_4\)mpyr]\(^+\) acts as a redox mediator as the rate would have to be improbably high for the reduction process to be mass transport controlled at low [C\(_4\)mpyr]\(^+\) concentrations, based on a semi-quantitative estimation using simulation of the
voltammograms obtained with the DigiElch® software package (results not shown). Since CO₂ reduction occurs at a very negative potential which has to be much more negative than the potential of zero charge for a Ag electrode in MeCN, the electrochemical double layer will be dominated by cations. Since CO₂ reduction is an inner sphere process, the cations within the electrochemical double layer are expected to play an important role in the reduction reaction. Because [C₄mpyrd]⁺ is smaller than [n-Bu₄N]⁺, it may displace the latter cation in the electrochemical double layer. This can allow CO₂ to approach the electrode surface more closely and facilitate electron transfer. That is, the heterogeneous charge transfer constant for the CO₂⁰⁻ process may increase, as has been reported for other reactions.³⁴-³⁵ In addition to inducing an electrochemical double layer effect, [C₄mpyrd]⁺ also may promote the kinetics of CO₂ reduction by providing a nitrogen site for binding CO₂ and stabilizing the intermediate CO₂⁻ radical anion.

Electrochemical reduction of 2.0 mM [C₄mmim][BF₄] (Figure 4) at a Ag electrode under a N₂ atmosphere exhibited a reduction process with a peak potential of -3.02 V vs. Fc/Fc⁺. The voltammogram obtained under a CO₂ atmosphere had an E_onset,CO₂ value of -2.02 V vs. Fc/Fc⁺, which is similar to those obtained in the presence of pyrrolidinium-based ionic liquids, suggesting that [C₄mmim]⁺ also modifies the electrochemical double layer in a manner that favours CO₂ reduction.
Figure 4. Cyclic voltammograms obtained with a 3.0 mm diameter Ag electrode at a scan rate of 0.1 V s$^{-1}$ in MeCN (0.1 M n-Bu$_4$NPF$_6$) under N$_2$ (─) and CO$_2$ (─) atmospheres and in the presence of 2.0 mM [C$_4$mmim][BF$_4$] under N$_2$ (─) and CO$_2$ (─).

3.1.5 Catalysis with other ionic liquid cations

To further explore the catalytic influence of other ionic liquid cations on CO$_2$ reduction, the voltammetry in the presence of 2.0 mM concentrations of six other ionic liquids containing [TFSI]$^-$ as a common anion (structures are provided in Scheme 2) were studied in MeCN (0.1 M n-Bu$_4$NPF$_6$). Under a N$_2$ atmosphere, no reduction was observed prior to the cathodic potential limit for MeCN (0.1 M n-Bu$_4$NPF$_6$). Under a N$_2$ atmosphere, no reduction was observed prior to the cathodic potential limit for MeCN (0.1 M n-Bu$_4$NPF$_6$) in the presence of [N$_{1114}$][TFSI], ([P$_{2225}$][TFSI]), [NHHB][TFSI] and [C$_6$DABC][TFSI] (black curves, Figure 5). However, under a CO$_2$ atmosphere, the onset potentials for CO$_2$ reduction again shifted to significantly more positive values and the peak currents had mass transport limiting current characteristics (Figure 5). Thus the cations associated with all these ionic liquids also promote the electrochemical catalysis of
CO$_2$ reduction in a manner similar to [C$_4$mpyr]$.^+$ Interestingly, the magnitude of the potential shift is significantly larger for ionic liquids containing nitrogen heteroatoms than for those with phosphonium-based ones; implying CO$_2$ interacts more strongly with the more electronegative nitrogen heteroatom.

**Figure 5.** Cyclic voltammograms of 2.0 mM ionic liquids including [N$_{1114}$][TFSI], [P$_{2225}$][TFSI], [NHHB][TFSI] and [C$_6$DABCO][TFSI] obtained at a 3.0 mm diameter Ag electrode with a scan rate of 0.1 V s$^{-1}$ under N$_2$ (─) and CO$_2$ (—) atmospheres in MeCN (0.1 M $n$-Bu$_4$NPF$_6$). Cyclic voltammogram of CO$_2$ (—) in MeCN (0.1 M $n$-Bu$_4$NPF$_6$) obtained at a 3.0 mm Ag electrode with a scan rate of 0.1 V s$^{-1}$ is included in each figure for comparison.

For solutions containing 2.0 mM [C$_3$mpy][TFSI]) or [S$_{222}$][TFSI] and under a N$_2$ atmosphere, irreversible reduction processes associated with the cations were found at -1.76 V
and at -2.21 V vs. Fc/Fc⁺, respectively (Figure 6). However, in these cases, the irreversible reduction process remains unaffected under a CO₂ atmosphere (Figure 6), indicating the absence of interaction between the reduced species and CO₂. Furthermore, if the positive charge on the cation is removed upon reduction, it cannot modify the electrochemical double layer.

**Figure 6.** Cyclic voltammograms of 2.0 mM [C₃mpy][TFSI] and [S₂₂₂][TFSI] obtained at a 3.0 mm diameter Ag electrode with a scan rate of 0.1 V s⁻¹ under N₂ (─) and CO₂ (—) atmospheres in MeCN (0.1 M n-Bu₄NPF₆). Cyclic voltammogram of CO₂ (—) obtained under the same conditions is included in each figure for comparison.

In summary, the \(E_{\text{onset,CO}_2}\) values obtained in the presence of 2.0 mM ionic liquid promoters, decrease in the order: [C₁₀mim]⁺ (-1.95 V) > [C₄mpyrđ]⁺ (-1.98 V) > [C₁₆mim]⁺ (-1.99 V) > [N₁₁₁₄]⁺ (-2.0 V) > [C₄mmim]⁺ (-2.02 V) > [C₄mim]⁺ (-2.03 V) > [C₆DABCO]⁺ (-2...
2.04 V) > [NHB]⁺ (-2.11 V) > [P₂₂₂₃]⁺ (-2.17 V), suggesting that [C₁₀mim]⁺ and [C₄mpyr]⁺ are superior for this application.

3.1.6 Catalysis with ammonium cations

The results presented above show that catalysis of CO₂ reduction by addition of ionic liquids is not restricted to imidazolium based ones. To test if the cation induced catalysis is general, three simple ammonium-based salts having variable alkyl lengths in their cations were also examined with respect to their influence for the electroreduction of CO₂ at a Ag electrode. Voltammetric results from studies of 2.0 mM Me₄NCl, CTAB and n-Hex₄NBr in MeCN (0.1 M n-Bu₄NPF₆) under N₂ and CO₂ atmospheres are shown in Figure 7. Under a N₂ atmosphere, Me₄N⁺ form Me₄NCl is reduced at -2.86 V vs. Fc/Fc⁺. By contrast, the other two additives n-Hex₄NBr and CTAB are more difficult to reduce based on their reduction onset potentials of -2.95 and -3.15 V vs. Fc/Fc⁺.
Figure 7. Cyclic voltammograms recorded on a 3.0 mm diameter Ag electrode with a scan rate of 0.1 V s⁻¹ in MeCN (0.1 M n-Bu₄NPF₆) containing 2.0 mM Me₄NCl, CTAB and n-Hex₄NBr, respectively, under N₂ (─) and CO₂ (─) atmospheres. Cyclic voltammogram of CO₂ (─) in MeCN (0.1 M n-Bu₄NPF₆) under the same conditions is included in each figure for comparison.

Under a CO₂ atmosphere, $E_{\text{onset,CO}_2}$ shifts positively in the presence of Me₄NCl or CTAB and the CO₂ reduction process is mass transport controlled. Again, catalysis is attributed to a modification of the electrochemical double layer. Even though [Me₄N]⁺ can be electrochemically reduced to a compound that could act as an electron transfer mediator, any contribution from this mechanism should be insignificant. No impact on CO₂ reduction was observed in the presence of 2.0 mM n-Hex₄NBr. However, this cation is larger and has a lower
charge density than \([n-\text{Bu}_4\text{N}]^+\), so at a 2.0 mM concentration it is not expected to modify the double layer to any significant extent.

To systematically vary the size of the cation and identity of the anion in ammonium-based salts, voltammetric reduction of CO\(_2\) in MeCN was undertaken in 0.1 M solutions of six tetraalkylammonium salts. The cation size difference was probed by cyclic voltammograms obtained in the presence of \(n\)-Hex\(_4\)NBr, \(n\)-Bu\(_4\)NPF\(_6\) and Et\(_4\)NI and the anion identity using \(n\)-Bu\(_4\)NPF\(_6\), \(n\)-Bu\(_4\)NBF\(_4\) and \(n\)-Bu\(_4\)NBr. Results are summarized in Figure S5. Utilizing this tetraalkylammonium group, \(E_{\text{onset,CO}_2}\) was most positive when the smallest cation was used (\([n\text{-Et}_4\text{N}]^+) and became more negative as the cation size increased. This trend is consistent with an electrochemical double layer effect since the smaller tetraalkylammonium cations also have a higher charge density and they can more effectively stabilize CO\(_2^-\), which facilitates CO\(_2\) reduction. The identity of the anions ([PF\(_6\)]^-, [BF\(_4\)]^-, [Br]) used does not significantly affect the reduction reaction with the \([n\text{-Bu}_4\text{N}]^+\) series of salts (inset Figure in Figure S5).

### 3.1.7 The influence of water

Proton coupling to electron transfer is known to lower the overpotential for CO\(_2\) reduction\(^1\). Adventitious water, a proton source, is always likely to present and may play a role. The impact of deliberately added water on the reduction of CO\(_2\) in the presence of 2.0 mM [C\(_{10}\text{mim}\)][BF\(_4\)] or [C\(_4\text{mpyr}\)][BF\(_4\)] in MeCN (0.1 M \(n\)-Bu\(_4\)NPF\(_6\)) was therefore examined.

As described above, the reduction of 2.0 mM [C\(_{10}\text{mim}\)][BF\(_4\)] with no deliberately added water and in the presence of CO\(_2\) exhibits an irreversible catalytic reduction process with an \(E_{p,\text{CO}_2}\) value of -2.30 V vs. Fe/Fe\(^+\) (black trace, Figure 8a). Upon addition of 0.5% water, the peak current increases significantly confirming that water promotes the catalytic activity of imidazolium. However, the potential for direct reduction of CO\(_2\) at a Ag electrode also becomes more positive (olive green trace, Figure 8a), so that the mediated and direct CO\(_2\) reduction
processes overlap. Upon addition of more H$_2$O, the extent of overlap increased and with 2.0% added H$_2$O, the two processes fully merged giving rise to an overall mass transport controlled process with an $E_{p,CO_2}$ value of -3.09 V. However, the addition of water does not significantly alter the onset potential for CO$_2$ reduction.

**Figure 8.** The impact of water on cyclic voltammograms obtained with a 3.0 mm diameter Ag
electrode at a scan rate of 0.1 V s$^{-1}$ in MeCN (0.1 M $n$-Bu$_4$NPF$_6$) containing 2.0 mM of [C$_{10}$mim][BF$_4$] (a) or [C$_4$mpyr][BF$_4$] (b) under a CO$_2$ atmosphere: no added water (—), 0.5% added water (—), 1.0% added water (—), 2.0% added water (—) and without IL but with 0.5% (—) or 1.0% (—) added water.

Results from experiment with 2.0 mM [C$_4$mpyr][BF$_4$] under a CO$_2$ atmosphere are shown in Figure 8b. Without added water, introduction of the pyrrolidinium cation shifts the onset potential for CO$_2$ reduction in a positive direction and catalyses CO$_2$ reduction. When water is now added to this solution, the peak current and the onset potential are almost unchanged. This different response to that with imidazolium reinforces the conclusion drawn previously that the mechanisms by which pyrrolidinium and imidazolium cations catalyse CO$_2$ reduction are not the same. The slightly diminishes peak current found when 2.0% H$_2$O was added may reflect a decrease in the solubility of CO$_2$ as the water concentration increases$^{37}$.

3.2 Bulk electrolysis and mechanistic analysis

Catalysis of CO$_2$ reduction can affect not only voltammetric characteristics, but may also influence the product distribution. To investigate the identity of the cation additive in this context, bulk electrolysis experiments were undertaken in a divided cell using a large surface area Ag wire as the cathode in MeCN (0.1 M $n$-Bu$_4$NPF$_6$) along with 2.0 mM [C$_{10}$mim][BF$_4$] or [C$_4$mpyr][BF$_4$]. Water (1.0%) was deliberately added in some of these experiments. Unless otherwise stated, the applied potential ($E_{\text{appled}}$) was -2.30 V vs. Fe/Fe$^+$, which corresponds to $E_{p,CO_2}$ in the presence of 2.0 mM [C$_{10}$mim]$^+$ under voltammetric conditions with a scan rate of 0.1 V s$^{-1}$. This potential was selected to avoid any significant contribution from the direct reduction of CO$_2$ at a Ag electrode, which could be particularly significant in the presence of 1.0% H$_2$O. After electrolysis, the gaseous products (CO and H$_2$) were detected by gas chromatography and the liquid phase products (formate and oxalate) were concentrated before detection by NMR spectroscopy. The products obtained under different conditions and their faradaic efficiencies (FE) are summarized in Table 3. It should be noted that to calculate the
FE, the charge used to reduce the co-catalyst, \([C_{10}\text{mim}]^+\) was ignored since its magnitude insignificant relative to the total charge consumed.

Under all conditions examined, reduction of \(\text{CO}_2\) forms \(\text{CO}\) and \(\text{C}_2\text{O}_4^{2-}\) as the major products, with only a small amount of formate (\(\text{FE} < 1.0\%\)). In the absence of either ionic liquid or added water, an \(E_{\text{appied}}\) value of -2.6 V was used instead of -2.3 V to obtain adequate current density. The major products under this condition are \(\text{CO}\) and \(\text{C}_2\text{O}_4^{2-}\) with \(\text{FE}\) values of 53.9\% and 39.3\%, respectively. The \(\text{FE}\) for \(\text{H}_2\) is negligible due to the aprotic environment. Upon addition of 2.0 mM ionic liquid, \(\text{CO}\) and \(\text{C}_2\text{O}_4^{2-}\) remain the major products although their \(\text{FE}\) values do depend on the identity of ionic liquid with a higher \(\text{FE}\) value for \(\text{CO}\) detected in the presence of \([\text{C}_4\text{mpyrld}][\text{BF}_4]\).

### Table 3 Products formed by bulk electrolysis of \(\text{CO}_2\) at a Ag cathode in MeCN (0.1 M \(n\)-\(\text{Bu}_4\text{NPF}_6\)).

<table>
<thead>
<tr>
<th>Additives</th>
<th>(E_{\text{appied}}/V) vs. (\text{Fc/Fc}^+)</th>
<th>Charge /C</th>
<th>(\text{H}_2)</th>
<th>(\text{CO})</th>
<th>(\text{C}_2\text{O}_4^{2-})</th>
<th>(\text{HCO}_2^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>without IL</td>
<td>-2.6(^b)</td>
<td>12.5</td>
<td>0.2</td>
<td>53.9</td>
<td>39.3</td>
<td>0.8</td>
</tr>
<tr>
<td>2.0 mM ([C_{10}\text{mim}][\text{BF}_4])</td>
<td>-2.3</td>
<td>28.5</td>
<td>0</td>
<td>45.1</td>
<td>53.4</td>
<td>0.4</td>
</tr>
<tr>
<td>2.0 mM ([\text{C}_4\text{mpyrld}][\text{BF}_4])</td>
<td>-2.3</td>
<td>50.1</td>
<td>0</td>
<td>66.4</td>
<td>28.4</td>
<td>0.8</td>
</tr>
<tr>
<td>without IL + 1.0% (\text{H}_2\text{O})</td>
<td>-2.3</td>
<td>15.3</td>
<td>87.4</td>
<td>9.5</td>
<td>3.5</td>
<td>---</td>
</tr>
<tr>
<td>2.0 mM ([C_{10}\text{mim}][\text{BF}_4]) + 1.0% (\text{H}_2\text{O})</td>
<td>-2.3</td>
<td>61.8</td>
<td>1.8</td>
<td>70.4</td>
<td>27.1</td>
<td>0.4</td>
</tr>
<tr>
<td>2.0 mM ([\text{C}_4\text{mpyrld}][\text{BF}_4]) + 1.0% (\text{H}_2\text{O})</td>
<td>-2.3</td>
<td>50.2</td>
<td>0.4</td>
<td>58.4</td>
<td>42.6</td>
<td>0.8</td>
</tr>
</tbody>
</table>

\(^a\) Water content: 5.0 mM.
\(^b\) This more negative potential was chosen to achieve a reduction rate that is comparable to that found in the presence of IL additive.

With added water, but in the absence of ionic liquid, \(\text{H}_2\) is the main product (\(\text{FE} = 87.4\%\)). The hydrogen evolution reaction (HER) is almost completely suppressed by addition of ionic liquids. Since HER is an inner-sphere process, the presence of any surface active species is expected to hinder its formation. In the presence of water and imidazolium-based ionic liquid, the \(\text{FE}\) for \(\text{CO}\) formation is also significantly enhanced.

CO formation can occur regardless of proton availability \(\text{via}\) either homogenous or heterogeneous pathways. In the homogeneous pathway and in the absence of protons, \(\text{CO}_2\) is
first reduced to $\text{CO}_2^-$ at the electrode surface. If this intermediate becomes detached, it can then react with dissolved $\text{CO}_2$ to form CO via a multi-step pathway (Scheme 5\textsuperscript{23}). If $\text{CO}_2^-$ remains attached, it can dimerise to form oxalate (Scheme 6\textsuperscript{23}). In the presence of $\text{H}^+$, a proton coupled heterogeneous reaction occurs to form CO (Scheme 7\textsuperscript{1, 23}). In the presence of added water and ionic liquids, clearly, Scheme 6 is dominant.

\begin{align*}
\text{CO}_2 + e^- & \rightleftharpoons \text{CC}_2^-(1) \\
\text{CC}_2^- + \text{C}_2 & \rightleftharpoons \text{CO}_3(2) \\
\text{CO}_3^- + \text{e}^- & \rightleftharpoons \text{C}_4 + \text{CC}_2^2-(3) \\
\text{CC}_3^- + \text{CO}_2^- & \rightleftharpoons \text{C}_4 + \text{CO}_3^2^- + \text{C}_2(4)
\end{align*}

**Scheme 5.** Homogeneous pathway for CO formation

\[ 2\text{CO}_2^- \rightarrow \text{C}_2\text{O}_4^{2-} \]

**Scheme 6.** The dimerization of the carbon dioxide radical anion in the absence of $\text{H}^+$

\[ \text{CC}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CC} + \text{H}_2\text{O} \]

**Scheme 7.** Heterogeneous pathway for CO formation in the presence of $\text{H}^+$.

To investigate the stability of ionic liquids under bulk electrolysis conditions, the amount of CO formed and FE were measured as a function of time (or overall charge consumed) with $E_{\text{applied}}$ -2.3 V and in the presence of 2.0 mM ionic liquid (Figure 9). With 2.0 mM [C\textsubscript{10}mim][BF\textsubscript{4}] and no added H\textsubscript{2}O, the current initially remains relatively constant and the amount of CO formed is approximately proportional to the charge passed up to 20 C. However, when the electrolysis proceeds further, both the current passed and FE for CO production fall rapidly, most probably because [C\textsubscript{10}mim]$^+$ is consumed during bulk electrolysis. Once 28.5 C
of charge had been passed, the catalytic current is essentially zero. However, catalytic activity of imidazolium is recovered by addition of 1.0% water. In contrast, in the presence of \([C_4mpyr]^{+}\), the FE for CO formation is almost independent of electrolysis time, with the small diminution in the reduction current at long times probably due to the consumption of CO_2.

![Graph](image)

**Figure 9.** The quantity of CO formed and FE for CO formation at a Ag wire cathode during bulk electrolysis of CO_2 in the presence of 2.0 mM [C_{10}mim][BF_4] or [C_4mpyr][BF_4] in MeCN (0.1 M \(n\)-Bu_4NPF_6).

The addition of 1.0 % water to 2.0 mM [C_{10}mim][BF_4] solutions significantly increases the FE for CO formation. Moreover, the current now remains almost constant when up to 60 C of charge is passed. Clearly, the presence of water significantly extends the catalytic lifetime of imidazolium for CO_2 reduction, indicating that a catalytic active form of the imidazolium cation is regenerated when water is present and that this is important in the catalytic reduction
of CO₂. By contrast, the addition of 1.0 % water to 2.0 mM solutions of [C₄AMILY][BF₄] does not increase the FE for CO formation or the stability of [C₄AMILY]⁺ to any appreciable extent.

The stability of the ionic liquid cations was assessed by examining the solutions before and after electrolysis by cyclic voltammetry. As seen in Figure S6a, in the absence of deliberately added water, the catalytic reduction process associated with [C₁₀mim]⁺ has essentially disappeared after bulk electrolysis, even though the unreacted CO₂ is still ~ 79% of the original solution concentration, as judged from the magnitude of the mass-transport limited current for CO₂ reduction. By contrast, in 2.0 mM [C₄AMILY][BF₄] solutions (Figure S6b) the onset potential for reduction remains unchanged after electrolysis and the CO₂ reduction peak current decreases by about 32 % due to the consumption of CO₂. In the presence of 1.0 % added water, the onset potential and voltammetric features were almost the same before and after bulk electrolysis when the charges listed in Table 3 were passed (Figures S6c, d). The magnitude of the peak reduction current after electrolysis decreases because the concentration of dissolved CO₂ decreases. These observations again suggest that in the absence of water, imidazolium cations are consumed during bulk electrolysis, while the presence of water extends the catalytic lifetime for CO₂ reduction. By contrast, the stability of [C₄AMILY]⁺ for CO₂ reduction is unaffected by the presence of water.

3.3 NMR investigation of the deactivation mechanism for imidazolium cations

To better understand the deactivation mechanism associated with the imidazolium cation under bulk electrolysis conditions, ¹H NMR spectra were used to identify the products generated. The ¹H NMR spectrum for a control solution containing 12.5 mM [C₁₀mim][BF₄] in MeCN is shown in Figure 10a. On the basis of the ¹H proton chemical shifts reported in the literatures¹⁰,²⁵, H₁, H₂ and H₃ resonances are assigned to the hydrogens from the imidazolium ring, and H₄ and H₅ resonances are the hydrogens from the alkyl groups.
Figure 10. $^1$H NMR spectra of (a) 12.5 mM [C$_{10}$mim][BF$_4$] in MeCN, (b) a concentrated solution of 2.0 mM [C$_{10}$mim][BF$_4$] in MeCN (0.1 M n-Bu$_4$NPF$_6$) after electrolysis (28.5 C) under a CO$_2$ atmosphere and (c) as for (b) but with 1.0% added water.

After reductive electrolysis (28.5 C) of a 2.0 mM solution of [C$_{10}$mim][BF$_4$] in MeCN (0.1 M n-Bu$_4$NPF$_6$) new resonances were detected in the spectrum, labelled H', H', H', H' and H', while the resonance for H$_1$ had shifted from 8.97 to 9.35 ppm (Figure 10b) due to the solution becoming more basic during the course of the bulk electrolysis experiment. The heights of all the resonances related to the imidazolium cation significantly decreased. Similar new resonances have been reported after the electrochemical reduction of CO$_2$ in the presence of 100 mM [C$_2$mim][TFSI] in MeCN$^{10}$. This study identified the formation of a carboxylate complex formed between an imidazolium carbene and CO$_2$. This species is also well documented as a product arising from a complexation reaction between an imidazolium
carbene and CO$_2$. Thus, it is concluded that the C2-H of the imidazolium cation is consumed during bulk electrolysis to form carbene, which reacts with CO$_2$ to generate the carboxylate complex that gives rise to the H’$_2$, H’$_3$, H’$_4$ and H’$_5$ resonances, derived from H$_2$, H$_3$, H$_4$ and H$_5$, respectively.

It is also notable in Figure 10b, that the imidazolium dimer is not detected. The bulky alkyl group on the imidazolium cation would hinder dimerization. Apparently, imidazolium dimers do not act as co-catalysts for CO$_2$ reduction under our bulk electrolysis conditions. The integrated $^1$H NMR resonances (a) and (b) in Figure 10 show that the majority of the [C$_{10}$mim]$^+$ cations were converted to the carboxylate complex during bulk electrolysis. Upon addition of 1.0% water (Figure 10c), the integrated resonance for the $^1$H in imidazolium increases, as expected if [C$_{10}$mim]$^+$ is regenerated by protonation of the carbene in the carboxylate complex. This result is consistent with the fact that the catalytic activity of the deactivated [C$_{10}$mim]$^+$ is recovered upon addition of water. On the basis of the NMR data, it is concluded that the imidazolium carboxylate formed between carbene and CO$_2$ does not catalyse reduction of CO$_2$, and results a deactivated form of the imidazolium cations. These conclusions are consistent with the experimental observations of Sun et. al.$^{10}$ and Watkins et. al.$^{19}$ The former authors suggested that CO and imidazolium carboxylate are major products in the electrochemical reduction of CO$_2$ at a Pb cathode in MeCN solution containing 0.1 M [C$_2$mim][TFSI] as the supporting electrolyte.$^{10}$ The latter authors reported the electrochemical reduction of 1,3-dimethylimidazolium-2-carboxylate ([C$_1$mim-CO$_2$]) in dry 1-ethyl-3-methylimidazolium trifluoroacetate.$^{19}$ No catalytic activity for CO$_2$ reduction was found under either argon or CO$_2$ atmospheres. These results are also consistent with the fact that imidazolium carboxylates are formed by a complexation reaction between carbene and CO$_2$, and that they are the precursors for generating of $N$-heterocyclic carbene catalysts in relevant area of organic syntheses.$^{39}$
In summary, a combination of data obtained by voltammetry and bulk electrolyses of solutions containing imidazolium ionic liquids with $^1$H NMR detection of products allows a mechanism for catalytic reduction of CO$_2$ to be proposed (Scheme 8) using CO formation as an example. In this scheme, all imidazolium related species are assumed to be adsorbed on the silver electrode surface since clear evidence (Figures 1 and 2) suggests that the electrode material also plays a decisive role in the catalytic reduction of CO$_2$. This scheme is analogous to that proposed by Wang et al. on the basis of theoretical calculations. According to this mechanism, an imidazolium cation is reduced to generate a neutral radical. This radical then forms a complex with CO$_2$ that is more easily reduced at the Ag electrode leading to formation of CO through a multi-step reaction pathway. This catalytic mechanism also implies a source of proton is essential for imidazolium to act as a catalyst. Reduction of imidazolium also can form carbene, which then forms a catalytically inactive complex with CO$_2$, which deactivates the catalytic action of imidazolium on CO$_2$ reduction. This competing deactivation process is slowed down when proton availability increases. Furthermore, the imidazolium carboxylate can be reactivated, if formed, to regenerate the imidazolium co-catalyst if a proton source, such as water, is present, as suggested by the NMR data. This reaction with water explains why imidazolium ionic liquids are excellent catalysts for the electrochemical reduction of CO$_2$ in aqueous media.
**Scheme 8.** Mechanism associated with [C_{10}mim]^+ catalysis of the electrochemical reduction of CO_2 to CO along with its deactivation pathway.

**Conclusion**

The electrochemical reduction of CO_2 at a Ag electrode has been investigated in MeCN (0.1 M n-Bu_nNPF_6) in the presence of 13 ionic liquids or salts that contain imidazolium, pyrrolidinium, ammonium, phosphonium, borate, pyridinium and sulfonium-based cations, and 7 ammonium cations of variable alkyl chain lengths. The results show many cations can significantly catalyse the electrochemical reduction CO_2 along with a Ag electrode. Thus, catalytic CO_2 reduction is not restricted to the widely reported imidazolium ionic liquids and is a property associated with many other cations, although the mechanism for catalysis varies with the nature of the cation. Imidazolium cations act as co-catalysts at a Ag electrode, and after reduction form a complex between the electrogenerated imidazolium radical and CO_2. The imidazolium radical is the key species for catalysing CO_2 reduction rather than the imidazolium carboxylate complex formed by a reaction between an imidazolium carbene and CO_2. NMR results suggest that the formation of imidazolium carboxylate leads to deactivation of the co-catalyst, but addition of water leads to catalysis recovery. Other catalytically active cations are believed to enhance CO_2 reduction by an electrochemical double layer effect. In terms of the stability for long-term applications, pyrrolidinium-based ionic liquids are recommended for catalytic reduction of CO_2 in the absence of water, while both imidazolium and pyrrolidinium are both very effective in the presence of water.

**Associated Content**

**Supporting Information**
Supporting data include voltammograms of ionic liquids and salts under N\textsubscript{2} and CO\textsubscript{2} atmospheres (Figures S1-S6). This material is available free of charge via the Internet at http://pubs.acs.org

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Notes
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References


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