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Electrochemical and IR Spectroelectrochemical Studies of the Electrocatalytic Reduction of Carbon Dioxide by $[Ir_2(dimen)_4]^{2+}$ (dimen = 1,8-Diisocyanomenthane)

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The electrocatalytic reactions of carbon dioxide that are catalyzed by $[Ir_2(dimen)_4]^{2+}$ (dimen = 1,8-diisocyanomenthane) were studied with cyclic voltammetry and infrared spectroelectrochemistry. The hexafluorophosphate (PF_6^-) salt and the tetraphenylborate ($B(C_6H_5)_4^-$) salt are electrocatalysts for carbon dioxide reduction. Infrared spectroelectrochemistry allowed the identification of the carbon dioxide reduction products and provided information about the mechanism(s) of the reduction. Bicarbonate and formate were identified as the electrocatalytic carbon dioxide reaction products by comparing the infrared bands observed by spectroelectrochemistry with authentic samples of tetrabutylammonium formate, tetrabutylammonium oxalate, and tetrabutylammonium bicarbonate. Formate arises from a net two-electron reduction of carbon dioxide that produces free formate and a formate complex of $[Ir_2(dimen)_4]^{2+}$. Bicarbonate results from the reaction of hydroxide (produced when residual water is reduced to hydrogen) with carbon dioxide.

Introduction

Carbon dioxide is the end product of many industrial and biological processes; however, only plants can effectively regenerate useful products from the abundant low-energy molecule. The electrocatalytic recycling of carbon dioxide into high-energy organic molecules has drawn the attention of several research groups.[1−17] Metal complexes, mainly mononuclear compounds, have been tested as potential electrocatalysts for carbon dioxide reduction. The typical products reported in these studies (carbon monoxide/carbonate and formate) have been identified by gas chromatography (GC) or IR spectroelectrochemistry. In a few studies, oxalate has also been observed.[5,b,c,6b]

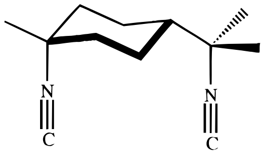

Figure 1. dimen = 1,8-diisocyano-*n*-menthane.

In this paper, we use GC and infrared spectroelectrochemistry to study the catalysis of carbon dioxide reduction with the binuclear complex $[Ir_2(dimen)_4]^{2+}$ (see Figure 1). Christensen et al. have applied infrared spectroelectrochemistry techniques to study the reduction of carbon dioxide catalyzed by several different metal complexes.[6] Their studies point out the difficulties of determining the reduction products with only IR spectroscopy. Comparisons with authentic samples of TBA oxoanions have been used by several research groups for the assignment of the infrared bands,[6d,18,19] but even so, inconclusive

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or ambiguous results were obtained. To minimize these problems, we have synthesized TBA oxoanion salts and carefully characterized them by IR spectroscopy *under catalytic conditions* for comparison with the products observed in electrocatalytic experiments.

Experimental Section

General Methods. Acetonitrile was distilled from P_2O_5 under a nitrogen atmosphere prior to use. Tetrabutylammonium hexafluorophosphate ($TBA^+PF_6^-$) (Southwestern Analytical) was dried overnight under vacuum and stored in a glovebox. Electrolyte solutions were prepared and dried by passage through a column of activated alumina. $[Ir_2(dimen)_4]((B(C_6H_5)_4)_2$[20] and $[Ir_2(dimen)_4](PF_6)_2$[21] were prepared from $[Ir(COD)Cl]_2$.[22] The carbon dioxide gas was bone-dry grade (Matheson). ^1H and ^{13}C NMR spectra were obtained on Bruker AC 200 and Varian VXR 300 spectrometers.

Electrochemistry. Cyclic voltammetry (CV) and bulk electrolysis experiments were performed with a Bioanalytical System (BAS) Model 100 electrochemical analyzer. A normal three-electrode configuration was used (CV). The working electrode was a highly polished glassy-carbon-disk electrode with a surface area of 0.07 cm^2. The Ag/AgCl reference electrode was attached to the working electrode compartment through a modified Luggin capillary. The auxiliary electrode was a platinum wire that was separated from the working compartment with a ground-glass frit. CV was performed under an argon or carbon dioxide atmosphere. Bulk electrolysis was also performed in the three-electrode configuration except platinum gauze was used as the working electrode. Typically, the working compartment was filled with 30 mL of the electrolyte solution. The solution was purged with carbon dioxide for at least 20 min before the electrolysis began. A very slow flow of carbon dioxide was maintained during electrolysis.

Spectroelectrochemistry. Infrared spectral changes during thin-layered bulk electrolyses were observed with a reflectance thin-layer flow-through spectroelectrochemical cell previously described.[23] Infrared data were collected with a Nicolet Magna Model 550 IR spectrometer. Bulk electrolyses in the thin-layer cell were controlled by the BAS 100 electrochemical analyzer. The working electrode was a glassy carbon electrode and was referenced vs a platinum pseudo-reference electrode. The potential of this pseudo reference is very stable and has E_{ref} within a few millivolts of the Ag/AgCl reference electrode used in CV experiments. A platinum wire outside the thin-layer solution was used as the auxiliary electrode.

Gas Chromatography. Gas chromatograms were determined with a Perkin-Elmer Sigma 3B capillary chromatograph equipped with a flame ionization detector and a Hewlett Packard 3390A integrator. The carbon dioxide reduction products were analyzed by reacting a bulk electrolyzed solution with benzyl chloride to convert the oxoanions into volatile esters. Helium carrier gas (25 psi) was used with a flow rate of 2.8 mL/min with the products esterified with benzyl chloride. The column, injection port, and detector temperatures were kept at 80, 125, and 125 °C, respectively.

Preparations. $(TBA)_2$(oxalate), TBA(formate), and TBA(bicarbonate) were synthesized for comparison of their IR spectra with the carbon dioxide reduction products.

$(TBA)_2$(oxalate). A 5 mL volume of 1 M tetrabutylammonium hydroxide (5 mmol) was mixed with 0.3152 g of oxalic acid$\cdot 3H_2O$ (2.5 mmol) in methanol. The solution was stirred until a gelatinous white solution formed. The solvent was removed by rotorary evaporation. The thick suspension was washed with diethyl ether three times and dried under vacuum at 60−70 °C overnight. The yield was not determined because the solid was extremely hygroscopic. The acetonitrile solution IR spectrum of the solid exhibits strong bands at 1566 and 1290 cm^{-1}.

Table 1. Electrochemical Data[a] for $[Ir_2(dimen)_4](PF_6)_2$ and $[Ir_2(dimen)_4](B(C_6H_5)_4)_2$

$[Ir_2(dimen)_4](X)_2$	$E_{p,a}$	$E_{p,c}$	$E^{\circ\prime}$ [b]
$X = PF_6^-$	0.70	−0.76	*c*
	−1.32	−1.38	−1.35
	−1.51	−1.57	−1.54
$X = B(C_6H_5)_4^-$	0.93	−0.88	*c*
	−1.30	−1.41	−1.36
	−1.49	−1.60	−1.54

[a] Under an argon atmosphere with a glassy-carbon electrode; potentials reported in V vs Ag/AgCl. [b] $E^{\circ\prime} = (E_{p,a} + E_{p,c})/2$. [c] Not calculated for the irreversible process.

TBA(formate). A 5.0 mL volume of 1 M tetrabutylammonium hydroxide (in methanol) was mixed with 0.2710 g of formic acid (88% in water). The solvent was removed under vacuum. The resulting solution was mixed with dichloromethane and activated alumina. After the alumina was removed by gravity filtration, the dichloromethane was removed under vacuum. The pale yellow solution was washed with diethyl ether 3 times before drying under vacuum in a warm water bath for 1 h. The light yellow product was stored in a desiccator. The yield was not determined because the product is extremely hygroscopic. The solution IR spectrum of the solid showed a band at 1607 cm^{-1} ($\epsilon = 820 \pm 80$ cm^{-1} M^{-1}) and 1333 cm^{-1}.

TBA(bicarbonate). Carbon dioxide was bubbled into a solution of tetrabutylammonium hydroxide (1 M in methanol) for 10 min. The solvent was removed under vaccum. The white residue was washed with diethyl ether and dried in a vacuum desiccator for 24 h. The resulting viscous solution was then dried further under vacuum at 25 °C (pale yellow, hygroscopic paste) or in a 110 °C oven for 16 h (brown liquid). Samples obtained by both methods exhibit identical IR bands (solution IR in CH_3CN) at 1685, 1646, and 1304 cm^{-1}. A ^1H NMR spectrum of a CD_3CN solution of TBA(bicarbonate) exhibited a broad peak at 3.5−5.5 ppm that was concentration dependent. Upon addition of D_2O, the peak disappeared. The ^{13}C NMR spectrum showed a peak at 162.9 ppm.

Results

A previous study showed that the hexafluorophosphate (PF_6^-) salt of $[Ir_2(dimen)_4]^{2+}$ possesses interesting electrochemical properties[24] that might make it useful as an electrocatalyst for the reduction of carbon dioxide. Additionally, we investigated the tetraphenylborate salt ($B(C_6H_5)_4^-$), which has nearly identical reductive electrochemical properties in comparison with the PF_6^- salt but is air stable and easier to handle.

Electrochemical oxidations are somewhat different for $[Ir_2(dimen)_4](PF_6)_2$ and $[Ir_2(dimen)_4](B(C_6H_5)_4)_2$ (Table 1). At glassy carbon, the PF_6^- salt is oxidized irreversibly at 0.70 V, while the $B(C_6H_5)_4^-$ salt irreversibly oxidized at 0.93 V. The sensitivity of the oxidation processes in other Rh and Ir binuclears to the nature of the supporting anion is well documented and is caused by strong axial interactions between the two electron oxidized forms of the binuclears and the anion.[25−27] The anodic peak current for the oxidation of the $B(C_6H_5)_4^-$ salt is almost 4 times higher than that of the PF_6^- salt. The additional peak current is probably due to the oxidation of the $B(C_6H_5)_4^-$ anion.[28]

A CV study of the reductive electrochemistry of the PF_6^- salt was also carried out in the previous study.[24] At platinum, this compound exhibits two closely spaced processes at $E^{\circ\prime} = -1.34$ and -1.53 V vs Ag/AgCl in acetonitrile solutions. These

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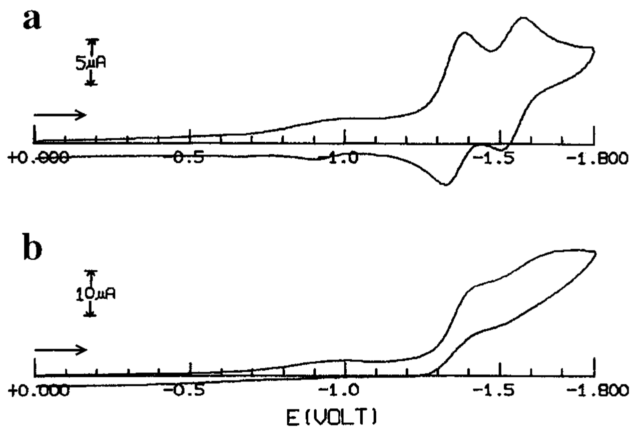

Figure 2. Cyclic voltammograms of 0.6 mM of $[Ir_2(dimen)_4]$-$(B(C_6H_5)_4)_2$ in 0.1 M $(TBA)PF_6/CH_3CN$ at a glassy-carbon working electrode: (a) Under argon; (b) under carbon dioxide. Scan rate = 100 mV/s.

two quasi-reversible reduction processes are also observed for $[Ir_2(dimen)_4](B(C_6H_5)_4)_2$ with minimal differences in redox potentials and peak currents in comparison to the PF_6^- salt. In the previous study, spectroelectrochemical measurements suggested that the first reduction product is a delocalized mixed-valence species that contains the Ir_2^+ core, while the second reduction product ($Ir_2(dimen)_4$) contains a valence localized Ir^+Ir^- core. The first reduction product was very reactive in dichloromethane solutions, where a single two-electron irreversible CV process is observed. This reactivity with dichloromethane suggested that one or more of these reduced $[Ir_2(dimen)_4]^{n+}$ ($n+ = +1$, 0) species might be capable of reducing carbon dioxide. Indeed, we found that both the hexafluorophosphate and the tetraphenylborate salts of the iridium compound are electrocatalysts for the reduction of carbon dioxide.

The CV of $[Ir_2(dimen)_4](B(C_6H_5)_4)_2$ at a glassy carbon electrode under an argon atmosphere is shown in Figure 2a. After the solution was saturated with carbon dioxide, the CV changed dramatically (Figure 2b). While the irreversible oxidation process was invariant, the two reversible reduction processes became irreversible. More importantly, there was a 2-fold increase in the anodic peak current with either the PF_6^- or $B(C_6H_5)_4^-$ salts. The increase in current flow results from a slow electrocatalytic reduction of carbon dioxide. If the CV scan in the negative direction is reversed at a potential between the two processes, the first process is no longer reversible, suggesting that the catalytically active species is produced after the first reduction process.

Infrared spectroelectrochemistry was used to investigate the reduction products and the role of the metal complex in the catalytic reaction. A solution of 0.6 mM of $[Ir_2(dimen)_4]^{2+}$ in 0.1 M $(TBA)PF_6/CH_3CN$ was purged with carbon dioxide for 15 min and injected into the thin-layer flow cell. Large currents ($\sim$150 μA) were observed when the solution was electrolyzed at -1900 mV vs a platinum pseudoreference electrode.[29] The spectral changes in the ν(CN) stretching region are shown in Figure 3. The new bands observed in the ν(CN) stretching region were very different from those observed upon reduction of $[Ir_2(dimen)_4]^{2+}$ in argon-saturated CH_3CN.[27,30] Upon reductive electrolysis of the CO_2-saturated solution, the ν(CN) stretch of the isocyanide ligands of $[Ir_2(dimen)_4](PF_6)_2$ *increased* from 2157 to 2161 cm^{-1}; in a similar experiment, those of the $B(C_6H_5)_4^-$ salt also increased to 2161 cm^{-1}. Further, a very weak peak at 1917 cm^{-1} grew in with the appearance of the 2161 cm^{-1} band.

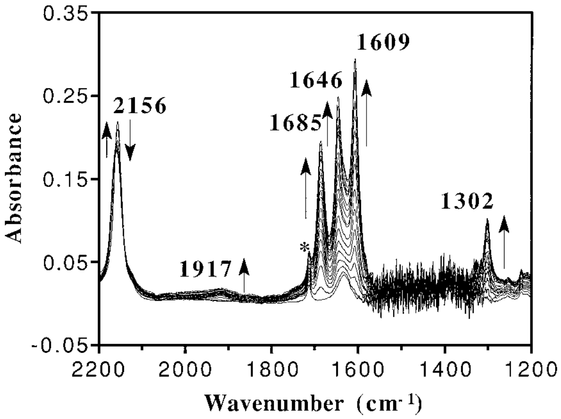

Figure 3. Infrared spectroelectrochemical changes observed during a thin-cell bulk electrolysis of carbon dioxide in the presence of 0.6 mM $Ir_2(dimen)_4](B(C_6H_4)_4)_2$. The potential at the glassy-carbon working electrode was held at -1900 mV vs a Pt wire pseudoreference electrode. Arrows show the direction of intensity change during the electrolysis. The starred peak is due to an acetone impurity introduced while cleaning the cell.

In the ν(C−O) stretching region, three peaks at 1685, 1646, and 1607 cm^{-1} grew in during the thin-layer electrolysis. Although the absorbance from the 1607 cm^{-1} peak is observed at early times in the electrolysis, it increases in intensity faster than the 1685 and 1646 cm^{-1} bands at later times. A band for carbon monoxide at 2138 cm^{-1}, a commonly observed CO_2 reduction product, is not observed.[31] The absence of this peak suggests that CO is not a product of the electrocatalytic carbon dioxide reduction by $[Ir_2(dimen)_4]^{2+}$.

TBA(formate), $(TBA)_2$(oxalate), and TBA(bicarbonate) were synthesized to unambiguously assign the infrared spectral bands observed in the electrocatalysis experiments. $(TBA)_2$(oxalate) exhibits a peak at 1566 cm^{-1}, ruling it out as a reduction product. Authentic TBA(formate) shows a C=O stretching band at 1607 cm^{-1}, strongly suggesting that the 1607 cm^{-1} band observed in the electrocatalysis experiments is formate. This assignment is further confirmed by GC/MS comparisons of an authentic sample of the benzyl ester of formate with the esterification product of the electrocatalysis solution. Comparison of the IR spectrum of our TBA(bicarbonate) sample synthesized by the literature procedure with the spectroelectrochemical results (Figure 3) suggest that bicarbonate is indeed an electrocatalytically generated product. The IR characterization[32] of our TBA(bicarbonate) sample agrees with the work of Christensen et al.[6c] Our infrared spectrum is similar to those of Christenson et al. except for slight differences in the fingerprint region that we attribute to the hygroscopic nature of the salt.

As mentioned previously, the production of formate in the thin-layer electrocatalytic reduction slightly lags the formation of bicarbonate. Studies to determine whether the formation of formate arises from the reduction of bicarbonate were made. Addition of TBA(bicarbonate) to a solution of $[Ir_2(dimen)_4]^{2+}$ under an argon atmosphere had no effect on the cyclic voltammogram. Reduction of $[Ir_2(dimen)_4]^{2+}$ in the presence of TBA(bicarbonate) in the thin-layer solution IR cell produced

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(29) Control experiments, identical except $[Ir_2(dimen)_4]^{2+}$ was not present, did not pass significant currents and gave no evidence of CO_2 reduction products.

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(32) The IR spectrum of our sample shows considerable differences to those of Tyler et al.[20] We speculate that these differences are due to hydration effects. They report that TBA(bicarbonate) has a strong band at 1673 cm^{-1}.

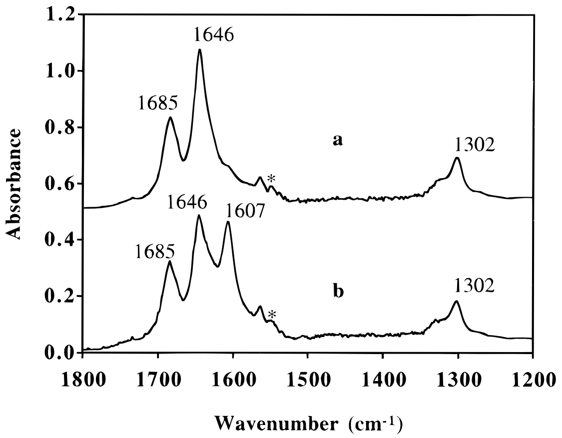

Figure 4. Infrared spectrum of a bulk electrolysis solution of carbon dioxide in 0.1 M $(TBA)PF_6/CH_3CN$ with 0.3 mM $[Ir_2(dimen)_4](B(C_6H_5)_4)_2$ present: Curve a, after 65 C of charge consumed; curve b, after 80 C of charge consumed. The starred peak (and additional absorbance at 1646 cm^{-1}) are due to 2,4,6-trimethyl-1,3,5-triazine formed inadvertently by oxidation of acetonitrile at the auxiliary electrode.[35]

no decrease in the bicarbonate bands or new bands due to the production of formate. These experiments suggest that formate does not arise from the reduction of bicarbonate.

The role of residual water on the electrocatalytic reactions was investigated with spectroelectrochemical reductions of carbon dioxide saturated acetonitrile solutions that also contained 0.02 M D_2O.[33] The spectral changes in the 1500−2200 cm^{-1} infrared region were only slightly different from those obtained in the absence of D_2O. Three bands at 1682, 1643, and 1609 cm^{-1} grow into the spectrum.[32] The 1682 and 1643 cm^{-1} bands grew in together and are assigned to DCO_3^-. These deuteriobicarbonate bands are shifted to lower energy by 3 cm^{-1} relative to those observed for HCO_3^-. The formate band at 1609 cm^{-1} is unshifted (within experimental error) relative to its position in H_2O-containing solutions. When the electrocatalytic reduction was performed at a less negative potential (−1000 mV), the formate band appears at later times during the electrolysis. More interesting, the appearance of the formate band coincides with the slight shift in the ν(CN) of the metal complex to higher energy. This suggests an interaction between formate and the metal complex (vide infra). The production of bicarbonate does not produce any shift in ν(CN) of the metal complex.

The products and the electrocatalytic nature of the carbon dioxide reduction reaction were confirmed by bulk electrolysis of carbon dioxide at a Pt gauze working electrode in the presence of $[Ir_2(dimen)_4]^{2+}$. The solution was electrolzyed at −1900 mV vs Ag/AgCl until ca. 65 C of charge was passed.[30] The infrared spectrum of the resulting solution showed two bands at 1685 and 1646 cm^{-1} while the 1607 cm^{-1} band was missing (Figure 4a). The 1607 cm^{-1} band was *not* observed even when identical solutions were electrolyzed at −1800 or −1950 mV up to the point where 65 C of charge was passed. However, when an otherwise identical solution was electrolyzed for a longer time such that over 80 C of charge was consumed, the 1607 cm^{-1} band arises (Figure 4b) during the time when the last 15 C is passed. No substantial drop in current was observed through out the electrolysis. Assuming that the first 65 C of charge is used in the conversion of CO_2 to HCO_3^-, then the last 15 C of charge was consumed in the 2-electron reduction of CO_2 to produce 7.7×10^{-5} mol of formate. This corresponds to approximately 8 turnovers of CO_2 to formate based on the iridium complex. These bulk electrolysis experiments and the spectroelectrochemical results suggest that the 1685 and 1646 cm^{-1} bands (bicarbonate) and the 1607 cm^{-1} band (formate) arise from two different electrocatalytic mechanisms and formate is not produced from bicarbonate. The passage of the first 65 C of charge in the bulk electrolysis experiments results from the reduction of residual amounts of water left in the solvent. Apparently, all of the water in these large-scale bulk electrolysis experiments must be used up before formate can be formed.

To further confirm the identity of the electrocatalytically produced products, the oxoanions produced in these bulk electrolysis solutions and standard samples of TBA(formate) and $(TBA)_2$(oxalate) were esterified by addition of benzyl chloride. Both types of samples were then analyzed by gas chromatography. The reaction product of benzyl chloride and authentic tetrabutylammonium formate showed a sharp peak due to benzyl formate in the gas chromatogram. The bulk electrolysis solution with a prominent IR band at 1607 cm^{-1} after treatment with benzyl chloride possessed a peak with identical characteristics (shape, retention time) in the gas chromatogram. The peaks in both cases were confirmed by GC/MS to be benzyl formate. No GC evidence for the electrocatalytic production of oxalate was obtained.

The slight shift in the ν(CN) IR peaks due to $[Ir_2(dimen)_4]^{2+}$ and the weak peak at 1917 cm^{-1} that occur during the electrolysis of CO_2-saturated solutions suggest that an interaction between formate and $[Ir_2(dimen)_4]^{2+}$ might occur. When an excess of TBA(formate) was added to $[Ir_2(dimen)_4]^{2+}$, the ν(CN) stretch shifted from 2157 to 2167 cm^{-1} and a new peak at 1918 cm^{-1} was observed in addition to the band at 1607 cm^{-1} due to formate. The addition of aliquots of TBA(formate) to a solution of $[Ir_2(dimen)_4]^{2+}$ was followed by IR spectroscopy. The ν(CN) stretch at 2157 cm^{-1} gradually decreased in intensity as a new band at 2167 cm^{-1} grew into the spectrum. All of these experiments are consistent with the formation of a complex between formate and $[Ir_2(dimen)_4]^{2+}$ which does not involve the dissociation of any of the dimen ligands. Further characterization of this species is planned in future work.

Discussion

Gas chromatography has previously been used as the primary method to detect the presence of formate and oxalate as products of the electrocatalytic reduction of carbon dioxide. More recently, infrared spectroelectrochemical methods have been used to obtain *in-situ* mechanistic information to support the GC studies. In addition to applying these techniques to investigate the products of the electrocatalytic solutions, we have prepared authentic samples of the tetrabutylammonium oxoanions so direct comparisons could be made. On the basis of the combination of these methods, we identify the 1685 and 1646 cm^{-1} bands in the electrocatalysis solutions as arising from bicarbonate. No oxalate was detected by infrared spectroscopy or by GC. Because all of the oxoanions of carbon have somewhat similar structural features (C═O) that are sensitive to protonation and/or H-bonding, confusion has been introduced in the literature by simply identifying the C═O stretch as a value “near 1600 cm^{-1}”. In addition to these ∼1600 bands, our data show that each of the three oxoanions also has a well-characterized band around 1300 cm^{-1} which greatly aids the assignment and interpretation of the spectroelectrochemistry results.

Our data suggest that $[Ir_2(dimen)_4]^{2+}$ catalyses two carbon dioxide reactions (to formate and bicarbonate) each by a discrete mechanism that branches after reaction 2. (See Scheme 1.)

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(33) See supplementary Figure 1 in the Supporting Information.

Scheme 1. Mechanisms for the Formation of Formate and Bicarbonate

$$[\mathrm{Ir_2(dimen)_4}]^{2+} + e^- \rightarrow [\mathrm{Ir_2(dimen)_4}]^{+} \qquad (1)$$

$$[\mathrm{Ir_2(dimen)_4}]^{+} + e^- \rightarrow [\mathrm{Ir_2(dimen)_4}]^{0} \qquad (2)$$

formate formation

$$[\mathrm{Ir_2(dimen)_4}]^{0} + \mathrm{CO_2} \rightarrow [\mathrm{Ir_2(dimen)_4(CO_2)}] \qquad (3)$$

$$[\mathrm{Ir_2(dimen)_4(CO_2)}] + [\mathrm{H^+}] \rightarrow [\mathrm{Ir_2(dimen)_4(HCO_2)}]^{+} \qquad (4)$$

$$[\mathrm{Ir_2(dimen)_4(HCO_2)}]^{+} \rightarrow \mathrm{HCO_2}^{-} + [\mathrm{Ir_2(dimen)_4}]^{2+} \qquad (5)$$

bicarbonate formation

$$[\mathrm{Ir_2(dimen)_4}]^{0} + 2\mathrm{H_2O} \rightarrow \mathrm{H_2} + 2\mathrm{OH}^- + [\mathrm{Ir_2(dimen)_4}]^{2+} \qquad (6)$$

$$\mathrm{OH}^- + \mathrm{CO_2} \rightarrow \mathrm{HCO_3}^- \qquad (7)$$

We suggest that formate probably results from the catalytic reduction of the metal complex, followed by reaction with CO_2 to form a putative CO_2 complex. The exact sequence of steps after the initial electron transfer step has not been determined, so that the order of addition of CO_2, H^+, and the second e^- could in fact be different than depicted here. It is likely that the putative CO_2 intermediate formed in reaction 3 has a weak Ir−C interaction between the iridium center and the carbon dioxide rather than an Ir−O interaction, as this later mode of complexation usually favors the formation of oxalate. The observation of formate complexation by the resting form of the electrocatalyst (i.e. $[Ir_2(dimen)_4]^{2+}$) is accounted for if reaction 5 does not go to completion.

A question of interest is the source of the nascent protons used in reaction 4 of this mechanism. Following the previous suggestion of Meyer and co-workers,[12d] a Hofmann degradation of the TBA electrolyte is a likely source, so that a more complete version of reaction 4 is as follows:

$$[\mathrm{Ir_2(dimen)_4(CO_2)}] + (\mathrm{C_4H_9})_4\mathrm{N}^+ \rightarrow \text{1-butene} + [\mathrm{Ir_2(dimen)_4(HCO_2)}]^{+} + (\mathrm{C_4H_9})_3\mathrm{N} \qquad (8)$$

We believe that the mechanism which produces bicarbonate does not involve the reduction of CO_2 because no evidence for the concomitant production of CO (that usually arises from disproportionation of $CO_2^{\bullet-}$) is observed. Rather, we propose that bicarbonate is formed in this system when hydroxide ion is produced via catalytic reduction of the residual water in the solvent by a reduced form of $[Ir_2(dimen)_4]^{2+}$ (probably $[Ir_2(dimen)_4]^{0}$) followed by the attack of hydroxide on CO_2 to produce bicarbonate. This mechanism is consistent with the production of DCO_3^- when D_2O is present in the catalytic solution and follows the suggestions of Meyer[12b] and others, who have previously suggested that bicarbonate forms via catalytic reduction of water to hydroxide ion by putative reduced metal hydrides. In the Meyer system, the metal hydride (an osmium hydride complex) also produces formate via a hydride transfer to carbon dioxide.

Conclusions

The electrocatalytic reduction of carbon dioxide with $[Ir_2(dimen)_4]^{2+}$ was studied with IR spectroelectrochemistry and gas chromatography. The major electrocatalytically produced products (formate and bicarbonate) are generated by reduction of CO_2 and by reduction of residual water, respectively. The reaction pathways that produce these products are not necessarily required to be those suggested by Amatore and Saveant.[34]

$$\mathrm{CO_2} + e^- \rightarrow \mathrm{CO_2}^{\bullet-} \qquad (9)$$

$$2\mathrm{CO_2}^{\bullet-} \rightarrow \mathrm{CO} + \mathrm{CO_3}^{2-} \qquad (10)$$

$$2\mathrm{CO_2}^{\bullet-} \rightarrow \mathrm{C_2O_4}^{2-} \qquad (11)$$

$$\mathrm{CO_2}^{\bullet-} + \mathrm{H}^+ + e^- \rightarrow \mathrm{HCO_2}^{-} \qquad (12)$$

The Saveant mechanism applies when CO_2 is reduced directly at the surface of an inert electrode at very negative potentials but may not apply to catalytic processes that involve solution species which could stabilize reaction intermediates. For example, the production of formate in the system we have studied here may involve an interaction between carbon dioxide and a reduced iridium compound, followed by protonation and then release of formate. If the metal complex catalytic scheme does not produce free $CO_2^{\bullet-}$, reactions 10 and 11 are much less favorable (carbon monoxide and oxalate are not observed as products) and the production of formate must occur via a reaction somewhat different than reaction 12.

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Supporting Information Available: An IR spectrum of changes during the reduction of CO_2 under the conditions of Figure 3 in the presence of 0.02 M D_2O, an IR spectrum of tetrabutylammonium bicarbonate in acetonitrile, and an IR spectrum of ca. 0.5 mM $[Ir_2(dimen)_4](B(C_6H_5)_4)_2$ in acetonitrile with excess TBA(formate) added (4 pages). Ordering information is given on any current masthead page.

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