Electrocatalysis of CO$_2$ Reduction in Aqueous Media at Electrodes Modified with Electropolymerized Films of Vinylterpyridine Complexes of Transition Metals

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4-Vinyl- and 6-vinylterpyridine (4-v-tpy; 6-v-tpy) complexes of chromium, nickel, cobalt, iron, ruthenium and osmium have been prepared. These materials can be electropolymerized onto glassy carbon electrodes and the resulting films have been characterized, by cyclic voltammetry and rotated disk electrode voltammetry in aqueous media and under nitrogen and carbon dioxide atmospheres. The electropolymerized films exhibit electrocatalytic activity toward the reduction of CO$_2$ with formaldehyde as virtually the only product. The magnitude of the catalytic effect and the efficiency are a function of the metal center and the location of the vinyl group(s) within the ligand. The catalytic activity of complexes having metal-based redox processes at negative potentials was superior to that of complexes where the relevant redox processes were ligand based. Complexes of first row transition metals were more active than those of the second or third row owing to the lower stability of the complexes. The presence of coordinating anions suppressed the electrocatalytic activity with HPO$_4^{-2}$ causing a complete inhibition. Electropolymerized films of [Cr(4-v-tpy)$_2$]$^{2+}$ exhibited a current efficiency of 87%. Turnovers in excess of 15 000 were achieved with electropolymerized films of [Fe(4-v-tpy)$_2$]$^{2+}$. The kinetics of the reaction were relatively slow, especially when compared to the analogous process in non-aqueous solvents such as DMF. This has been ascribed to differences in the overall reaction and products.

Introduction

Because of the increasing need for new and/or alternative sources of fuel, the abundance of CO$_2$ in the atmosphere, and potential environmental concerns, there continues to be a great deal of interest in the design of electrocatalysts for the reduction of carbon dioxide[1] to useful fuel products. In general, these processes are difficult to catalyze as they typically involve not only multiple electron transfers but also are often coupled to chemical steps such as protonation. In addition, there can be multiple competing reaction pathways giving rise to a variety of reaction products. In the case of carbon dioxide, products can include carbon monoxide, formic acid, formaldehyde, methanol, and methane among others. These products differ in the number of redox equivalents required, and the kinetics for their formation can vary broadly and can depend on factors such as proton availability. Although thermodynamically these processes should take place at moderately negative potentials, the direct reduction of carbon dioxide at electrode surfaces typically requires very large overpotentials because of the formation of high energy intermediates such as CO$_2^{1-}$.[2] For example, the reduction of carbon dioxide in DMF takes place at about −2.0 V vs SCE.

A variety of catalysts such as semiconductor electrodes and transition metal electrocatalysts[3] have been employed in order to circumvent the formation of high energy intermediates such as CO$_2^{1-}$ and thus decrease the activation energy barrier. In addition, a number of transition metal complexes have been shown to be effective in the electrocatalytic reduction of carbon dioxide. Co and Ni tetraazamacrocycles,[4] whose catalytic activity for CO$_2$ reduction was initially reported by Fisher and Eisenberg,[5] have been found to diminish the potential for carbon dioxide reduction by about 0.5 V in non-aqueous media while Ni(cyclam)$^{2+}$ (cyclam is 1,4,8,11-tetraazatetradecane) has been used as an electrocatalyst in aqueous media.[6] Phthalocyanine and porphyrin complexes,[7] phosphine complexes[8] such as Rh(diphos)$_2$Cl[9] (diphos is 1,2-bis(diphenylphosphino)ethane), and polypyridyl-type transition metal complexes[10] have also been studied for their potential catalytic activity for CO$_2$ reduction. In many of these examples, the catalyst is capable

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of undergoing more than one reduction and thus storing multiple redox equivalents. In addition, the catalyst has or can make available upon reduction at least one open coordination site where carbon dioxide can ostensibly bind.

The use of electrodes modified with immobilized electrocatalysts is especially attractive and a number of reports on systems exhibiting electrocatalytic activity toward CO_2 have appeared.[11] The use of surface-bound catalysts is advantageous from a number of standpoints. The effective (volume) concentration of electroactive material can reach levels (ca. 0.5 M) that are simply not accessible in homogeneous solution. At such high effective concentrations, the distance between adjacent metal complexes is sufficiently short that cooperativity effects are enhanced. In addition, the use of surface-immobilized electrocatalysts allows for the easy removal of the catalyst from the reaction vessel.

An important type of surface-immobilized electrocatalysts for CO_2 reduction has been metallophthalocyanines deposited onto glassy carbon electrodes. For example, cobalt phthalocyanines immobilized in this manner have been shown to reduce carbon dioxide to carbon monoxide at potentials as low at −0.65 V vs SCE at pH 5.[12]

An alternative and powerful method for immobilizing catalysts onto electrode surfaces has been through the use of complexes containing polymerizable, vinyl substituted ligands. For example, electropolymerization of $[Re(CO)_3(v\text{-}bpy)Cl]$ (v-bpy is 4-vinyl-4′-methyl-2,2′-bipyridine) gives rise to the formation of redox active polymeric films which can reduce carbon dioxide to carbon monoxide electrocatalytically.[13]

We have previously shown that electropolymerized layers of $[Co(4\text{-}v\text{-}tpy)_2]^{2+}$ (4-v-tpy is 4′-vinyl-2,2′:6′,2″-terpyridine) are electrocatalytically active in the reduction of carbon dioxide to formic acid (in DMF) and of oxygen to water and hydrogen peroxide in aqueous media.[14] In DMF solution, $[Co(tpy)_2]^{2+}$ (tpy is 2,2′:6′,2″-terpyridine) can reduce carbon dioxide at −1.70 V. However, electrodes modified with polymeric films of $[Co(4\text{-}v\text{-}tpy)_2]^{2+}$, can reduce CO_2 under similar conditions at −0.90 V. This difference in reactivity appears to be the result of generation of empty coordination sites on the cobalt once it is reduced to Co(I) and possibly to cooperativity effects.

We also prepared the 7-coordinate vinyl quinquepyridine (v-qpy) (v-qpy is 4′, 4‴-divinyl-2, 2′: 6′, 2″: 6″, 2‴: 6‴, 2⁗-quinquepyridine) derivative $[Co(v\text{-}qpy)Cl_2]$.[15] Analogous to the 4-v-tpy complex, this material could be easily electropolymerized to give rise to electrodes modified with electroactive polymeric films of the complex. Unfortunately, such modified electrodes only exhibited modest electrocatalytic activity. These findings prompted us to take a closer look at various transition metal complexes and to try to determine what aspects, in terms of coordination, affect electrocatalytic activity. From these studies we have found that terdentate coordination, especially around first row transition metals, favored such electrocatalytic activity.[16]

As part of our continued interest in the electrocatalytic reduction of carbon dioxide, we have prepared and characterized electrodes modified with electropolymerized films of 4- and 6-vinylterpyridine (4-v-tpy, 6-v-tpy) complexes of Fe, Co, Ni, Cr, Ru, and Os and have characterized their electrocatalytic activity for CO_2 reduction in aqueous media. We report here on the electrocatalytic behavior of such electrodes with emphasis on the potential at which CO_2 is reduced, the current efficiency and product distribution. We have also determined the effects of different supporting electrolytes on the catalytic activity. In addition we have carried out rotated disk electrode experiments to investigate the kinetics of these processes.

Experimental Section

2,2′:6′,2″-Terpyridine (referred to in the text as tpy) from Aldrich was used as received. The ligands 4′-vinyl-2,2′:6′,2″-terpyridine and 6′-vinyl-2,2′:6′,2″-terpyridine were prepared according to literature methods.[14] These will be referred to in the text as 4-v-tpy and 6-v-tpy, respectively. Formaldehyde (37% solution from Aldrich; ACS reagent grade) and chromotropic acid (Aldrich; ACS reagent grade) were used as received. Electrochemical measurements were performed in water (purified by passage through a Milli-Q purification system), acetonitrile or dimethyl formamide, (the latter two were Burdick & Jackson distilled in glass, dried over 4 Å molecular sieves). For nonaqueous solvents (acetonitrile, DMF) the supporting electrolyte was tetrabutylammonium perchlorate (TBAP) (G. F. S. Chemicals, recrystallized three times from ethyl acetate and dried under vacuum for 72 h). In aqueous media, sodium perchlorate (Aldrich, recrystallized twice from water) sodium nitrate, sodium acetate, sodium chloride, and sodium dihydrogen phosphate (all from Fisher) were employed. All other reagents were of at least reagent grade quality and were used as received. Carbon dioxide was passed through hydrocarbon and Oxysorb (to remove traces of oxygen) columns.

Elemental analysis (C, H, N) were carried out by Quantitative Technologies Inc., Bound Brook, NJ.

Synthesis of Metal Complexes. The synthesis of tpy complexes of transition metals is well established in the literature.[17] In addition, we have previously reported on the preparation and characterization (by elemental analysis, NMR, and fast atom bombardment mass spectrometry) of a number of the materials employed in this study.[14] In those cases, only a brief description of the synthesis is included here. The interested reader is referred to our previous work which contains detailed descriptions of synthesis and characterization of those complexes.

1. $\mathbf{[Co(4\text{-}v\text{-}tpy)_2]^{2+}(PF_6)_2}$ was prepared and characterized as described previously.[14a] Briefly, to a degassed aqueous solution of cobalt (II) chloride were added 2.3 equivalents of 4-v-tpy. Complex formation was immediately apparent form the resulting color change. The solution was allowed to stir at room temperature for 30 min. The complex was precipitated by the addition of an aqueous, saturated solution of ammonium hexafluorophosphate. The complex was collected by filtration, washed and dried with diethyl ether, and recrystallized from acetone/ether.

2. $\mathbf{[Fe(4\text{-}v\text{-}tpy)_2]^{2+}(PF_6)_2}$ was prepared by mixing a degassed aqueous solution of ferrous ammonium sulfate with 2.3 equiv of 4-v-tpy. Complex formation was immediately apparent form the resulting color change. The solution was allowed to stir at room temperature

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for 30 min. The complex was precipitated by the addition of an aqueous, saturated solution of ammonium hexafluorophosphate. The complex was collected by filtration, washed and dried with diethyl ether, and recrystallized from acetone/ether.

Elemental analysis for $[Fe(4\text{-v-tpy})_2]^{2+}(PF_6)_2$ follows. Anal. Calcd for $C_{34}H_{26}F_{12}N_6FeP_2$: C;, 47.26; H, 3.03; N, 9.73. Found: C, 47.02; H, 3.03; N, 9.52.

3. $[Ni(4\text{-v-tpy})_2]^{2+}(PF_6)_2$. $NiCl_2{\cdot}6H_2O$ was combined with 2.3 equiv of 4-v-tpy in 1:1 ethanol/water. The solution was vigorously bubbled with prepurified nitrogen for 20 min and heated at reflux for 3 h. The dark yellow solution was allowed to cool and filtered to remove any unreacted ligand. Upon addition of an aqueous, saturated solution of ammonium hexafluorophosphate, a white precipitate formed and was collected by filtration. The product was washed with diethyl ether and recrystallized from acetone/ ether.

Anal. Calcd for $C_{34}H_{26}F_{12}N_6NiP_2$: C, 47.09; H, 3.02; N, 9.69. Found: C, 47.27; H, 2.94; N, 9.45.

4. $[Ru(4\text{-v-tpy})_2]^{2+}(PF_6)_2$, and $[Ru(6\text{-v-tpy})_2]^{2+}(PF_6)_2$ were prepared and characterized as described previously.[14a] Briefly, $RuCl_3{\cdot}xH_2O$ was combined with 2.3 equiv of the ligand in 1:1 ethanol/water. The solution was vigorously bubbled with prepurified nitrogen for 20 min and heated at reflux for 3 h. The deep orange solution was allowed to cool and filtered to remove any unreacted ligand. Upon addition of an aqueous, saturated solution of ammonium hexafluorophosphate, an orange precipitate formed and was collected by filtration. The product was washed with diethyl ether and recrystallized from acetone/ether.

5. $[Os(4\text{-v-tpy})_2]^{2+}(PF_6)_2$: $[Os(Cl)_6](NH_4)_2$ was combined with 2.3 equiv of 4-v-tpy in ethylene glycol. The solution was vigorously bubbled with prepurified nitrogen for 20 min and heated at reflux for 3 h. After cooling, an equivalent volume of water was added and the deep green solution filtered to remove any unreacted ligand. Upon addition of an aqueous, saturated solution of ammonium hexafluorophosphate, a green precipitate formed and was collected by filtration. The product was washed with diethyl ether and recrystallized from acetone/ether.

Anal. Calcd for $C_{34}H_{26}F_{12}N_6OsP_2$: C, 40.89; H, 2.62; N, 8.42. Found: C, 40.82; H, 2.74; N, 8.20.

6. $[Ru(tpy)(4\text{-v-tpy})]^{2+}(PF_6)_2$. $[Ru(tpy)Cl_3]$, prepared according to a published procedure[18] was combined with 1.1 equiv of 4-v-tpy in 1:1 ethanol/water. The solution was vigorously bubbled with prepurified nitrogen for 20 min and heated at reflux for 3 h. The deep orange solution was allowed to cool and filtered to remove any unreacted ligand. Upon addition of an aqueous, saturated solution of ammonium hexafluorophosphate, an orange precipitate formed and was collected by filtration. The product was washed with diethyl ether and recrystallized from acetone/ether. The product was further purified by chromatography in neutral alumina with 15% methanol in toluene as eluent.

Anal. Calcd for $C_{32}H_{24}N_6RuP_2F_{12}$: C, 43.49; H: 2.72; N, 9.51. Found: C, 43.42; H: 2.61; N, 9.39.

Instrumentation. Electrochemical experiments were performed using a glassy carbon disk electrode (A = 0.045 cm^2), or a rotated glassy carbon disk electrode (A = 0.283 cm^2) (Pine Instruments). For bulk electrolysis experiments, a large area (ca. 6 cm^2) glassy carbon rod was employed as a working electrode. Electrodes were polished prior to use with 1 μm diamond paste (Buehler) and rinsed thoroughly with water and acetone. Potentials are referenced to a Ag/AgCl (saturated with sodium chloride) (+0.222 vs NHE) electrode without regard for the liquid junction. A coiled platinum wire was used as counterelectrode in voltammetric studies and a large area (>20 cm^2) platinum gauze electrode was employed as a counterelectrode in bulk electrolysis experiments. Three compartment electrochemical cells of conventional design were employed. In bulk electrolysis experiments the working electrode compartment was saturated with CO_2 by bubbling for at least 45 min and sealed with a serum cap to prevent escape and/ or contamination of gaseous products. The atmosphere above the solution was sampled with a Hamilton Teflon-coated gastight syringe.

Solutions for electrochemistry were typically 0.5 mM in the redox species and were deoxygenated by purging with prepurified nitrogen for at least 15 min.

The electrochemical instrumentation utilized was either a Pine Instrument Company Electrochemical Analyzer Model RDE3 or a PAR Model 173 potentiostat in conjunction with a PAR Model 175 universal programmer. Data were recorded on a Soltec Model VP-6423S recorder.

Electropolymerization of the complexes was carried out in acetonitrile as previously described.[14] The surface coverage was controlled to the desired value, via the time of polymerization. Surface coverages were determined from integration of the area under the voltammetric waves. For these complexes, a coverage of one monolayer corresponds to approximately 1×10^{-10} mol/cm^2 of monomer units. Afterward, the modified electrodes were thoroughly rinsed with acetone and water and subsequently transferred to aqueous solutions and allowed to equilibrate for at least 30 min. The electrocatalytic activity of the electropolymerized metal complexes toward the reduction of carbon dioxide was tested by comparing their voltammetric response under an atmosphere of nitrogen and carbon dioxide, respectively.

The detection and quantification of formaldehyde and formate (formic acid) was through the chromotropic acid test.[19] For the determination of formaldehyde, a 1.0 mL sample of electrolyzed solution was diluted to 10 mL with sulfuric acid. Chromotropic acid was subsequently added and the solution was heated in a water bath at 60 °C for 30 min. The absorbance of the solution at 484 and 578 nm was obtained and the values compared with those obtained from a calibration curve using standard formaldehyde solutions prepared from ACS reagent formaldehyde. For the determination of formate, the electrolyzed solution was initially reduced with Mg/HCl and the same procedure as described above was subsequently followed. The amount of formate generated was determined by difference. The generation of CO was determined by gas chromatography on a Hewlett-Packard Model 5890 gas chromatograph using a column packed with carbospheres and with He as the carrier gas. Blank experiments were carried out with the identical procedure except that the electrode was not modified with electropolymerized films of the metal complex.

After bulk electrolysis, the electrodes were rinsed with water and acetone, and the coverage was again determined in acetonitrile in order to determine the amount of material lost. In general, losses after electrolysis were typically small (10−15%) as long as potentials more negative than about −1.30 V were avoided. Electropolymerized films of $[Fe(4\text{-v-tpy})_2]^{2+}$ proved to be quite sensitive to the potential applied during bulk electrolysis so that significant (over 50%) losses were observed for potentials more negative than −1.10 V.

Current efficiencies were estimated from the charge consumed during electrolysis and from a knowledge of the surface coverage and the products (formaldehyde, formic acid and CO) and their distribution.

Results and Discussion

1. Preliminary Electrochemical Characterization. The electrochemical behavior of terpyridine complexes of transition metals is relatively well-known,[17] and only a brief description is given here. This is followed by a discussion of the behavior of electropolymerized films.

In solution, the complexes exhibited both metal-localized as well as ligand-localized processes. For the iron and osmium complexes,[17,20] one metal-based redox process was observed at +1.06 and +0.77 V, respectively. For the ruthenium complexes, the potential of the metal localized ($Ru^{II/III}$) oxidation was dependent on the nature of the ligands. $E^{\circ\prime}$ values for the specific complexes were as follows: $[Ru(4\text{-v-tpy})_2]^{2+}$, +1.26 V; $[Ru(4\text{-v-tpy})(tpy)]^{2+}$, +1.29 V; and $[Ru(6\text{-v-tpy})_2]^{2+}$, +1.36 V. The $[Co(4\text{-v-tpy})_2]^{2+}$ [21] and $[Ni(4\text{-v-tpy})_2]^{2+}$ [22] complexes, as anticipated, exhibited two metal-based redox processes at

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Table 1. Formal Potentials (vs Ag/AgCl) for Solutions of 4-v-tpy and 6-v-tpy Complexes of Transition Metals at a Glassy Carbon Electrode in MeCN Containing 0.1 M TBAP

complex	metal-based $E^{\circ\prime}$ (v) [ΔE_p (mV)]	ligand-based $E^{\circ\prime}$ (v) [ΔE_p] (mV)]
$[Cr(4\text{-v-tpy})_2]^{2+}$	−0.15 [80] Cr(II)/Cr(I) −0.51 [70] Cr(I)/Cr(0) −0.94 [70][a]	−1.29 [70] −1.47 [70]
$[Fe(4\text{-v-tpy})_2]^{2+}$	+1.06 [80] Fe(III)/Fe(II)	−1.19 [80] −1.32 [80]
$[Co(4\text{-v-tpy})_2]^{2+}$	+0.26 [60] Co(III)/Co(II) −0.79 [60] Co(II)/Co(I)	−1.70 [60]
$[Ni(4\text{-v-tpy})_2]^{2+}$	+1.62 [110] Ni(III)/Ni(II) −1.25 [80] Ni(II)/Ni(I)	−1.45 [100]
$[Ru(4\text{-v-tpy})_2]^{2+}$	+1.26 [70] Ru(III)/Ru(II)	−1.20 [70] −1.41 [70]
$[Ru(4\text{-v-tpy})(tpy)]^{2+}$	+1.29 [70] Ru(III)/Ru(II)	−1.20 [70] −1.45 [70]
$[Ru(6\text{-v-tpy})_2]^{2+}$	+1.36 [70] Ru(III)/Ru(II)	−1.18 [70] −1.44 [70]
$[Os(4\text{-v-tpy})_2]^{2+}$	+0.77[60] Os(III)/Ru(II)	−1.31 [70] −1.41 [70]

[a] Intermediate case where the redox process is metal/ligand localized.

+0.26 and −0.79 V for the cobalt and +1.62 and −1.25 V for the nickel complex, respectively. The chromium complex $[Cr(4\text{-v-tpy})_2]^{2+}$ exhibited three metal-based redox processes at −0.15, −0.51, and −0.94 V, respectively.

In addition, all the complexes exhibited ligand localized reductions over the range of −1.10 to −1.70 V. Table 1 presents a compilation of the electrochemical data determined by cyclic voltammetry in acetonitrile. All redox processes involved one-electron transfers unless otherwise indicated.

As we have reported earlier[14] for 4-v-tpy and 6-v-tpy complexes of transition metals, these materials undergo electroreductively initiated polymerization (in non-aqueous solvents such as acetonitrile) to give rise to electrodes modified with an electroactive polymeric film of the complex. The polymeric films generally exhibit redox processes at approximately the same potentials as those observed in solutions of the complexes and these data are presented in Table 2. In a number of cases (e.g., for $[Co(4\text{-v-tpy})_2]^{2+}$, $[Fe(4\text{-v-tpy})_2]^{2+}$, $[Ni(4\text{-v-tpy})_2]^{2+}$, and $[Ru(6\text{-v-tpy})_2]^{2+}$) the electropolymerized films exhibited additional redox processes not present for the complexes in homogenous solution (see Tables 1 and 2). We have previously documented such behavior (the case of $[Co(4\text{-v-tpy})_2]^{2+}$ has been investigated in detail[14b]), which we believe is due to the generation of complexes where there is partial displacement of the terpyridine ligand and coordination by acetonitrile, which is a moderately strong coordinating solvent. When electropolymerizations are carried out in DMF (or the electrode with an electropolymerized film is transferred to a DMF/0.1 M TBAP solution) which; relative to acetonitrile, is a much weaker coordinating solvent, these additional waves are absent, consistent with the above statement.[14b,e] Parts a and b of Figure 1 present, respectively, consecutive voltammetric scans for acetonitrile/0.1M TBAP solutions of $[Co(4\text{-v-tpy})_2]^{2+}$ and $[Fe(4\text{-v-tpy})_2]^{2+}$, and it can be seen that they readily undergo electroinitiated polymerization and that there are additional voltammetric waves that appear as the polymerization progresses. Qualitatively similar behavior was observed for $[Ni(4\text{-v-tpy})_2]^{2+}$.[14e]

The $[Ru(6\text{-v-tpy})_2]^{2+}$ exhibited somewhat anomalous behavior. First of all, as reported previously,[14a] this complex undergoes electroinitiated polymerization at a much slower rate than any of the other complexes. In fact, we had previously reported[14a] that this complex undergoes electropolymerization at a rate that is more than 2 orders of magnitude (150 times) slower than that for the $[Ru(4\text{-v-tpy})_2]^{2+}$ complex. In addition, and as mentioned above, as polymerization progresses, we also see the appearance of additional redox waves at formal potentials of +0.11 and −0.22 V, respectively, which are likely metal-localized redox processes since the potentials are much too positive for the processes to be ligand-based. Relative to the other complexes of ruthenium investigated; mainly $[Ru(4\text{-v-tpy})_2]^{2+}$ and $[Ru(tpy)(4\text{-v-tpy})]^{2+}$, the electrochemical behavior of this complex is unusual and we believe that it is due to the fact that having the vinyl groups in the 6-position gives rise to a significant degree of steric repulsion making electropolymerization more difficult and the complex more susceptible to substitution. The main panel in Figure 1c depicts both the electropolymerization of $[Ru(6\text{-v-tpy})_2]^{2+}$ as well as the appearance of the additional waves at formal potentials of +0.11 and −0.22 V, respectively which we ascribe to metal-localized

Table 2. Formal Potentials (vs Ag/AgCl) for Electropolymerized Films of 4-v-tpy and 6-v-tpy Complexes of Transition Metals at a Glassy Carbon Electrode in MeCN Containing 0.1 M TBAP and Potential for Electrocatalytic Reduction of CO_2 in Aqueous 0.10 M $NaClO_4$

complex	metal-based $E^{\circ\prime}$ (v) [ΔE_p (mV)]	ligand-based $E^{\circ\prime}$ (v) [ΔE_p (mV)	CO_2 reduction potential[a] (v)
$[Cr(4\text{-v-tpy})_2]^{2+}$	−0.14 [50] Cr(II)/Cr(I) −0.49 [60] Cr(I)/Cr(0) −0.93 [60][b]	−1.26 [90] −1.45 [100]	−0.86
$[Fe(4\text{-v-tpy})_2]^{2+}$	+1.16 [60] Fe(III)/Fe(II)	−1.13 [80] −1.25 [80	−1.10
$[Co(4\text{-v-tpy})_2]^{2+}$	+0.26 [60] Co(III)/Co(II) −0.03 [60][c] −0.76 [70] Co(II)/Co(I) −1.12 [60][d]	−1.62 [60]	−0.87
$[Ni(4\text{-v-tpy})_2]^{2+}$	+1.65 [100] Ni(III)/Ni(II) −1.14 [70] Ni(II)/Ni(I)	−1.45 [100]	−1.12
$[Ru(4\text{-v-tpy})_2]^{2+}$	+1.25 [70] Ru(III)/Ru(II)	−1.18 [80] −1.38 [90]	−1.20
$[Ru(4\text{-v-tpy})(tpy)]^{2+}$	+1.26 [70] Ru(III)/Ru(II)	−1.16 [80] −1.37 [80]	−1.17
$[Ru(6\text{-v-tpy})_2]^{2+}$	+1.40 [70] Ru(III)/Ru(II) +0.11 [80][e] −0.22 [80][e]	−1.14 [60] −1.38 [60] −1.87 [60]	−1.13
$[Os(4\text{-v-tpy})_2]^{2+}$	+0.80[60] Os(III)/Ru(II)	−1.29 [90] −1.39 [90]	−1.22
bare glassy carbon electrode			−1.80[f]

[a] Peak potential value for the first redox wave whose current increases in the presence of CO_2 relative to N_2 in 0.10 M aqueous $NaClO_4$ solution. [b] Intermediate case where the redox process is metal/ligand localized. [c] Co(III)/Co(II) process with coordinated acetonitrile. [d] Co(II/I) process with coordinated acetonitrile. [e] Likely metal based processes. [f] In DMF due to solvent limit.

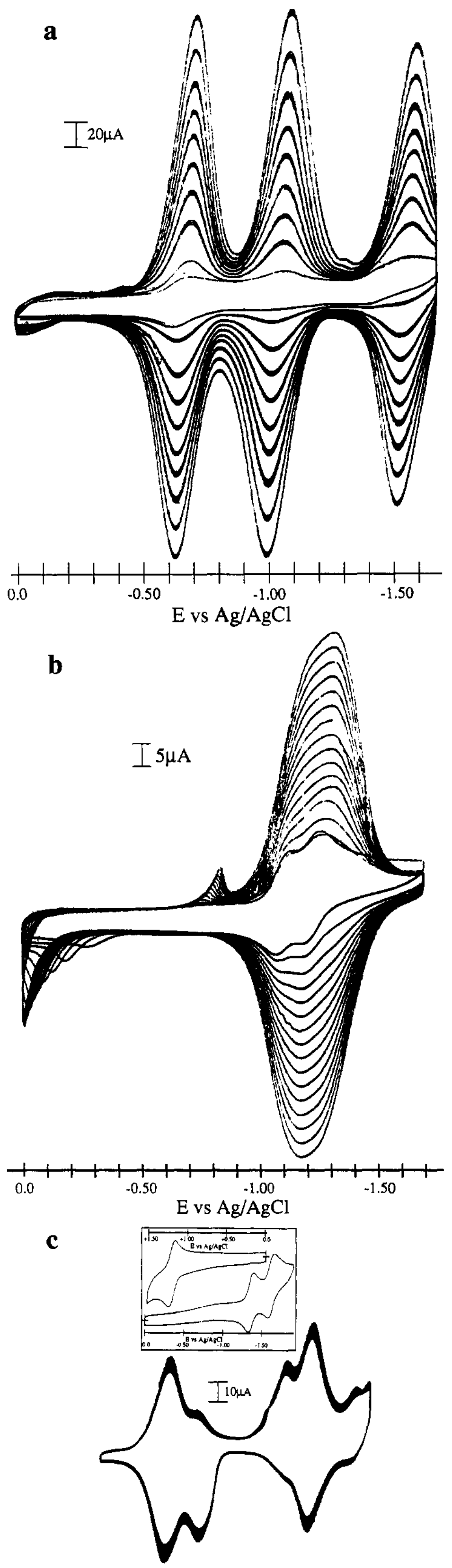

Figure 1. Consecutive cyclic voltammograms at a sweep rate of 100 mV/s depicting electropolymerization for a glassy carbon electrode in contact with a 0.10 M TBAP/ACN solution containing (a) [Co(4-v-tpy)$_2$](PF$_6$)$_2$, (b) [Fe(4-v-tpy)$_2$](PF$_6$)$_2$, and (c) [Ru(6-v-tpy)$_2$](PF$_6$)$_2$. Note: Because of the very slow rate of polymerization, scans were recorded over approximately a 2-h period. Inset: Initial cyclic voltammograms depicting the metal-based oxidation and the two ligand-based reductions. Notice the absence of any voltammetric features at +0.11 and −0.22 V.

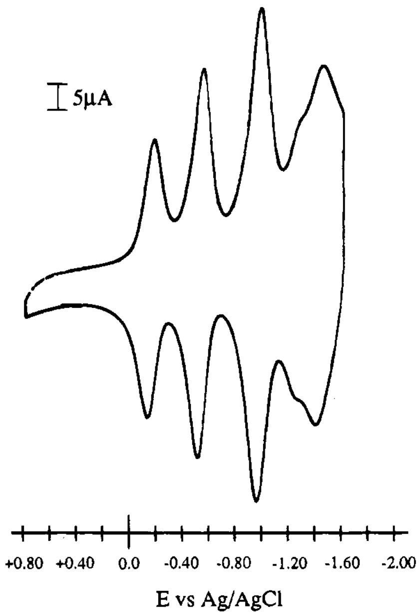

Figure 2. Cyclic voltammogram in 0.10 M TBAP/ACN at a sweep rate of 100 mV/s for a glassy carbon electrode modified with an electropolymerized film of [Cr(4-v-tpy)$_2$](PF$_6$)$_2$.

processes. These voltammograms were taken over a time period of about 2 h. which is much longer than the time required for electropolymerization of the other complexes (e.g. see Figure 1a,b) and is, again consistent with previous results.[14a] The inset to Figure 1c depicts the initial voltammograms were the metal localized oxidation as well as the two ligand-based reductions are clearly evident as in the absence of the waves at formal potentials of +0.11 and −0.22 V, respectively.

The other complexes ([Ru(4-v-tpy)$_2$]$^{2+}$, [Ru(4-v-tpy)(tpy)]$^{2+}$, [Cr(4-v-tpy)$_2$]$^{2+}$, and [Os(4-v-tpy)$_2$]$^{2+}$ also underwent electroinitiated polymerization and gave rise to redox-active films with no additional redox waves.

The redox response for electrodes modified with electropolymerized films of the complexes exhibited shapes characteristic of surface-bound species. For example, Figure 2 presents the cyclic voltammogram in acetonitrile/0.10 M TBAP for a glassy carbon electrode modified with an electropolymerized film of [Cr(v-tpy)$_2$](PF$_6$)$_2$. The voltammetric waves are sharp and symmetrical as would be anticipated. For sweep rates of up to about 200 mV/s the waves are symmetrical and ΔE_p is small. At higher sweep rates the waves take on a more "difussional" shape with a concomitant increase in ΔE_p. Plots of peak current vs sweep rate were linear as anticipated for surface-bound species for sweep rates up to about 200 mV/s. At higher sweep rates some deviations were noted especially when high surface coverages (e.g. 100 equivalent monolayers) were employed. As mentioned earlier, surface coverages were determined by integration of the area under the redox waves. The electropolymerized films were found to be quite robust and resistant to continuous washings with water, acetone, and acetonitrile. In addition, they were also quite stable to potential cycling with less that 10% loss after 6 h of continuous cycling.

In aqueous solution (0.10 M NaClO$_4$) the films remained electroactive although the redox responses were typically broader. For example trace A in Figure 3a depicts the voltammetric behavior of an electrode modified with a film of [Co(4-v-tpy)$_2$]$^{2+}$ in 0.10 M NaClO$_4$ saturated with nitrogen. When compared to those for voltammograms in acetonitrile (e.g. Figure 2), it is clear that the redox responses in aqueous environments are broader. However, the sharp voltammetric response is restored when the electrode is placed back in acetonitrile solution. This would suggest that charge propaga-

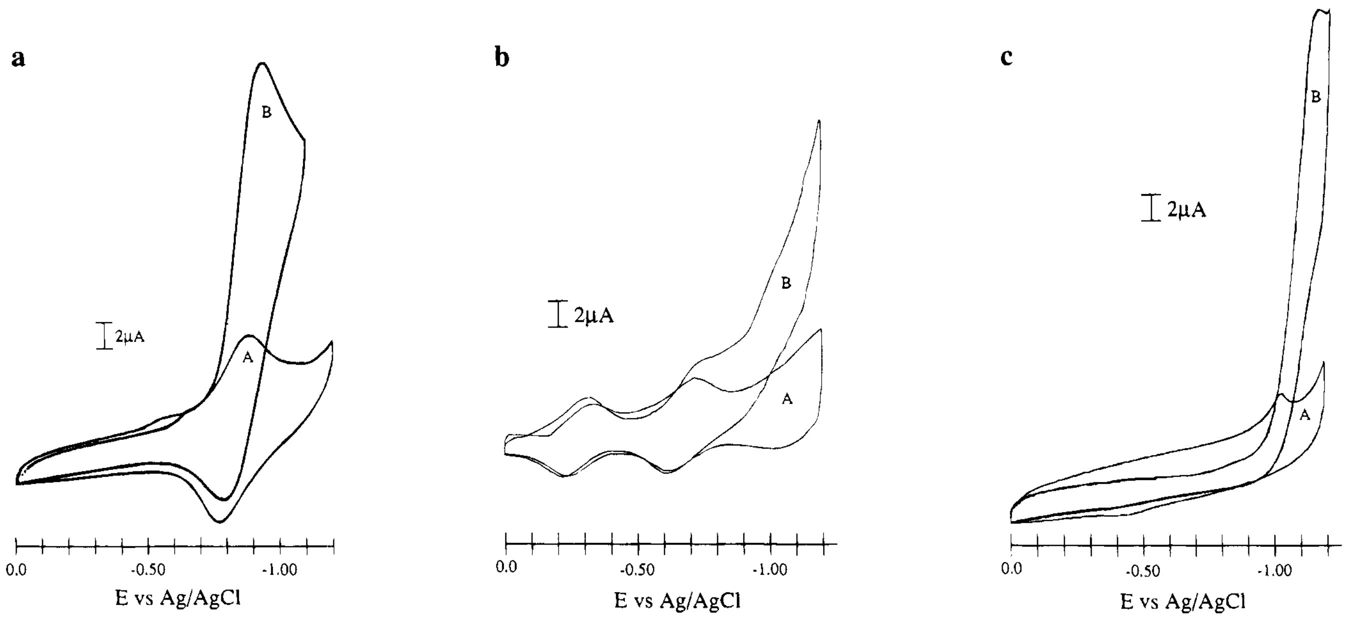

Figure 3. (a) Cyclic voltammograms at 10 mV/s in aqueous 0.10 M $NaClO_4$ for a glassy carbon electrode modified with an electropolymerized film of $[Co(4\text{-v-tpy})_2](PF_6)_2$ under nitrogen (A) and carbon dioxide (B) atmospheres. (b) Cyclic voltammograms at 10 mV/s in aqueous 0.10 M $NaClO_4$ for a glassy carbon electrode modified with an electropolymerized film of $[Cr(4\text{-v-tpy})_2](PF_6)_2$ under nitrogen (A) and carbon dioxide (B) atmospheres. (c) Cyclic voltammograms at 10 mV/s in aqueous 0.10 M $NaClO_4$ for a glassy carbon electrode modified with an electropolymerized film of $[Fe(4\text{-v-tpy})_2](PF_6)_2$ under nitrogen (A) and carbon dioxide (B) atmospheres.

tion is slower in aqueous media perhaps due to differences in solvation and/or permeability of the film in aqueous vs nonaqueous solvents. Such effects have been previously documented.[11]

2. General Electrocatalytic Activity of Electropolymerized Films. The electrocatalytic activity of electropolymerized films was evaluated by comparing the voltammetric response in an atmosphere of CO_2 with that obtained under an atmosphere of N_2 under otherwise identical conditions. In all cases tested, the electropolymerized films exhibited electrocatalytic activity toward the reduction of CO_2. For example, parts a–c of Figure 3 depict the voltammetric responses in aqueous 0.1M $NaClO_4$ solutions under CO_2 and N_2 atmospheres for glassy carbon electrodes modified with electropolymerized films of $[Co(4\text{-v-tpy})_2]^{2+}$, $[Cr(4\text{-v-tpy})_2]^{2+}$, and $[Fe(4\text{-v-tpy})_2]^{2+}$, respectively. In all three cases there is a dramatic shift in the potential at which CO_2 is reduced (relative to the potential at a bare electrode; -1.80 V; note that this value is in DMF solvent; see below) as well as an enhancement in current consistent with an electrocatalytic process.

The potential at which the catalysis occurs is dependent on the nature of the metal center. As a point of comparison we take the peak potential value for the first redox wave whose current increases in the presence of CO_2 relative to N_2. For the chromium, cobalt, and iron complexes these potentials were -0.86, -0.87 and -1.10 V, respectively. The shift in the potential for CO_2 reduction employing electropolymerized films of the chromium and cobalt complexes was approximately 1 V, which is a very dramatic diminution in the activation energy. However it is also clear that the relative increase in current in the presence and absence of CO_2 is much larger for electropolymerized films of the cobalt complex relative to the chromium complex.

The last column in Table 2 shows the potentials for the reduction of CO_2 in aqueous 0.10 M $NaClO_4$ solutions at electrodes modified with electropolymerized films of the various complexes. As mentioned above, this potential represents the peak potential value for the first redox wave whose current increases in the presence of CO_2 relative to N_2. For comparison purposes, the reduction of CO_2 at a bare glassy carbon electrode in DMF is also included. DMF was employed since in aqueous solution the direct reduction of CO_2 at a glassy carbon electrode is beyond the solvent limit.

As can be ascertained from the table, the potential at which CO_2 is reduced is strongly dependent on the nature of the metal center. The most positive potential (largest diminution in the activation energy) is observed for electropolymerized films of $[Cr(4\text{-v-tpy})_2]^{2+}$ (-0.86 V), whereas the most negative value is obtained for electropolymerized films of $[Os(4\text{-v-tpy})_2]^{2+}$ (-1.22 V). In addition it can also be observed that, in general, the potentials for complexes of metals of the first row are significantly less negative than for metals of the second (e.g. Ru) or third (e.g. Os) rows. Such an effect is indeed anticipated and will be discussed in more detail below.

3. Product Analysis and Yield of the Catalytic Process. With the aim of determining the products and the yield of the catalytic reaction, CO_2 saturated (215 mM)[23,24] aqueous $NaClO_4$ solutions were electrolyzed at glassy carbon electrodes modified with electropolymerized films of $[Co(4\text{-v-tpy})_2]^{2+}$, $[Fe(4\text{-v-tpy})_2]^{2+}$, and $[Cr(4\text{-v-tpy})_2]^{2+}$ at potentials of -1.10, -1.075, and -1.10 V, respectively. The lower potential employed in the case of the iron complex was due to instabilities of the film as mentioned earlier. We tested for the production of formaldehye and formic acid using the chromotropic acid test and for the production of carbon monoxide using gas chromatography. In all cases, formaldehyde was detected as virtually the only reaction product. Neither formic acid nor carbon monoxide was detected to within the limits of the chromotropic acid test and gas chromatography, respectively.

This is rather different from results for the electrocatalytic reduction of CO_2 in non-aqueous media (DMF) using electropolymerized films of these materials where formate was virtually the only reaction product.[14c,d] We ascribe this rather marked difference to the aprotic nature of the solvent.

In order to determine the yield of the electrocatalytic process,

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(23) Stephen, H.; Stephen, T. *Solubilities of Inroganic and Organic Compounds*; Pergamon Press: New York, 1963; Vol. 1, p 1063.

(24) Linke, W. F. *Solubilities of Inooganic and Metallorganic Compounds*, 4th ed.; American Chemical Society: Washington, DC, 1965; Vol. 11, p 1229.

Table 3. Yield of Formaldehyde in CO_2-Saturated Aqueous 0.10 M $NaClO_4$ Solution for Glassy Carbon Electrodes Modified with Electrpolymerized Films of $[Co(4\text{-v-tpy})_2]^{2+}$, $[Fe(4\text{-v-tpy})_2]^{2+}$, and $[Cr(4\text{-v-tpy})_2]^{2+}$

complex	charge (Coul.)	HCHO generated (mol × 10^6) [equiv Q (coulomb)[a]]	applied potential (V)	turnovers[b]	yield (%)
$[Co(4\text{-v-tpy})_2]^{2+}$	2.31	2.33 [0.90]	−1.100	11,000	39
$[Fe(4\text{-v-tpy})_2]^{2+}$	2.88	2.07 [0.80]	−1.075	15,000	28
$[Cr(4\text{-v-tpy})_2]^{2+}$	1.10	2.49 [0.96]	−1.100	6,100	87

[a] Charge corresponding to the number of moles of formaldehyde detected. [b] Estimated from the amount of charge consumed and the surface coverage.

the amount of formaldehyde generated (obtained from a calibration curve) was compared to the amount of charge passed during the electrolysis and assuming a four-electron process. The results are presented in Table 3. The highest yield (87%) was obtained for the chromium complex. On the other hand, the yield for the iron complex was rather low (27%) which, could be due to the fact that the potential employed was actually below E_{cat} by about 25mV. This potential was chosen because of the instability of the films at potentials around −1.10 V mentioned earlier. In the case of the cobalt complex, the yield was also rather low (39%) even though the applied potential was similar to that of the chromium complex. At this time, we are uncertain as to the final fate of the redox equivalents unaccounted for.

Table 3 also presents values of the turnover numbers estimated from the surface coverage for the electropolymerized films of the various complexes and the amount of charge consumed during the electrolysis. In all cases very high turnover numbers were obtained as can be ascertained from Table 3.

4. Kinetics of Electrocatalysis of CO_2 Reduction with Electropolymerized Films. In an effort to further characterize the electrocatalytic process and in order to determine the rate constant, rotated disk electrode voltammetry experiments were carried out with electrodes modified with electropolymerized films of 4-v-tpy complexes of various metals and at various coverages. Plots of i_l vs $\omega^{1/2}$ (Levich plots) were linear at low rotation rates (typically up to 1000 rpm) implying that, under these conditions, the reaction is under mass transport control. However, at fast rates of rotation (beyond 1000 rpm), the limiting currents were below the values anticipated (from extrapolation) for a mass transport controlled process suggesting that there was a kinetic limitation. Under these conditions, the Koutecky−Levich[25] equation can be used to determine the rate constant for the process. The Koutecky−Levich equation can be formulated as follows:

$$1/i_{\text{lim}} = 1/(nFAk\Gamma C_b) + 1/(0.62nFA\nu^{-1/6}D^{2/3}\omega^{1/2}C_b) \qquad (1)$$

where C_b is the bulk concentration of the reactant in solution (in this case the solution concentration of CO_2 at saturation was estimated to be 215 mM [23,24]), Γ is the total surface coverage, ν is the kinematic viscosity, ω is the rate of rotation, and k is the rate constant with all other symbols having their conventional meaning. From equation 1 it is apparent that the value of k can be determined from the intercept of a plot of $1/i_{\text{lim}}$ vs $1/\omega^{1/2}$ (or a so-called Koutecky−Levich plot).

A typical Koutecky−Levich plot for an electrode modified with an electropolymerized film of $[Cr(4\text{-v-tpy})_2]^{2+}$ is presented in Figure 4. In this particular case the rate constant was determined to be 24 M^{-1} s^{-1}. Data for the other materials tested and the coverage employed (in equivalent monolayers) are presented in Table 4. In the case of electrodes modified with electropolymerized films of $[Co(4\text{-v-tpy})_2]^{2+}$ the rates were extremely low. This is in stark contrast to similar measurements carried out in DMF where values in the neighborhood of 10^3 M^{-1} s^{-1} were obtained for coverages between 50−100 equivalent monolayers.[14c,d]

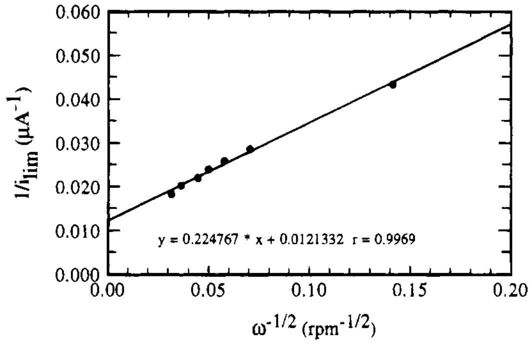

Figure 4. Koutecky−Levich plot for the reduction of carbon dioxide in CO_2 saturated aqueous 0.10 M $NaClO_4$ at a glassy carbon electrode modified with an electropolymerized film of $[Cr(4\text{-v-tpy})_2](PF_6)_2$ at a coverage of 18 equivalent monolayers.

Table 4. Rate Constants for the Reduction of CO_2 by Electropolymerized Films of 4-v-tpy Complexes of Transition Metals in CO_2 Saturated Aqueous 0.10 M $NaClO_4$ Solution

complex	surface coverage (equivalent monolayers)	K (M^{-1} s^{-1})
$[Os(4\text{-v-tpy})_2]^{2+}$	92	6
$[Ru(4\text{-v-tpy})_2]^{2+}$	41	12
$[Ru(4\text{-v-tpy})_2]^{2+}$	81	4
$[Ru(4\text{-v-tpy})_2]^{2+}$	92	4
$[Fe(4\text{-v-tpy})_2]^{2+}$	66	8
$[Co(4\text{-v-tpy})_2]^{2+}$	10−200	
$[Cr(4\text{-v-tpy})_2]^{2+}$	18	24
$[Cr(4\text{-v-tpy})_2]^{2+}$	62	6
$[Cr(4\text{-v-tpy})_2]^{2+}$	213	3

Looking at the values for the rate constants (Table 4) we note that they ranged from 3 to 24 M^{-1} s^{-1}. In all cases, the values for the rate constants were significantly smaller than those measured in DMF.[14c] These differences in the rate constants could be due to the fact that whereas in DMF the reaction product is formate, which is a 2-electron reduction, in aqueous media the product is formaldehyde which is a 4-electron process. The fact that the rate in the former is much larger than in the latter, suggests that the 4-electron reduction to formaldehye is kinetically a much more difficult process, as would be anticipated.

It can also be observed from Table 4 that for different coverages using the same modifier (e.g. $[Cr(4\text{-v-tpy})_2]^{2+}$ or $[Ru(4\text{-v-tpy})_2]^{2+}$) the rate is significantly higher at low coverages than at high coverages. For example for films of $[Cr(4\text{-v-tpy})_2]^{2+}$ a rate of 24 M^{-1} s^{-1} is obtained for a coverage of 18 equivalent monolayers whereas at a coverage of 213 equivalent monolayers, the rate drops to 3 M^{-1} s^{-1}. A similar trend is observed for films of $[Ru(4\text{-v-tpy})_2]^{2+}$ as seen in Table 4. This could be due to slower rate of charge propagation through the thicker polymeric films or that only part of the electrodeposited material is electrocatalytically active.[11] Although such behavior could also be due, in principle, to a slower rate of permeation of CO_2, we do not feel that this is the case since the permeation of a gaseous species would be anticipated to be relatively high

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(25) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods Fundamentals and Applications*; Wiley, New York, 1980.

Table 5. Effect of Supporting Electrolyte anions on the Metal-Based Co(II/I) Potential and on the Electrocatalytic Reduction of CO_2 in CO_2-Saturated Aqueous 0.1 M $NaClO_4$ Solution at Electrodes Modified with Electropolymerized Films of $[Co(4\text{-v-tpy})_2]^{2+}$

supporting electrolyte (0.10 M)	Co(II)/Co(I) reduction E_p(V)	potential forCO_2 Reduction (V)	$i_p(CO_2)/i_p(N_2)$ [surface coverage (equiv monolayers)]
$NaNO_3$	−0.83	−0.87	4.0 [72]
$NaClO_4$	−0.83	−0.87	4.9 [75]
pH 5 acetate buffer	−0.78	−0.87	1.8 [84]
NaCl	−0.77	−0.87	1.2 [54]
NaH_2PO_4	−0.72	...	... [92]

and thus not rate limiting. However, we have no direct evidence in support of this.

5. Effect of Supporting Electrolyte on the Electrocatalytic Process. From our earlier studies[14] we have found that the electrocatalytic activity of these films hinges on the ability of generating an empty coordination site so that the substrate (e.g., CO_2) can bind to the metal center. This implies that one of the ligands must be displaced and CO_2 must bind to the metal center. We have found that such a process is much more facile for electropolymerized films than for the analogous complexes in homogeneous solution (e.g. electropolymerized films of $[Co(4\text{-v-tpy})_2]^{2+}$ are much more electrocatalytically active than $[Co(tpy)_2]^{2+}$ in solution) and we ascribed this difference in reactivity to steric constraints present in the film as well as to the much higher effective concentration (over 0.2 M) of the catalyst as an electropolymerized film. However, the binding process represents a competition, among all the species present in solution and the substrate, for the available coordination sites. Thus the nature of the solvent and other species in solution can play a very significant role. In fact, we have previously demonstrated[14c] that, in non-aqueous solvents, the electrocatalytic activity of electropolymerized films of $[Co(4\text{-v-tpy})_2]^{2+}$ toward CO_2 reduction is much higher in DMF than in acetonitrile, and we ascribed this difference to the much higher coordinating strength of acetonitrile relative to DMF.

Similarly, one would expect that the nature of other species in solution could also affect the electrocatalytic behavior of these electropolymerized films. Of particular relevance in this case would be the supporting electrolyte ions. In order to evaluate this effect, we have employed various supporting electrolytes in aqueous media (all at 0.10 M concentration) and have studied the effects on the potential of the Co(II/I) couple under a nitrogen atmosphere as well as the electrocatalytic behavior toward the reduction of CO_2 of electropolymerized films of $[Co(4\text{-v-tpy})_2]^{2+}$. The results are presented in Table 5.

As can be ascertained from the table, the formal potential of the Co(II/I) couple under a nitrogen atmosphere varies according to the nature of the anion. The value of the formal potential becomes increasingly negative over the series: $H_2PO_4^-$ (−0.72 V), Cl^- (−0.77 V), $HOAc/OAc^-$ (pH 5) (−0.78 V), NO_3^- (−0.83 V), and ClO_4^- (−0.83 V). In addition, the electrocatalytic activity (defined as the ratio of currents under CO_2 and N_2 atmospheres) increased in the same order, being lowest (no catalysis) for $H_2PO_4^-$ and highest for ClO_4^-. In general, one would anticipate that the more negative the formal potential, the stronger the interaction between the anion and a Co(II) center. The opposite would be true for Co(I). The observed trend would suggest that the anions are interacting more strongly with Co(I), which would be contrary to expectation. However, the electrocatalytic activity follows the trend anticipated from the strength of interaction (as reflected by formation constants[26]) of the anion with the metal center. These observations would suggest that there must be other factors affecting the potential of the Co(II/I) couple.

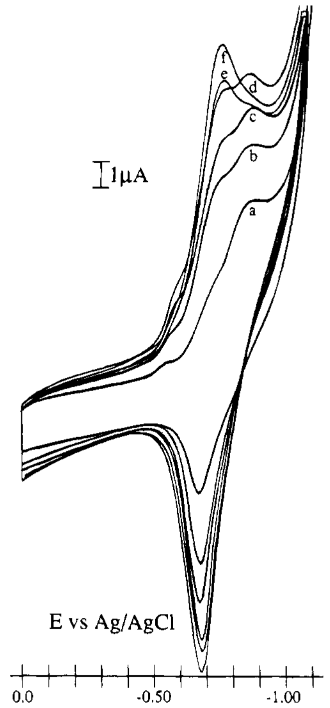

Figure 5. Cyclic voltammograms as a function of sweep rate for a glassy carbon electrode modified with an electropolymerized film of $[Co(4\text{-v-tpy})_2](PF_6)_2$ in CO_2 saturated aqueous 0.10 M KCl. Sweep rates in mV/s: a, 5; b, 10; c, 12; d, 15; e, 17; f, 20.

We also have additional electrochemical evidence in support of competitive binding effects and this comes from sweep rate dependent studies of the electrocatalytic reduction of CO_2 in 0.10 M aqueous NaCl at electrodes modified with electropolymerized films of $[Co(4\text{-v-tpy})_2]^{2+}$. The voltammetric responses, presented in Figure 5, exhibit two peaks. The most positive of these two peaks is present under both nitrogen and carbon dioxide atmospheres whereas the more negative one is present only under an atmosphere of carbon dioxide. Thus we ascribe the first wave to the Co(II/I) process where chloride is bound to the metal and the second wave to the electrocatalytic reduction of carbon dioxide bound to the cobalt center. It is also apparent from the figure that the relative amplitudes of these two processes are sweep rate dependent. At low sweep rates (5, 10, and 12mV/s; curves a, b, and c, respectively) the most negative redox process, associated with the electrocatalytic reduction of carbon dioxide is dominant whereas at fast sweep rates (15, 17, and 20 mV/s; curves d, e, and f), the first wave, ascribed to the Co(II/I) reduction with bound chloride has a higher amplitude. In a qualitative sense, this is the behavior anticipated for an $ECEC_{cat}$ process where the chemical step is not very fast. We have not attempted a more quantitative analysis because of the significant overlap between these two processes.

Although the above mentioned statements and observations are clearly of a qualitative nature, they can provide guidelines for future work.

6. Reactivity Differences among the Various Complexes. A. Complexes of First Row Metals. There are significant differences in the reactivity of the various complexes studied

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(26) Sillén, L. G.; Martell, A. E. *Stability Constants of Metal-Ion Complexes*; The Chemical Society Special Publication No. 17; The Chemical Society: London, 1964.

including those between complexes of metals from different rows; especially first vs second and third. There are also differences for complexes within a row. For electropolymerized films of $[Cr(4\text{-}v\text{-}tpy)_2]^{2+}$ and $[Co(4\text{-}v\text{-}tpy)_2]^{2+}$, the electrocatalytic reduction of CO_2 occurs at about −0.87 V whereas for films of $[Fe(4\text{-}v\text{-}tpy)_2]^{2+}$ and $[Ni(4\text{-}v\text{-}tpy)_2]^{2+}$ the process takes place at about −1.10 V. Such behavior is depicted in Figure 3a,c which shows the voltammetric responses under nitrogen and carbon dioxide atmospheres for electrodes modified with electropolymerized films of $[Co(4\text{-}v\text{-}tpy)_2]^{2+}$ and $[Fe(4\text{-}v\text{-}tpy)_2]^{2+}$, respectively.

The difference in electrocatalytic activity likely arises as a result of the existence (absence) of metal-based redox processes at the appropriate potentials for the electrocatalytic reduction of CO_2. The cobalt complex has two reversible metal-based redox processes at formal potentials of +0.26 and −0.76 V, which correspond to Co(III/II) and Co(II/I) processes, respectively. Similarly, the chromium complex has two reversible metal-based redox processes at formal potentials of −0.14 and −0.49 V, which correspond to Cr(III/II) and Cr(II/I), respectively. The presence of metal-based redox processes at the appropriate potentials would increase the catalytic activity since it would enhance the interaction between the metal center and the ostensibly bound CO_2 thus facilitating the overall reaction.

Another aspect that needs to be kept in mind is that because the effective concentration of these electropolymerized films can reach values of over 0.2 M, cooperativity effects between two (or more) metal complexes can be favored and/or enhanced.

In the present case the predominant reduction product is formaldehyde which requires the transfer of four electrons per molecule of CO_2. Thus, one would need the interaction of either two or four molecules depending on whether they can act as one or two electron donors. This clearly favors molecules that can act as two-electron donors such as the chromium and cobalt complexes and is consistent with their higher reactivity.

In the case of electropolymerized films of $[Ni(4\text{-}v\text{-}tpy)_2]^{2+}$ the Ni(III/II) process is at a very positive potential (+1.65 V) so that it is unable to participate in the electrocatalytic process. On the other hand, the Ni(II/I) process is at −1.14 V, a value that coincides with the onset of the electrocatalytic reduction of CO_2 at electrodes modified with electropolymerized films of this complex. Since it is most unlikely that the nickel complex can act as a two-electron donor, we believe that in this case the process takes place through sequential one-electron transfers.

The iron complex $[Fe(4\text{-}v\text{-}tpy)_2]^{2+}$ represents a case that is distinctly different from those considered previously in that the only metal-based (Fe(III/II)) redox process is at a very positive potential (+1.16 V), precluding its participation in the catalytic process. On the other hand, the complex exhibits ligand-based reductions at potentials that are appropriate for the electrocatalytic reduction of CO_2. The ligand orbitals where these electrons reside are predominantly π^* in character. Since the e_g orbitals of the metal are π in character, there might be sufficient interaction between these ligand- and metal-based orbitals for the electrocatalytic reaction to take place.

B. Complexes of Fe, Ru, and Os. We next consider electropolymerized films of $[Fe(4\text{-}v\text{-}tpy)_2]^{2+}$, $[Ru(4\text{-}v\text{-}tpy)_2]^{2+}$, and $[Os(4\text{-}v\text{-}tpy)_2]^{2+}$ since they reflect variations arising from the fact that the metal centers are from different rows in the transition series. As mentioned above for the iron complex, these materials do not have metal-based redox processes at potentials appropriate for the electrocatalytic reduction of CO_2. However, they all have ligand-based redox processes at potentials appropriate for the electrocatalytic reduction of CO_2. The potentials for these processes are generally around −1.20 V, a value which is significantly negative of the metal-based redox processes of the Cr, Co, and Ni complexes discussed earlier. As a result, the potentials for the electrocatalytic reduction of CO_2 at electrodes modified with electropolymerized films of $[Fe(4\text{-}v\text{-}tpy)_2]^{2+}$, $[Ru(4\text{-}v\text{-}tpy)_2]^{2+}$ and $[Os(4\text{-}v\text{-}tpy)_2]^{2+}$ tend to be more negative as is evident from Table 2.

There are also differences in the potentials, and reactivity that we believe arise from the fact that the metals belong to different rows in the transition series. For example, the potentials for the electrocatalytic reduction of CO_2 at electrodes modified with electropolymerized films of $[Fe(4\text{-}v\text{-}tpy)_2]^{2+}$, $[Ru(4\text{-}v\text{-}tpy)_2]^{2+}$ and $[Os(4\text{-}v\text{-}tpy)_2]^{2+}$ are −1.10, −1.20, and −1.22 V, respectively, consistent with their belonging to the first, second, and third row. The largest difference is between Fe and Ru (first and second) as would be anticipated. These differences reflect the fact that the stability of the tpy complexes increases as one goes down a column (Fe−Ru−Os) so that the generation of an empty coordination site; which we believe is necessary for binding and subsequent electrocatalytic activity, is rendered more difficult. Thus, a more negative potential would be required as was indeed observed.

C. Complexes of Ru with Vinyl Groups in Different Positions. Finally, we considered the effects of having the vinyl group(s) in different positions on the ligand. Specifically we considered Ru complexes with one or two (one on each ligand) vinyl group(s) in the 4-position (para to the pyridine nitrogen; 4-v-tpy) as well as complexes with vinyl groups (one on each ligand) in the 6-position (6-v-tpy). As was mentioned earlier, the ability of these three materials to polymerize is quite different with the relative polymerization rates being 150:30:1 for $[Ru(4\text{-}v\text{-}tpy)_2]^{2+}$, $[Ru(4\text{-}v\text{-}tpy)(tpy)]^{2+}$, and $[Ru(6\text{-}v\text{-}tpy)_2]^{2+}$, respectively.[14a] The potentials at which CO_2 is reduced at electrodes modified with electropolymerized films of these complexes are −1.20, −1.17, and −1.13 V, respectively. These potential shifts are ascribed to the different stability of the resulting complexes; especially $[Ru(6\text{-}v\text{-}tpy)_2]^{2+}$. This material has the vinyl groups in the 6-position, placing them in a position α to the ring nitrogen. This gives rise to a significant extent of steric strain so that it is easier to generate an empty coordination site which, as mentioned earlier, we believe to be a requisite to electrocatalytic activity. We believe that this is also responsible for the observation of additonal redox waves for electropolymerized films as mentioned earlier. The potential for electropolymerized films of $[Ru(4\text{-}v\text{-}tpy)_2]^{2+}$ was the most negative (−1.20 V), consistent with its higher stability.

Conclusions

We have prepared and characterized, by cyclic voltammetry and rotated disk electrode voltammetry in aqueous media and under nitrogen and carbon dioxide atmospheres, electropolymerized films of 4- and 6-vinyl terpyridine complexes of chromium, nickel, cobalt, iron, ruthenium, and osmium. These materials exhibit electrocatalytic activity toward the reduction of CO_2 with formaldehyde as virtually the only product. The magnitude of the catalytic effect and the efficiency are a function of the metal center and the location of the vinyl group(s) within the ligand. The catalytic activity of complexes having metal-based redox processes at negative potentials was superior to that of complexes where the relevant redox processes were ligand-based. Complexes of first row transition metals were more active that those of second or third row owing to the lower stability of the complexes. The presence of coordinating anions suppressed the electrocatalytic activity with HPO_4^{2-} causing a complete inhibition. The current efficiency for formaldehyde production was highest (87%) for the chromium complex. Turnovers in excess of 15 000 were achieved. The kinetics of the reaction were relatively slow, especially when compared to the analogous process in non-aqueous solvents such as DMF. This has been ascribed to differences in the overall reaction and products.

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