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Formation of Polymeric [$\{Ru^0(bpy)(CO)_2\}_n$] Films by Electrochemical Reduction of [$Ru(bpy)_2(CO)_2$](PF_6)$_2$: Its Implication in CO_2 Electrocatalytic Reduction

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Introduction

Polypyridylcarbonylruthenium(II) complexes are known to act as efficient homogeneous catalysts for the electrochemical and photochemical reduction of CO_2 to CO and/or formate anion. For instance, mono(bipyridine) complexes *trans*-(Cl)-[$Ru^{II}(bpy)(CO)_2Cl_2$] and *trans*-(CH_3CN) [$Ru^{II}(bpy)(CO)_2(CH_3CN)_2$]$^{2+}$ (bpy = 2,2′-bipyridine) catalyze the reduction of CO_2 in aqueous CH_3CN solution to produce CO almost quantitatively.[1,2] We have recently demonstrated that the formation of an electroactive polymeric film occurring during the reduction is the key step in the electrocatalytic process.[2–4] These strongly adherent films have been identified as an open cluster polymeric [$\{Ru^0(bpy)(CO)_2\}_n$] complex and result from the bielectronic reduction of the complexes associated with the loss of two ligands (Cl^- or CH_3CN). We have also demonstrated, in separate experiments, that these new materials exhibit an outstanding catalytic efficiency either in aqueous CH_3CN solution or in pure aqueous electrolyte. They display an high selectivity of the process (only CO is formed with a quantitative faradic yield) and a good accessibility of the applied potential ($E = -1.2$ V vs SCE).[2,3]

These results have prompted us to examine in details the electrochemical behavior of the bis(bipyridine) complex *cis*-[$Ru(bpy)_2(CO)_2$]$^{2+}$, which is also known to be an efficient homogeneous electrocatalyst and photocatalyst for CO_2 reduction in various electrolytes.[1,5–9] We report here that the electroreduction of this complex in CH_3CN leads to the formation of a similar [$\{Ru^0(bpy)(CO)_2\}_n$] polymeric film on the electrode surface. We have also studied its implication in the CO_2 reduction electrocatalytic process in this solvent.

Experimental Section

Electrochemical Instrumentation and Procedures. Acetonitrile (Rathburn, HPLC grade) was used as received. Tetrabutylammonium perchlorate (TBAP) from Fluka was recrystallized from ethyl acetate and dried under vacuum at 80 °C for 3 days. Water was doubly distilled. Electrochemical experiments were carried out with a Princeton Applied Research Model 273 potentiostat–galvanostat and a Sefram TGM 164 X-Y recorder. Potentials are relative to the Ag/10 mM Ag^+ electrode in CH_3CN. Potentials referenced to that system can be converted to the SCE by adding 0.3 V. All experiments were run under an Ar or CO_2 atmosphere in a conventional three electrode cell. Working electrodes for cyclic voltammetry were platinum or vitreous carbon discs (5- or 3-mm diameter, respectively) polished with 1-μm diamond paste. Exhaustive electrolyses for the [$\{Ru^0(bpy)(CO)_2\}_n$] film formation were carried out with a 5 cm^2 platinum foil or on a carbon felt piece (10 × 10 × 4 mm; RVC 2000 from Le Carbone Lorraine) for electrocatalytical experiments. Anal. Calcd for [$\{Ru^0(bpy)(CO)_2\}_n$]: C, 46.01; H, 2.57; N, 8.94. Found: C, 45.89; H, 2.38; N, 8.79.

Analyses. CO was analyzed on a Delsi Model 30 gas chromatograph with a flame ionization detector, with 120-cm long 5-Å molecular sieve column followed by a catalytic oven. Formate ions were analyzed on a Waters Associates HPLC with a Bio Rad HPX-87 H cation exchange resine column eluted with a 10^{-2} M H_2SO_4 solution. A UV detector at 224 nm was used. TBAP was removed prior to analyses.

Spectroscopies. Electronic absorption spectra were recorded on a Hewlett Packard 8452 A diode array spectrophotometer. Spectroelectrochemical measurements on films were made using a conventional sandwich-type cell.[10] The optically transparent electrode (OTE) was doped indium–tin oxide (ITO). IR and FAB-MS spectra were recorded on a Brucker FTIR IFS 25 spectrometer and on a ZAB HF-VG analytical apparatus, respectively (positive mode using *m*-nitrobenzylalcohol (*m*-NBA) as matrix).

Compounds. [$Ru(bpy)(CO)_2Cl_2$],[11] [$Ru(bpy)(CO)_2(OCOCH_3)_2$],[12] and [$Ru(bpy)(CO)_2$ ($CH_3CN)_2$](PF_6)$_2$[12] were prepared by an adaption of literature procedures. The synthesis of *cis*-[$Ru(bpy)_2(CO)_2$](PF_6)$_2$ has previously been reported,[13] but an improved experimental procedure has been used.

Preparation of *cis*-[Ru(bpy)$_2$(CO)$_2$](PF$_6$)$_2$. To 25 mL of argon-degassed absolute ethanol in a Schlenk tube were added [Ru(bpy)-($CO)_2(CH_3CN)_2$](PF_6)$_2$ (0.5 g, 0.73 mmol), bpy (0.34 g, 2.18 mmol), and 5 mL of freshly distilled *N*-ethylmorpholine. The mixture was heated at reflux over 5 h while vigorous magnetic stirring was maintained. During the course of the reaction, a fine precipitate appeared. After 5 h the reaction was cooled to room temperature, and the white powder which had appeared was filtered. The product was washed with 3 × 20 mL portions of Et_2O and vacuum-dried affording 330 mg of *cis*-[$Ru(bpy)_2(CO)_2$](PF_6)$_2$. Addition of Et_2O to the filtrate afforded an additional amount of the desired complex (140 mg); global yield 98%. ^{1}H NMR spectral data (δ, recorded in CD_3CN): 9.10 (d, 2 H, ^3J = 5.7 Hz), 8.60 (d, 2 H, ^3J = 8.0 Hz), 8.46 (overlapping multiplets, 4 H), 8.22 (td, 2 H, ^3J = 7.8 Hz, ^4J = 1.6 Hz), 7.93 (td, 2 H, ^3J = 6.6 Hz, ^4J = 1.5 Hz), 7.51 (td, 2 H, ^3J = 6.6 Hz, ^4J = 1.2 Hz), 7.42 (dd, 2 H, ^3J = 8.6 Hz). $^{13}C\{^1H\}$ NMR spectral data (δ, recorded in CD_3CN): 190.81 (CO), 157.65 (CH), 156.34 (CC), 155.61 (CC), 150.34 (CH), 142.84 (CH), 130.33 (CH), 129.50 (CH), 126.66 (CH), 125.87 (CH). IR (KBr pellets): 2093, 2040 cm^{-1} (ν_{CO}); 838 (ν_{PF}) cm^{-1}. FAB$^+$ (*m*-NBA): 615 [M − PF_6]$^+$, 470 [M − 2PF_6], 459 [M − PF_6 − bpy]$^+$, 442 [M − 2PF_6 − CO], 414 [M − 2PF_6 − 2CO] (all patterns have expected isotopic profiles). UV–vis λ_{max} recorded in CH_3CN,

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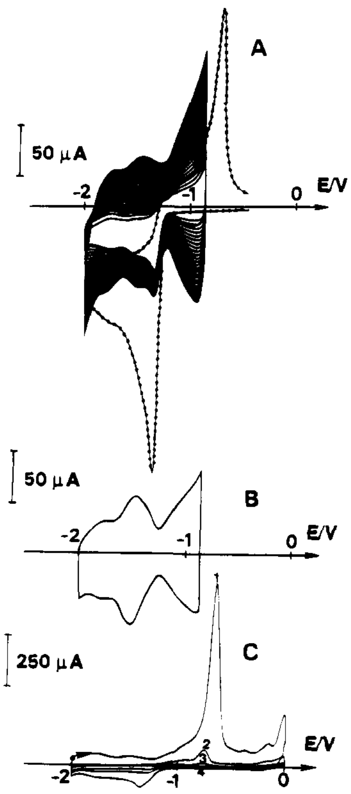

Figure 1. Cyclic voltammograms in CH_3CN solution containing 0.1 M TBAP under an argon atmosphere at a scan rate of 100 mV s^{-1}: (A) $[Ru^{II}(bpy)_2(CO)_2](PF_6)_2$ (1 mM) at a Pt electrode (19.6 mm^2) showing (• — •) initial sweep and (—) 2nd to 29th successive scans between −0.85 and −2.0 V; (B) resulting Pt/$[\{Ru^0(bpy)(CO)_2\}_n]$ modified electrode transfered in an Ar-purged electrolyte solution; (C) curves 1−4 showing four successive scans of the resulting Pt$[\{Ru^0(bpy)(CO)_2\}_n]$ between 0.0 and −2.0 V.

nm (ε, L mol^{-1} cm^{-1}): 208 (49 560), 252 (37 160), 306 (34 810), 312 (sh), 318 (sh).

Results and Discussion

Film Formation under Argon. The cyclic voltammogram of a solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (10^{-3} M) in 0.1 M TBAP in CH_3CN reveals that this complex is not electroactive in the anodic area while its behavior in the cathodic area is quite similar to that of *trans*-Cl$[Ru(bpy)(CO)_2Cl_2]$ or $[Ru(bpy)(CO)_2(CH_3CN)_2](CF_3SO_3)_2$.[2-4] The voltammetric curve under argon exhibits an intense irreversible peak at −1.36 V associated with an anodic peak at −0.78 V on the reverse scan. The shape of this peak system is typical of an electroprecipitation redissolution phenomenon due to a film formation. This can be displayed by continuously cycling the potential. Figure 1A shows the growth of an electroactive film as the potential is repeatedly scanned from −0.85 to −2.0 V. Three clear reversible peak systems appear ($E_{1/2}$ = −0.90, −1.50, −1.76 V) which increase in size continuously. If after a period of scanning, the resulting modified electrode is transferred to a pure electrolyte solution, the two first systems persist (Figure 1B). Extension of the scan to −2.4 V leads to the emergence of a partially reversible system at $E_{1/2}$ = −2.25 V. The electroactivity of this film is identical to that of poly-$[\{Ru^0(bpy)(CO)_2\}_n]$[2-4] and corresponds to the successive reduction of the bipyridine ligand to the $bpy^{\bullet-}$ ($E_{1/2}$ = −1.50 V) and bpy^{2-} ($E_{1/2}$ = −2.25 V) levels. The system located at $E_{1/2}$ = −0.90 V is associated with an intense desorption peak at −0.67 V and is attributed to the partial oxidation of the polymer into $[\{Ru^I(bpy)(CO)_2\}_n]^{n+}$ inducing the break of the Ru—Ru bonds and the desorption of the film (Figure 1C). Further oxidations induce the formation of the soluble complex $[Ru(bpy)(CO)_2(CH_3CN)_2]^{2+}$ as previously shown.[2] Films having similar electrochemical signal can be also deposited by potentiostating the electrode at −1.45 V after a few millicoulombs have been passed.

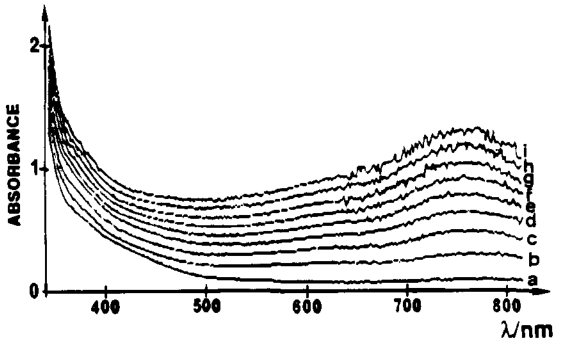

Figure 2. Development of the absorption spectra at an OTE during the electrodeposition at −1.45 V of a solution of 10^{-3} M $[Ru(bpy)_2(CO)_2]^{2+}$ in CH_3CN containing 0.1 M TBAP (charge passed Q): (a−i) Q from 0 to 40 mC (in increments of 5 mC).

In view to confirm the identity of these electroactive films an exhaustive reduction has been carried out at −1.45 V on a platinum gauze. This leads to the covering of the working electrode by a copious, strongly adherent deep blue film. Analytical data of this coating are identical to those of an authentic sample of $[\{Ru^0(bpy)(CO)_2\}_n]$ obtained by electrochemical reduction of mono(bipyridine) complexes $[Ru^{II}(bpy)(CO)_2Cl_2]$ or $[Ru^{II}(bpy)(CO)_2(CH_3CN)_2]^{2+}$. Elemental analyses are consistent with this polymeric formulation (see experimental section). FAB-MS using *m*-NBA + CH_3CN as matrix exhibits peaks at *m*/*z* 1137 $[Ru_3(bpy)_3(CO)_6$(*m*-NBA)(CH_3CN) + H], 966 $[Ru_2(bpy)_3(CO)_5$(*m*-NBA) + H], and 794 $[Ru_2(bpy)_2(CO)_3$ (*m*-NBA)]. The absorption of the film developed during its electrodeposition on an ITO transparent electrode shows the typical bands of $[\{Ru^0(bpy)(CO)_2\}_n]$ at λ_{max} = 450 (sh), 650 (sh), 750 nm (Figure 2). FT-IR spectrum reveals the presence of the metal—metal-bound (Ru^0—Ru^0) at 170 cm^{-1} and carbonyl stretching vibrations at 2017 and 1977 cm^{-1}.

The electrochemical formation of $[\{Ru^0(bpy)(CO)_2\}_n]$ here comes from the addition of two electrons per mole of $[Ru(bpy)_2(CO)_2]^{2+}$ associated with the loss of one bpy ligand (eq 1).

$$n[Ru^{II}(bpy)_2(CO)_2]^{2+} + 2ne^- \rightarrow [\{Ru^0(bpy)(CO)_2\}_n] + \text{nbpy} \quad (1)$$

This is confirmed by the result of the exhaustive electrolysis at −1.45 V. The cyclic voltammogram of the resulting solution at a platinum disk electrode after removing of the working electrode shows that the initial response of the complex has completely vanished after 2 electrons have been consumed, while the typical reversible system of the free bpy ligand released appears at $E_{1/2}$ = −2.51 V.[14] Comparison of the intensity of those peaks system with that of a standard solution of bpy shows that around 0.9 molecule of bpy ligand per molecule of the initial complex is released during the reductive process. Furthermore a similar result is obtained by titration by UV−visible spectroscopy of this free bpy solution after addition of some Fe^{2+} ions to produce in situ $[Fe(bpy)_3]^{2+}$) (λ_{max} = 521 nm for $[Fe(bpy)_3]^{2+}$).

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(15) No CO was detected by GC analysis (<1%) after almost quantitative formation of the $[\{Ru(bpy)(CO)_2\}_n]$ blue film.

It should however be noted that some few amounts (~5% yield) of the hydrido derivative $[Ru^{II}(bpy)_2(CO)H]^+$ are also formed during the electrolysis. This complex is characterized by its typical electrochemical signal exhibiting two successive reversible processes[16] ($E_{1/2} = -1.76$ and -1.95 V) as compared to an authentic sample. $[Ru(bpy)_2(CO)H]^+$ results from the indirect reduction of residual water by the electrogenerated reduced form of $[Ru(bpy)_2(CO)_2]^{2+}$ by a similar process to that described for the reduction of $[Ru(bpy)_2(CO)(CH_3CN)]^{2+}$ for instance.[16]

Electrocatalytic Reduction of CO_2. (i) In pure acetonitrile saturation of a solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (1.1×10^{-3} M) in CH_3CN with CO_2 induces a strong modification of the cyclic voltammogram. Acidity brings about by the presence of CO_2 improves the formation of the hydrido complex as judged by the emergence of its typical peaks on the cyclic voltammogram of the solution while the intensity of the anodic redissolution peak of the $[\{Ru(bpy)(CO)_2\}_n]$ has decreased (Figure 3A, curve a). Moreover a quite large cathodic current starting at -1.90 V corresponding to the well-known electrocatalytic reduction of CO_2 by the reduced form of $[Ru(bpy)_2(CO)H]^+$ is also seen.[16] Controlled-potential electrolysis conducted at -1.45 V confirms these observations. After 2 electrons (Q = 1.6 C) per molecule of $[Ru(bpy)_2(CO)_2]^{2+}$ have been passed, no initial complex remains in solution. Analysis of the resulting solution (absorption spectroscopy and cyclic voltammetry) shows that 50% of $[Ru(bpy)_2(CO)H]^+$ has been formed while ~50% of the free bpy ligand is released resulting from the formation of $[\{Ru^0(bpy)(CO)_2\}_n]$ film on the working electrode.[17] On the other hand, an electrolysis ($Q = 60$ C) conducted on the catalytic current peak (-1.90 V) produced CO and formate with respectively 58 and 2% electrical yield. These data are close to those reported in literature for the catalytic reduction of CO_2 by a solution of $[Ru(bpy)_2(CO)H]^+$ in acetonitrile.[16] All these results indicate that in non aqueous acetonitrile the hydride derivative is the active species for the electrocatalyzed reduction of CO_2 by $[Ru(bpy)_2(CO)_2]^{2+}$.[18] (ii) In aqueous acetonitrile addition of 20% per volume of H_2O to the electrolyte induces a large increase of the catalytical current while its potential becomes markedly less negative (Figure 3A, curve b) and has an identical value to that observed for the electrocatalytic reduction of CO_2 by $[\{Ru^0(bpy)(CO)_2\}_n]$ films in a similar electrolyte.[2,5] Potentiostating the working electrode (C disk, diameter 3 mm) at -1.55 V induces formation of the $[\{Ru^0(bpy)(CO)_2\}_n]$ film as revealed by the typical signal of the resulting modified electrode obtained after 335 mQ has been passed and its transfer in an CH_3CN argon purged solution (Figure 2B). Exhaustive electrolysis at -1.55 V then affords almost quantitatively CO (97% current efficiency) as for experiments using $C/[\{Ru(bpy)(CO)_2\}_n]$ as cathodic material. Only a small amount of formate (3% current efficiency) is simultaneously produced.[19]

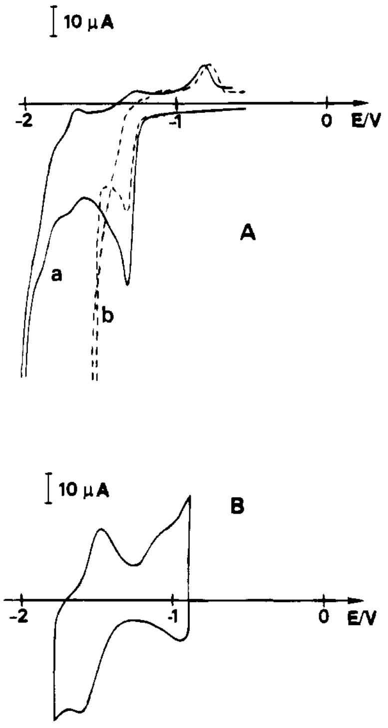

Figure 3. Cyclic voltammograms in CH_3CN solution containing 0.1 M TBAP at a carbon electrode (7.1 mm^2) at a scan rate of 100 mV s^{-1}: (A) curve a showing a CO_2-saturated solution of 1.1 mM $[Ru^{II}(bpy)_2(CO)_2](PF_6)_2$ curve b showing the same solution after 20% of H_2O has been added; (B) the resulting carbon/$[\{Ru^0(bpy)(CO)_2\}_n]$-modified electrode after electrolysis, at -1.55 V ($Q = 335$ mQ) and its transfer in an Ar-purged solution.

In conclusion, we clearly demonstrate that the electrocatalytic effect obtained toward reduction of CO_2 with a solution of *cis*-$[Ru(bpy)_2(CO)_2]^{2+}$ *in aqueous CH_3CN* is due, in large part, to the formation of a polymeric film of $[\{Ru^0(bpy)(CO)_2\}_n]$ occurring during the electroreduction of the complex.

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(17) It has been previously observed that controlled potential electrolysis of a CO_2 saturated anhydrous DMF solution of $[Ru(bpy)_2(CO)_2]^{2+}$ at -1.50 V vs SCE results in decomposition of the complex to yield a black precipitate, which was not characterized.[6]

(18) It should be noted that in any cases the potential of the catalytic peak is more cathodic than that of the reduction of $[Ru(bpy)_2(CO)_2]^{2+}$ indicating that the latter is not directly responsible of the catalytic effect. $[\{Ru^0(bpy)(CO)_2\}_n]$ is a poor catalyst in the absence of added water.[2,3]

(19) In a previous experiment[1] carried out under similar experimental conditions except that Hg pool was used instead carbon felt as working electrode, electrical yield for CO production was only 67%. This difference of catalytic efficiency can be resulted from the fact that $[\{Ru(bpy)(CO)_2\}_n]$ does not remain as a film on the working electrode.