Voltammetric Oxidation of Solution and Solid Phases of Salts of $[V(CO)_6]^-$ in Aqueous (Electrolyte) Media

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In the absence of water and oxygen the solution phase voltammetry of $[V(CO)_6]^-$ in organic solvents exhibits an extremely well-defined, reversible, one-electron redox couple $[V(CO)_6]^- \rightleftharpoons V(CO)_6 + e^-$; $E^r{}_{1/2} = -0.35$ V versus the ferrocenium/ferrocene (Fc^+/Fc) couple, where $E^r{}_{1/2}$ is the reversible half-wave potential. Addition of water or oxygen causes the response to become irreversible, but all components remain soluble. Simulations of the solution-phase voltammetry in acetone/water mixtures (no oxygen present) are consistent with the mechanism $V(CO)_6 + H_2O \rightarrow V(CO)_5(H_2O) + CO$. The sodium diglyme stabilized $[V(CO)_6]^-$ salt ($[Na(diglyme)_2][V(CO)_6]$) is slightly soluble in water without decomposition. In contrast, solid $V(CO)_6$ is insoluble in water, but reacts so slowly with it that solid state voltammetry of the $[V(CO)_6]^{0/-}$ system is possible in aqueous media. Oxidation of $[Na(diglyme)_2][V(CO)_6]$ dissolved in water (electrolyte) media gives insoluble $V(CO)_6$, which precipitates onto platinum, gold, or carbon electrodes. Cyclic voltammetry, electrochemical quartz crystal microbalance, chronocoulometric, and electron microscopy studies show that $V(CO)_6$ is precipitated as lumps of solid rather than as uniform layers. Voltammetric studies on $[Na(diglyme)_2][V(CO)_6]$ mechanically attached to electrodes that are then placed into aqueous (electrolyte) media show distinct relationships to the voltammetry of dissolved $[Na(diglyme)_2][V(CO)_6]$. However, in this case, ion exchange with the electrolyte cations and gradual dissolution of the mechanically attached solid occurs. The potentials are independent of the electrolyte anions, but change considerably (>600 mV) with the electrolyte cation. In the cases of the tetraalkylammonium cations (NR_4^+), the potentials are correlated with the solubility products of $[NR_4][V(CO)_6]$. Equations are presented relating the potentials of the processes and the concentration of the cations and the solubility products of the salts.

Introduction

In earlier studies from these laboratories it has been demonstrated that well-defined voltammetric responses may be observed for insoluble microcrystalline solids mechanically attached to electrodes immersed in water (electrolyte) media. However, the voltammetry is often different from that observed in the solution phase because of the associated ion transfer processes that accompany the electron-transfer process.[1−5] More recently, the use of the electrochemical quartz crystal microbalance (ECQCM) has been shown to be a powerful technique for determining mass changes at the electrode that directly relates to the ion transfer processes and provides considerable mechanistic information.[6−9] The ion transfer processes lead to large changes in the voltammetry, which are dependent on the electrolyte and may involve either anion or cation inclusion or expulsion to maintain the charge balance. However, so far, there has been no quantitative description of these phenomena. There have been two recent reviews by Scholz and Meyer[10,11] on the voltammetry of microcrystalline solids mechanically attached to electrodes.

There was an earlier detailed examination of the voltammetry of the $[V(CO)_6]^{0/-}$ system in acetone and dichloromethane solutions.[12] The one-electron redox couple

$$[V(CO)_6]^- \rightleftharpoons V(CO)_6 + e^- \qquad (1)$$

is fully reversible on the voltammetric time scale, but other irreversible oxidation processes were observed at more positive potentials.

In this paper, the voltammetry of the $[V(CO)_6]^{0/-}$ system is examined for solid compounds mechanically attached to electrodes that are then immersed in water (electrolyte) media. The starting material was the commercially available sodium diglyme (diglyme = 2-methoxyethyl ether, $\{CH_3OCH_2CH_2\}_2O$) stabilized $[V(CO)_6]^-$ salt, $[Na(diglyme)_2][V(CO)_6]$, and studies were confined to the potential region associated with the process described in eq 1. The combination of ECQCM, chronocoulometric, and electron microscopy studies provides new insights into the mechanism of the solid-state processes and for the first time a quantitative analysis of the mechanism is attempted. Importantly, this organometallic system is unusual because $[Na(diglyme)_2][V(CO)_6]$ is sparingly soluble in water. Therefore, for the first time for any system, a direct comparison can be made between solution and solid-state voltammetry in water (electrolyte) media.

Experimental Section

Chemicals. $[Na(diglyme)_2][V(CO)_6]$ was obtained from Strem (Newburyport, MA) and used without purification. Distilled water was used for preparation of all the aqueous electrolyte solutions. The solvents, acetone and acetonitrile,

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were HPLC grade (Mallinckrodt, Paris, KY). All electrolytes were of either electrochemical or analytical reagent grade.

Electrochemical Apparatus and Conditions. Cyclic voltammetric and chronoamperometric measurements were obtained with a Cypress CS 1090 system (Cypress Systems, Lawrence, KS). Multiple scan cyclic voltammograms were recorded on a BAS 100A (Bioanalytical Systems, West Lafayette, IN) electrochemical analyzer. Simultaneous cyclic (staircase) voltammetric and mass balance experiments were undertaken with an ECQCM consisting of an Elchema (Elchema, Postdam, NY) model EQCN-701 nanobalance and model PS-205 potentiostat. The system was controlled with a 486 PC running VOLTSCAN software (Intellect Software, Postdam, NY).

All experiments were undertaken at ambient temperatures of 20 ± 1 °C, and solutions were deoxygenated using high purity nitrogen (BOC Gases, Chatswood, NSW, Australia). Simulation of the solution-phase cyclic voltammetric responses was achieved with the computer package DIGISIM Version 2.1 (Bioanalytical Systems, West Lafayette, IN).

The reference electrode for aqueous and acetone experiments was Ag/AgCl (3 M KCl). This reference electrode was calibrated against the $[Fe(CN)_6]^{3-/4-}$ couple in aqueous 1 M KCl and the reversible half-wave potential $E^r_{1/2}$ was 0.270 ± 0.002 V versus Ag/AgCl (3 M KCl). All potentials recorded in aqueous (electrolyte) media are reported relative to this chemical system. In acetone, the potentials are quoted relative to that of the ferrocenium/ferrocene (Fc^+/Fc) couple. The reference electrode used for experiments in acetonitrile was Ag^+/Ag (10 mM $AgNO_3$ with 0.1 M Bu_4NPF_6 in acetonitrile). This reference electrode also was calibrated against the Fc^+/Fc couple, and all potentials in acetonitrile are reported relative to ferrocene. The auxiliary electrode was a platinum wire.

The range of working electrodes included a platinum disk electrode (1.6 mm diameter), a gold disk electrode (1.6 mm diameter), a glassy carbon disk electrode (3.0 mm diameter), a basal plane pyrolytic graphite disk electrode (5.0 mm diameter), and a platinum microdisk electrode (9.8 μm diameter). The working electrode for the ECQCM measurements was one side of a 13-mm diameter AT-cut quartz crystal (Bright Star Crystals, Rowville, Victoria, Australia) that had gold disks (5.0 mm diameter) vapor deposited on each side and that oscillated at a frequency of 10 ± 0.05 MHz. The calibration of the ECQCM was as previously described.[8] The $[Na(diglyme)_2][V(CO)_6]$ was readily attached to the electrode by rubbing the electrode surface onto the solid compound. The electrode containing the mechanically attached solid was then placed into the aqueous (electrolyte) medium in order to obtain the solid-state voltammograms.

Fourier Transform Infrared Spectroscopy. The Fourier transform infrared (FTIR) spectrum for the $[Na(diglyme)_2]$-$[V(CO)_6]$ was recorded on a Perkin-Elmer 1600 series FTIR spectrometer using a Nujol mull. For gas-phase FTIR measurements, the cell contained NaCl windows, and spectra were obtained with a resolution of 1 cm^{-1} using a BIORAD FTS-60 spectrometer.

Scanning Electron Microscopy. Samples of $[Na(diglyme)_2]$-$[V(CO)_6]$ for examination by scanning electron microscopy (SEM) were prepared by rubbing a freshly cleaved basal plane graphite plate (5 × 5 × 1 mm) onto a small amount of the carbonyl compound on a filter paper. The surface-modified carbon plate was fixed with double-sided sticky tape onto a stub and gold plated in a Belzers sputter-coating unit. An ETEC Autoscan system (20 KV accelerator voltage) was used for the SEM measurements.

***In Situ* Optical Microscopy.** To observe changes occurring during the redox reactions of $[Na(diglyme)_2][V(CO)_6]$, a video imaging system[13] consisting of a Nikon Epiphot Inverted Metallurgical Microscope fitted with a special long-working-distance objective lens, a CCD TV camera, and an Imaging Technology PCVision frame grabber was incorporated into an electrochemical apparatus controlled by a BAS 100A electrochemical analyzer. For these experiments, a special electrochemical cell with a 20-mm diameter quartz window bottom was used in which the distance between the working electrode and the quartz window could be adjusted to ≈0.1 mm.

Results and Discussion

A. Reactivity of $[Na(diglyme)_2][V(CO)_6]^-$ and $V(CO)_6$ with Oxygen and Water. In the absence of oxygen and water, the voltammetry of $[Na(diglyme)_2][V(CO)_6]$ in acetonitrile and acetone solutions (0.1 M Bu_4NPF_6) was well defined as previously reported.[12] Under the conditions of cyclic voltammetry (scan rates between 10 and 1000 mV s^{-1}), a reversible one-electron redox couple (eq 1) is observed at platinum (Pt), gold (Au) and carbon (C) electrodes for the oxidation of $[V(CO)_6]^-$ at a half-wave potential of −0.35 V versus Fc^+/Fc in acetonitrile and at −0.36 V versus Fc^+/Fc in acetone.

The value of the reversible half-wave potential implies that $[V(CO)_6]^-$ is likely to be air sensitive, and, in fact, a small percentage of $V(CO)_6$ is always present in the solid. However, oxidation of the solid $[Na(diglyme)_2][V(CO)_6]$ by molecular oxygen is a very slow process. A strong band at 1842 cm^{-1} in the infrared (IR) spectrum of the solid (Nujol mull)[12] and the observation of the expected migration current from steady-state voltammetry at a Pt microdisk electrode in the absence of electrolyte[14] confirm that the majority of the solid sample is in the anionic $[V(CO)_6]^-$ form.

The rate of reaction of $[V(CO)_6]^-$ with oxygen in solution also was found to be slow and of no significance on the voltammetric time scale. However, the presence of oxygen in solution causes the couple to become irreversible, due to the rapid reaction of oxygen with $V(CO)_6$ to give unidentified products. Consequently, thorough deoxygenation of solutions was maintained in all experiments.

Because the voltammetry of the $[V(CO)_6]^{0/-}$ system was to be studied at an aqueous (electrolyte) interface, the effect of added water to solutions also was investigated. Figure 1a shows the solution voltammetry of $[V(CO)_6]^-$ in acetone alone, whereas Figures 1b−d show that the addition of water significantly decreases the chemical reversibility of the $[V(CO)_6]^{o/-}$ couple. This result indicates that $V(CO)_6$ in solution reacts with water as well as with oxygen. Figure 2 shows the voltammograms at various scan rates of a solution of $[V(CO)_6]^-$ in acetone with 10% added water. The couple is reversible only at scan rates >1000 mV s^{-1}. Because Figure 1 shows the reaction rate of $V(CO)_6$ with water is dependent on the water concentration, the system was modeled with the DIGISIM computer program[15] as a pseudo-first-order EC reaction according to eqs 2a and 2b:

$$\text{(E)} \qquad [V(CO)_6]^- \rightleftharpoons V(CO)_6 + e^- \qquad \text{(2a)}$$

$$\text{(C)} \qquad V(CO)_6 \xrightarrow{k[H_2O]} \text{products} \qquad \text{(2b)}$$

The value of the pseudo-first-order rate constant, $k_{[H_2O]}$ was measured. The second-order rate constant, k' was calculated

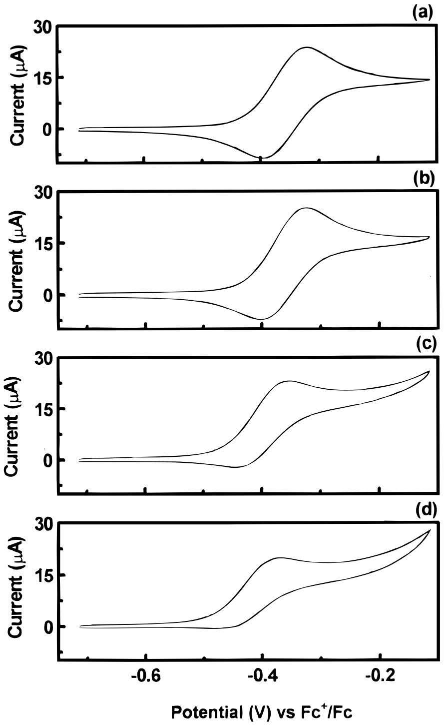

Figure 1. Cyclic voltammograms (100 mV s^{-1}) at a Pt macrodisk electrode (1.6 mm diameter) showing the effect of added water to an acetone (0.1 M Et_4NPF_6) solution of 2 mM $[Na(diglyme)_2][V(CO)_6]$: (a) 0%; (b) 3%; (c) 5%; and (d) 10% (v/v water added).

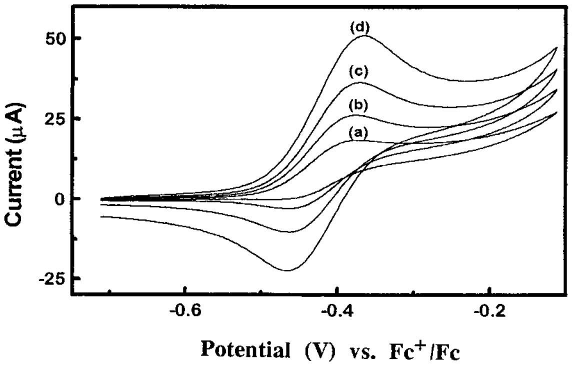

Figure 2. Cyclic voltammograms at a Pt macrodisk electrode (1.6 mm diameter) showing the effect of scan rate on an acetone (0.1 M Et_4NPF_6) solution of 2 mM $[Na(diglyme)_2][V(CO)_6]$ with 10% (v/v) of added water: (a) 100; (b) 200; (c) 500 (d) 1000 mV s^{-1}.

from the water concentration to give a constant value of 0.3 M^{-1} s^{-1} for the water concentration range 3−10%. According to this model, the chemical reversibility of cyclic voltammograms should be dependent on both the scan rate and the concentration of water. Comparison of Figure 1d with Figures 1b and 2 shows that decreasing the water concentration by a factor of $^{10}/_3$ is equivalent to an increase in the scan rate by $(^{10}/_3)^2$ or ≈10, as expected.

FTIR experiments show the release of small quantities of carbon monoxide ($\nu_{CO} = 2140$ cm^{-1})[16] upon addition of water to solid $[Na(diglyme)_2][V(CO)_6]$. In contrast, the addition of 10% water to an acetone solution of $[Na(diglyme)_2][V(CO)_6]$ had no significant effect on the *oxidative* peak current of cyclic voltammetric experiments (taking into account the dilution) even after 1 h. This result suggests that it is only the small amount of $V(CO)_6$ initially present in the solid that releases the carbon monoxide when in contact with water. Previously, the overall reactions of $V(CO)_6$ with coordinating solvents have been described as disproportionation reactions[12] where two-thirds of the vanadium is retained as $[V(CO)_6]^-$, and carbon monoxide gas is released on the synthetic time scale:

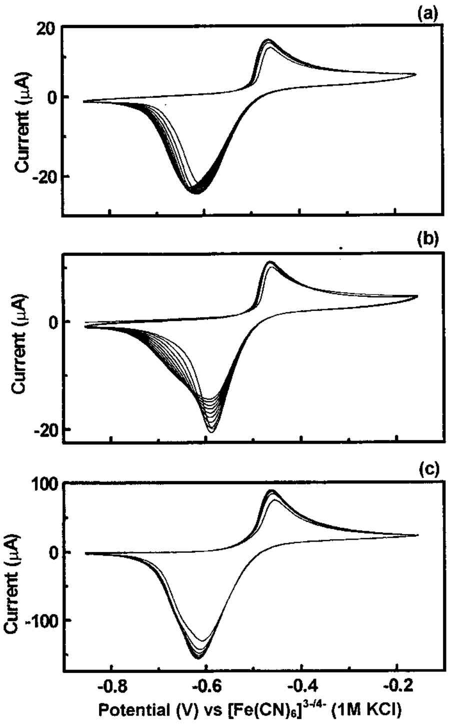

Figure 3. Ten voltammetric cycles of an aqueous (0.05 M $CsClO_4$) solution of 2 mM $[Na(diglyme)_2][V(CO)_6]$ with different electrodes: (a) Pt; (b) Au; and (c) pyrolytic graphite.

$$3V(CO)_6 \rightarrow 2[V(CO)_6]^- + V(II) + 6CO \qquad (3)$$

However, the pseudo-first-order kinetics observed on the voltammetric time scale indicate that the initial step in the decomposition of $V(CO)_6$ in the presence of water probably occurs via a rate-determining substitution reaction:

$$V(CO)_6 + H_2O \rightarrow V(CO)_5(H_2O) + CO \qquad (4)$$

with subsequent reactions leading to the overall stoichiometry shown in eq 3.

In summary, these initial studies show that solid $[Na(diglyme)_2][V(CO)_6]$ reacts slowly with oxygen to form $V(CO)_6$, which in turn reacts rapidly with water to produce carbon monoxide. In acetone solution, $[V(CO)_6]^-$ is stable to both molecular oxygen and water on the voltammetric time scale. However, the product of electrochemical oxidation, $V(CO)_6$, reacts slowly with water, but very rapidly with oxygen, on the voltammetric time scale. Importantly, because we have confirmed that $[V(CO)_6]^-$ is stable in the presence of water,[17] the aqueous (electrolyte) voltammetry of $[Na(diglyme)_2][V(CO)_6]$ can be explored.

B. Voltammetry of $[Na(diglyme)_2][V(CO)_6]$ in Aqueous (Electrolyte) Media. Although $[Na(diglyme)_2][V(CO)_6]$ is slightly soluble in water, the solid dissolves only very slowly. Consequently, both solution- and solid-state voltammetry in aqueous (electrolyte) are possible.

(a) Solution-Phase Voltammetry. Figure 3 shows multiple voltammetric scans for 2 mM $[Na(diglyme)_2][V(CO)_6]$ solution in water (0.05 M $CsClO_4$) at various macrodisk electrodes (Pt, Au, and basal plane pyrolytic graphite). In each case, a well-defined oxidation process with the shape associated with

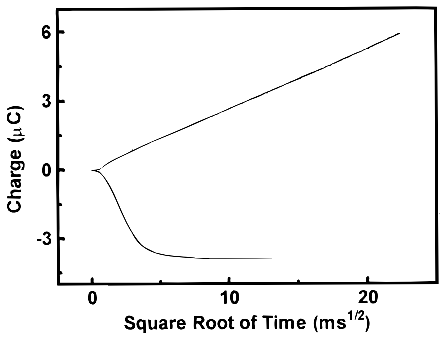

Figure 4. Anson chronocoulometric plot[19] for a solution of 2 mM $[Na(diglyme)_2][V(CO)_6]$ in water (0.1 M NaCl) at an Au electrode (1.6 mm diameter); $\tau = 500$ ms. Further details are given in the text.

features of diffusion control is seen on the forward potential scan. A larger reduction response (nondiffusion controlled) is observed on the reverse scan. The symmetrical nature of the reduction response indicates that the product of oxidation is insoluble in water and adsorbs or precipitates onto the electrode surface. The overall process is consistent with eq 5

$$[V(CO)_6]^-(aq) \rightleftharpoons V(CO)_6(surface) + e^- \qquad (5)$$

This surface confinement process prevents the oxidized species from reacting with the water on the voltammetric time scale; that is, in purely aqueous media the electrochemistry is described by eq 5 rather than eqs 2a and 2b.

The forward and reverse peak heights increase with cycling of the potential. The oxidation peak is similar to the responses observed in acetone/water (90:10) solvent mixtures, but the reduction response has a very different shape.

Confirmatory evidence for a surface deposition process was obtained by simultaneous cyclic voltammetry and ECQCM experiments. A cyclic voltammogram (one cycle only) was recorded for 2 mM $[Na(diglyme)_2][V(CO)_6]$ in water (0.1 M NaCl); scan rate, 100 mV s^{-1}) from −0.83 to −0.23 V versus $[Fe(CN)_6]^{3-/4-}$. Upon oxidation at the Au electrode, the mass increased as expected for deposition of the insoluble neutral species $V(CO)_6$. The mass deposited was (28 ± 3 ng). Upon reduction, the mass decreased by almost the same amount (26 ± 3 ng), corresponding to reduction of $V(CO)_6$ forming a soluble $[V(CO)_6]^-$ salt. Using the crystallographic data[18] for $V(CO)_6$, the radius the molecule was calculated to be 0.39 nm, and assuming a packing factor of 0.91 for a hexagonally close-packed flat layer, the mass increase corresponds to a surface coverage of approximately two (2.1 ± 0.2) layers on the electrode. There is a question of the validity of the Sauerbrey equation used to convert the frequency change in the ECQCM experiments to a mass change when more than a monolayer is deposited. However, these results suggest that $V(CO)_6$ is not simply adsorbed onto the electrode surface, but is deposited under conditions where the concentration of the neutral molecule exceeds the solubility limit in water and precipitates onto the electrode surface.

Chronocoulometric experiments for 2.25 mM $[Na(diglyme)_2][V(CO)_6]$ in water (0.1 M NaCl) at Pt, Au, and glassy C electrodes provide additional evidence for a surface-based process involving the reduction of deposited $V(CO)_6$ to water-soluble $[V(CO)_6]^-$. These double-step chronocoulometric experiments consist of an initial potential step from −0.76 to −0.26 V versus $[Fe(CN)_6]^{3-/4-}$ and a reverse step from −0.26 to −0.76 V versus $[Fe(CN)_6]^{3-/4-}$. Figure 4 shows an Anson plot[19] that confirms that the oxidation of $[V(CO)_6]^-$ to $V(CO)_6$ at an Au electrode is an uncomplicated diffusion-controlled process (upper straight line). However, during the reduction of $V(CO)_6$ (lower curve), there is an initially rapid increase in charge as a function of time, corresponding to the reduction of the majority of the surface-confined $V(CO)_6$, and dissolution of the resultant $[V(CO)_6]^-$. The plot then becomes horizontal when the reduction is completed.

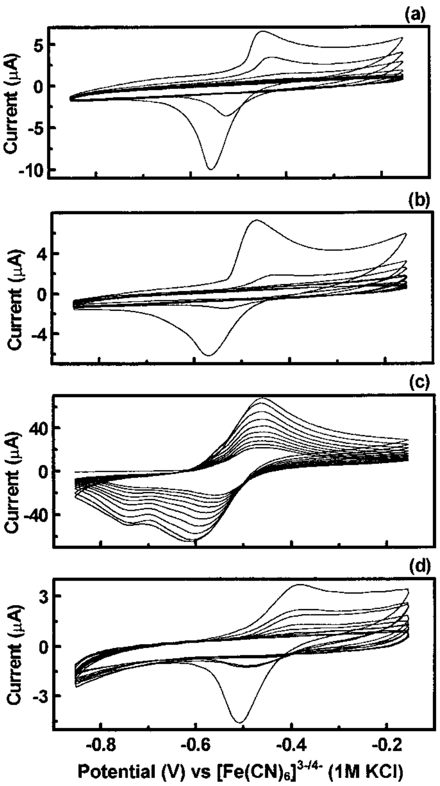

Figure 5. Solid-state cyclic voltammograms of mechanically attached $[Na(diglyme)_2][V(CO)_6]$ in an aqueous (0.05 M $CsClO_4$) solution with different electrodes (a) Pt; (b) Au; (c) pyrolytic graphite; and (d) glassy C.

Calculation of the surface coverage from the chronocoulometric data[19] and using the same packing factor assumptions as before showed that the quantity of $V(CO)_6$ deposited is much greater than a monolayer and also dependent on the step time, τ. At a 500 ms step time, the chronocoulometric data corresponds to 5.7 ± 0.2 (Pt), 5.5 ± 0.2 (Au) and 3.0 ± 0.2 (glassy C) layers of $V(CO)_6$, assuming the deposition is in the form of uniform flat layers. At 1500 ms step time, deposition on Pt was 9.6 ± 0.4 layers, on Au was 7.8 ± 0.8, but on glassy C was highly variable. Both the simultaneous cyclic voltammetry/ECQCM and chronocoulometric experiments are consistent with precipitation of solid $V(CO)_6$ onto the electrode surface.

(b) Solid-State Voltammetry. Even though $[Na(diglyme)_2][V(CO)_6]$ is sparingly soluble in water, the slow dissolution rate of material mechanically attached to the electrode surface enables the solid-state voltammetry to be obtained after the electrode is placed in aqueous (electrolyte) media. The practicality of solid-state voltammetry is improved because the product of the reduction reaction, $V(CO)_6$, is extremely insoluble in water.

Figure 5a shows successive voltammetric cycles for solid $[Na(diglyme)_2][V(CO)_6]$ attached to a Pt macrodisk electrode that has been placed in aqueous electrolyte (0.05 M $CsClO_4$). The first cycle gives well-defined oxidation and reduction responses, very similar to those observed in the solution-phase voltammetry of $[V(CO)_6]^-$. However, on successive scans, there are

TABLE 1: Influence of Electrolyte Anion on Half-Wave Potentials and Peak Separations for the Solid-State Voltammetry of the $[V(CO)_6]^{0/-}$ Process[a]

	Pt		Au		graphite	
electrolyte	$E_{1/2}$ (V)[b]	ΔE_p (V)[c]	$E_{1/2}$ (V)[b]	ΔE_p (V)[c]	$E_{1/2}$ (V)[b]	ΔE_p (V)[c]
KCl	−0.57	0.11	−0.59	0.11	−0.53	0.11
NaCl	−0.56	0.12	−0.60	0.12	−0.55	0.12
NaF	−0.55	0.21	−0.57	0.11	−0.54	0.10
$NaClO_4$	−0.53	0.10	−0.58	0.12	−0.55	0.12
$NaNO_3$	−0.54	0.10	−0.58	0.11	−0.60	0.13
Na_2SO_4	−0.60	0.12	−0.61	0.12	−0.57	0.11

[a] Electrolyte concentrations were 0.1 M with respect to the cation and all potentials are reported relative to the $[Fe(CN)_6]^{3-/4-}$ redox couple in 1 M $KCl_{(aq)}$. [b] Calculated as the average of the oxidation and reduction peak potentials. [c] Calculated as the difference in the oxidation and reduction peak potentials.

significant decreases in current for both responses. In addition, both responses move slightly to more positive potentials with each cycle, but the peak-to-peak separation remains essentially constant. Thus, there is some difficulty in assigning an $E_{1/2}$ value when defined as the average of the oxidation and reduction peak potentials. The shift of potential in the $E_{1/2}$ of the process can be as large as 50 mV. This shift introduces an uncertainty into the thermodynamic significance of the $E_{1/2}$ values that are reported in Tables 1 and 2. After three scans the response disappears. This disappearance is attributed to the dissolution of the $[Na(diglyme)_2][V(CO)_6]$ or $Cs[V(CO)_6]$ formed by a cation exchange phenomenon (see below). Cyclic voltammetry at an Au electrode (Figure 5b) is similar to that at Pt, but dissolution appears to be even more rapid. In contrast, many voltammetric cycles can be observed on basal plane pyrolytic carbon and this electrode surface dependence is attributed to a much slower dissolution rate from graphite. The much higher surface roughness of the graphite electrode minimizes the contact area between the solid and the solution, with a consequent decrease in the dissolution rate of the solid. In support of this suggestion, Figure 5d shows that at a glassy carbon electrode (a smooth-surfaced electrode), the dissolution rate is close to that at the relatively smooth Au and Pt electrodes.

The solid-state reaction is described by eq 6a or 6b:

$$[Na(diglyme)_2][V(CO)_6](s) \rightleftharpoons [Na(diglyme)_2]^+(aq) + V(CO)_6(s) + e^- \quad (6a)$$

$$Cs[V(CO)_6] \rightleftharpoons Cs^+(aq) + V(CO)_6(s) + e^- \quad (6b)$$

with the assumption being that the slow dissolution process

$$[Na(diglyme)_2][V(CO)_6](s) \rightleftharpoons [Na(diglyme)_2]^+(aq) + [V(CO)_6]^-(aq) \quad (7)$$

causes the peak height to decrease with continuous cycling.

In studies on other systems, it has been observed that both the $E_{1/2}$ and ΔE_p values can be strongly dependent on the nature and concentration of the anion and cation of the electrolyte.[4,5,7,8] Therefore, solid-state voltammetric data for $[V(CO)_6]^{0/-}$ were obtained in a variety of aqueous (electrolyte) media, and the results with several anions are summarized in Table 1. The $E_{1/2}$ values are independent of the anion and electrode material within the 50 mV uncertainty already mentioned.

Data in Table 2 illustrates the dependence of potentials on the electrolyte cation. It is obvious that the $E_{1/2}$ values are much more dependent on the cation than on the anion (Table 1). There is a spread in $E_{1/2}$ of ≈100 mV when the cation is an alkali metal H^+, NH_4^+, or $[NMe_4]^+$, but for the larger tetraalkylammonium cations, the variation is much greater. This dependence on the tetraalkylammonium cations is consistent with a mechanism involving ion exchange of the cation from the electrolyte with the cation in the solid. Any $[Na(diglyme)_2]^+$ ions expelled from the solid are expected to react with water to form the aquo sodium ion with release of free diglyme. In situ optical microscopy during the electrochemical process reveals that globules of a substance, assumed to be diglyme, are released from the electrode surface into the bulk solution.

TABLE 2: Influence of Electrolyte Cation on Half-Wave Potentials and Peak Separations for the Solid-State Voltammetry of the $[V(CO)_6]^{0/-}$ Process[a]

	graphite electrode	
electrolyte	$E_{1/2}$ (V)[b]	ΔE_p (V)[c]
NaCl	−0.55	0.12
$CsClO_4$	−0.54	0.14
KCl	−0.53	0.11
NH_4Cl	−0.53	0.10
$HClO_4$	−0.48	0.20
HCl	−0.44	0.12
NMe_4Cl	−0.43	0.17
NEt_4Cl	−0.15	0.24
NBu_4Cl	0.07	0.28

[a] Electrolyte concentrations were all 0.1 M except for $CsClO_4$, which was 0.05 M, and all potentials are reported relative to the $[Fe(CN)_6]^{3-/4-}$ redox couple in 1 M $KCl_{(aq)}$. [b] Calculated as the average of the oxidation and reduction peak potentials. [c] Calculated as the difference in the oxidation and reduction peak potentials.

Although ion exchange may occur when solid $[Na(diglyme)_2][V(CO)_6]$ is in contact with the electrolyte solution, this process will be greatly accelerated during redox cycling because the cation is expelled from the solid during oxidation. Upon reduction of $V(CO)_6$ to $[V(CO)_6]^-$, it is far more likely that an electrolyte cation will be incorporated into the solid forming $C[V(CO)_6]$, where C^+ is the electrolyte cation, especially because the concentration of sodium ions near the electrode will be reduced by diffusion away from the electrode. It follows therefore that if the solubility of $[Na(diglyme)_2][V(CO)_6]_{(s)}$ is greater than that of $C[V(CO)_6]_{(s)}$, then any formation of $[V(CO)_6]^-_{(aq)}$ from $[Na(diglyme)_2][V(CO)_6]^-_{(s)}$ may lead to precipitation of $C[V(CO)_6]_{(s)}$ on the electrode surface with sodium ions diffusing into the bulk of solution. Thus, after ion exchange is complete, the redox process that occurs upon cycling is that given in eq 8 rather than that in eq 6a:

$$C[V(CO)_6](s) \rightleftharpoons C^+(aq) + V(CO)_6(s) + e^- \quad (8)$$

If all processes are reversible and assuming the activity of $V(CO)_{6(s)}$ is unity, the thermodynamic potentials will be related to the solubility of $C[V(CO)_6]_{(s)}$ and the potentials given in Table 2 will be related to the solubility products by the following equation:

$$E^r_{1/2} = E^{\circ\prime}_{V(CO)_6/V(CO)_6^-} + \frac{RT}{F}\ln\left[\frac{[C^+]}{K_{sp}^{C[V(CO)_6]}}\right] \quad (9)$$

where $E^r_{1/2}$ is the reversible half-wave potential and $E^{\circ\prime}_{V(CO)6/V(CO)6-}$ is the formal potential of the redox couple given in eq 1. From the $E_{1/2}$ values in Table 2, which are assumed to be close to $E^r{}_{1/2}$, the calculated solubility product for $[NBu_4N]\cdot[V(CO)_6]$ is $\approx 3 \times 10^{-12}$ M^2. The present study suggests that although alkaline earth $[V(CO)_6]^-$ salts are soluble in water, the tetramethyl- and tetrabutylammonium salts are comparatively insoluble. This conclusion is supported by the observation that voltammetry of mechanically attached $[Na(diglyme)_2][V(CO)_6]$ onto a graphite electrode in water (NEt_4Cl or NBu_4Cl) remains essentially unchanged for many scans, in contrast to similar experiments in which the electrolyte is an alkali metal or ammonium chloride where the response rapidly decays with cycling the potential.

A further consequence of eq 9 is that the observed $E_{1/2}$ should also be dependent on the supporting electrolyte concentration (i.e., $[C^+]$), but the suggestion cannot easily be tested because of the relative instability of the tetraalkylammonium salts of $[V(CO)_6]^-$ on the synthetic time scale. However, studies have been made on other systems where a neutral species is oxidized to a cation and the relevant equation connecting $E^{r}_{1/2}$ with electrolyte anion is:

$$E^{r}_{1/2} = E^{\circ\prime}_{M/M^+} - \frac{RT}{F} \ln \left[\frac{[A^-]}{K^{MA}_{sp}} \right] \tag{10}$$

where M/M^+ is the redox couple and A^- is the electrolyte anion. The data for the oxidation of solid *trans*-$Cr(CO)_2(dpe)_2$[5] (dpe = 1,2-bis(diphenylphosphino)ethane) and decamethylferrocene[7] can be interpreted in terms of eq 10. Previously, the shift in potential with varying anion for these systems was related only to the hydrophobicity of the anion.

C. Electron Microscopy. Because the electrochemical responses of mechanically attached $[Na(diglyme)_2][V(CO)_6]$ and precipitated $V(CO)_6$ were closely related, it was suggested that $V(CO)_6$ may be precipitated as lumps on the electrode surface.

Examination of mechanically attached $[Na(diglyme)_2][V(CO)_6]$ on a graphite electrode by electron microscopy showed the presence of only a partially covered surface and the attached solid consists of lumps of approximate diameter 0.2−0.5 μm separated by distances of ≈1−2 μm.

Electron micrographs of $V(CO)_6$ deposited from aqueous solution after oxidation of $[Na(diglyme)_2][V(CO)_6]$ showed a similar appearance, although the particle size and the quality of the images was not as good as for the mechanically attached $[Na(diglyme)_2][V(CO)_6]$. Nevertheless, it is apparent that a nucleation/precipitation mechanism applies and the solid is not deposited as a uniform film.

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