

Voltammetry, Electron Microscopy, and X-ray Electron Probe Microanalysis at the Electrode-Aqueous Electrolyte Interface of Solid Microcrystalline *cis*- and *trans*-Cr(CO)₂(dpe)₂ and *trans*-[Cr(CO)₂(dpe)₂]⁺ Complexes (dpe = Ph₂PCH₂CH₂PPh₂) Mechanically Attached to Carbon Electrodes

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Abstract: Microcrystalline forms (size range 0.1–10 μm) of *cis*-Cr(CO)₂(dpe)₂ (*cis*⁰), *trans*-Cr(CO)₂(dpe)₂ (*trans*⁰), and *trans*-[Cr(CO)₂(dpe)₂]⁺ (*trans*⁺) (dpe = Ph₂PCH₂CH₂PPh₂) may be mechanically attached to carbon electrodes. The voltammetry of these water-insoluble materials produces exceedingly well defined processes over a wide scan rate range when the electrode is placed into aqueous media containing 0.1 M NaClO₄ or 0.1 M KClO₄ as the electrolyte. Electron probe microanalysis demonstrates that ClO₄⁻ partially covers the edges and the surface of the solid after oxidative electrolysis. This suggests that oxidative voltammetry of the uncharged complex occurs at the crystal-electrode-solution interface to form a perchlorate complex. The redox processes observed for the arrays of microcrystalline carbonyl compounds attached to the electrode may be summarized by the following reaction schemes: *cis*-Cr(CO)₂(dpe)₂ ⇌ *cis*-Cr(CO)₂(dpe)₂ + e⁻ and *trans*-Cr(CO)₂(dpe)₂ ⇌ *trans*-[Cr(CO)₂(dpe)₂]⁺ + e⁻ ⇌ *trans*-[Cr(CO)₂(dpe)₂]⁺ + e⁻ with *cis*-[Cr(CO)₂(dpe)₂]⁺ slowly isomerizing to *trans*-[Cr(CO)₂(dpe)₂]⁺. Interestingly, the *trans*⁰ complex may be reversibly oxidized to *trans*⁺ and *trans*²⁺ under most conditions, but not as readily reduced from *trans*⁺ back to *trans*⁰ if the potential is held for short periods of time at potentials intermediate between the *trans*^{+/0} and *trans*^{2+/+} processes. This indicates that the presence of a pure *trans*⁺ phase hinders reduction; however stepping the potential to a value more negative than the reduction potential of the *trans*^{+/0} couple and then scanning in the positive potential direction restores the current to its original value. The experimental results are in accord with an electrochemical process that takes place at the solid-solution interface to form a layer of oxidized material. Electron transfer is postulated to occur by electron hopping via self exchange and cross redox reactions with the rate (apparent diffusion coefficient) being dependent on the state of the electrode-compound-solution interface and the surface charge.

Introduction

Voltammetric methods have been widely employed to establish reversible potentials and other aspects of the redox chemistry of soluble organometallic compounds.^{5,6} However, since voltammetric studies of nonconducting solids have not generally been possible and the majority of organometallic compounds are completely insoluble in water, their redox properties in this important solvent are usually unknown. Obviously, conducting materials such as metals or semiconductors, which are also insoluble in water, can be used as electrodes and some aspects of their redox chemistry at the water-solid (electrode) interface have been established. Additionally, the voltammetry of insoluble mixed valent compounds can be studied when they are prepared as thin films on suitable electrode surfaces.⁷ Similarly, polymers have been adsorbed onto electrodes or electropolymerized to form thin films and the voltammetry of these insoluble materials also can be studied in detail.⁸⁻¹² The thin-film studies of insoluble materials form part of the well-established area of voltammetry

at chemically modified electrodes.^{13,14} Electrochemistry at the organic molecular crystal-aqueous electrolyte interface has been studied for a considerable period of time and the mass transport mechanism is reasonably well understood.¹⁵ Other solids such as Li_xCoO₂, Li_xV₂O₅, Li_xU₃O₈, Li_xMoO₃, and Li_xRuO₂ are now recognized as suitable cathodes in batteries because lithium and other ions can intercalate and de-intercalate from the oxide host structures.¹⁶⁻²² The electrochemistry of these oxide materials

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and their intercalation is often studied by mixing the oxide with graphite or other conducting material and making the mixed materials into conducting electrodes by pressing the powder under high pressure onto stainless steel. Voltammetry on these composite electrodes usually has to be undertaken at slow scan rates to minimize problems associated with ohmic (*iR*) drop. However, it was recently established²² that different forms of U₃O₈ when ground to micron size could be mechanically attached to conventional graphite electrodes to produce an array of microscopically small electroactive sites. By using electrodes formed in this way, the voltammetry of the intercalation process with ions present in the aqueous solution could be studied over wide scan rates with minimal problems associated with *iR* drop. This method of mechanically attaching material to electrode surfaces was originally developed²³ by Scholz et al. and applied to the abrasive stripping voltammetric analysis of metals and to water-insoluble compounds which could be oxidized or reduced to water-soluble species.²³

In principle, the method of mechanically attaching microcrystalline solids to graphite or other electrode surfaces leads to the formation of an array of microscopically small sites where redox chemistry can take place, provided a charge transport mechanism is available. Under these experimental conditions a large three-phase boundary electrode/solid/solution can be obtained and processes not readily detectable under normal conditions can be observed.

In this paper the water-insoluble and nonconducting neutral metal carbonyl compounds *cis*-Cr(CO)₂(dpe)₂ (*cis*⁰) and *trans*-Cr(CO)₂(dpe)₂ (*trans*⁰) and the positively charged complex *trans*-[Cr(CO)₂(dpe)₂]⁺ (*trans*⁺) (dpe = Ph₂PCH₂CH₂PPh₂) have been attached to polished pyrolytic basal plane graphite electrodes in microcrystalline form. When the electrode is transferred to an aqueous 0.1 M NaClO₄ or 0.1 M KClO₄ electrolyte solution, well-defined diffusion-controlled voltammetric processes are observed. Features of the mass transport mechanism, the electron-transfer step, and chemistry associated with the electron-transfer step for these solids are interrogated by voltammetry, scanning electron microscopy, and electron probe X-ray microanalysis and are compared to conventional voltammetry of the complexes when they are dissolved in organic solvents.²⁴

Experimental Section

Synthesis. *cis*- and *trans*-Cr(CO)₂(dpe)₂. Cr(CO)₆ was refluxed with 2 mol equiv of dpe in decane.²⁵ A typical reaction time of 65 h gave a crude product which was collected by filtration and then washed first with hexane followed by a small amount of dichloromethane to give red crystals of *trans*-Cr(CO)₂(dpe)₂. Addition of methanol to a dichloromethane solution of *trans*-Cr(CO)₂(dpe)₂ caused the yellow *cis*-Cr(CO)₂(dpe)₂ to separate from solution as reported previously.²⁶ The product was collected by filtration and stored in the dark. ¹³C and ¹H NMR studies on samples dissolved in suitable solvents indicate that the microcrystalline solids used for the voltammetric studies contain no solvent of crystallization.

The previously reported²⁷ method for the preparation of a range of *trans*-[Cr(CO)₂(dpe)₂]⁺ complexes was used to prepare the tetrafluoroborate, tetraphenylborate, hexafluorophosphate, and perchlorate analogues. A solution of NaBF₄, NaBPh₄, KPF₆, or NaClO₄ in methanol was added slowly to a solution of either *cis*- or *trans*-Cr(CO)₂(dpe)₂ in dichloromethane (equimolar quantities). The solvent was evaporated under reduced pressure until crystallization of the orange compound commenced. The solution was then cooled and the product collected by filtration.

Reagents and Voltammetric Instrumentation. Unless otherwise specified, all reagents were of analytical reagent or electrochemical grade

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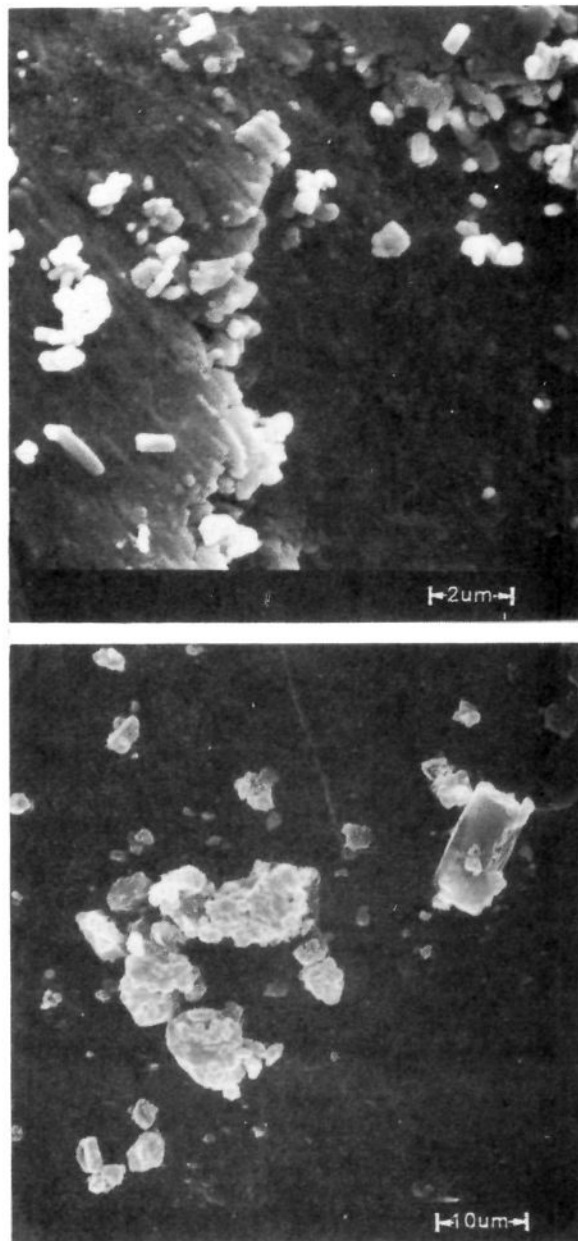


Figure 1. Electron microscopy of (a, top) *trans*-[Cr(CO)₂(dpe)₂]BPh₄ mechanically attached to a polished basal plane graphite disk electrode and (b, bottom) *cis*-Cr(CO)₂(dpe)₂ mechanically attached to a graphite plate electrode.

purity. Millipore water was used for the preparation of the electrolyte solution. The reference electrode was Ag/AgCl (3 M NaCl) and the auxiliary electrode was a platinum wire. Voltammetric experiments were performed at 20 ± 2 °C with a BAS 100 electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN). The supporting electrolyte was 0.1 M NaClO₄ or 0.1 M KClO₄ in aqueous media and 0.1 M Bu₄NClO₄ in dichloromethane. All solutions were degassed with high-purity nitrogen for 15 min prior to making the measurements.

The carbon disk electrodes used in this study were made from polished basal plane pyrolytic graphite (5 mm diameter) or glassy carbon (3 mm diameter) and the chromium carbonyl complexes were transferred to the surface of the carbon electrode as follows. Sample amounts of 1–3 mg of microcrystalline chromium carbonyl complex were placed on coarse grade filter paper. The carbon electrode was then pressed onto the substance and rubbed over the material causing some of the compound to be ground to a smaller size and to adhere to the electrode surface as an array of microcrystalline particles. To obtain well-defined voltammograms a high surface coverage of microcrystalline material must be achieved. Figure 1a shows the electron microscopy of *trans*-[Cr(CO)₂(dpe)₂]BPh₄ attached to a pyrolytic graphite electrode, and while particle

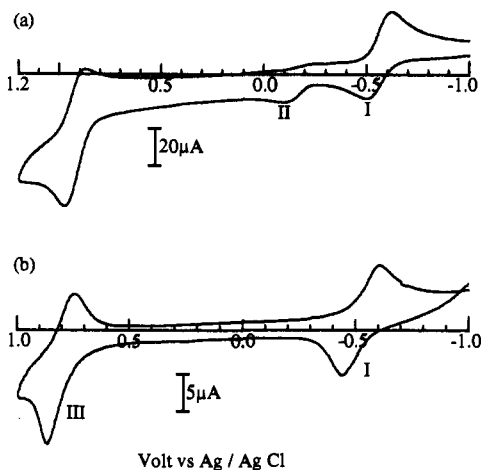


Figure 2. Cyclic voltammograms obtained at 20 °C at (a) a platinum disk electrode in dichloromethane (0.1 M Bu₄NClO₄) for a mixture of *cis*-Cr(CO)₂(dpe)₂ and *trans*-[Cr(CO)₂(dpe)₂]⁺ showing processes I, II, and III (scan rate = 200 mV s⁻¹) and (b) in aqueous (0.1 M NaClO₄) media at 20 °C for solid *trans*-Cr(CO)₂(dpe)₂ mechanically attached to a polished basal plane pyrolytic graphite electrode (scan rate = 50 mV s⁻¹). Initial and final potential = -1.0 V, switching potential = +1.0 V vs Ag/AgCl.

sizes and their distributions are not uniform, the average size of the microcrystalline material is approximately 0.1 μm. For electrochemical measurements, the electrode was transferred into the electrochemical cell containing the aqueous 0.1 M NaClO₄ or 0.1 M KClO₄ electrolyte solution. The electrode surface could be renewed after each measurement by cutting the electrode surface with a razor blade. Alternatively, the electrode may be cleaned by vigorously rubbing the electrode surface on dry filter paper to remove old sample or by dipping the electrode into dichloromethane and allowing the compound to dissolve in the solvent.

Electron Probe X-ray Microanalysis. Surface elemental analyses by electron probe X-ray measurements were carried out on a scanning electron microscope (JSM 840) coupled to a TN 5500 X-ray analyzer at an accelerating voltage of 15 kV with a probe monitor current ranging from 0.3 to 0.6 nA. A dead time of 25–30% is present under these conditions for a spectrum collection time of 100 s. Samples for analysis were prepared by rubbing a freshly cleaved basal plane carbon graphite plate (5 × 5 × 1 mm) onto a small amount of the carbonyl compound on a filter paper. The modified face of the graphite plate was then electrolyzed at the required potential for 120 s in aqueous 0.1 M NaClO₄ or KClO₄ prior to electron microscopy and electron probe analysis. The graphite plate was transferred into a cleaning bath of distilled water and then dried in air. The carbon plates were attached to the sample holder with conducting epoxy resin.

Scanning Electron Microscopy. An ETEC Autoscan system (20 kV accelerator voltage) was used for the scanning electron microscopy measurements. Sample preparation for examination by electron microscopy was similar to that described for the electron probe analyzer. The surface modified carbon plate was fixed with double sided sticky tape on a stub and gold plated in a Balzers sputter coating unit. Figure 1b shows the electron microscopy of the *cis*-Cr(CO)₂(dpe)₂ compound prepared in this way. The crystal size is up to 10 μm in these experiments and somewhat larger (Figure 1a) than the size used for other studies.

Resistivity Measurements. Pellets of the *cis*⁰ and *trans*⁰ chromium compounds (1 cm diameter, 0.5 mm thick) were prepared with the aid of a press and application of a pressure of 6 × 10⁹ Pa for 10 min. Electrical contact was made by adding conducting carbon lubricant (Acheson Dag 154) between the pellet and two metal plates (1 cm diameter). The resistance was measured with a Fluke 77 multimeter set on the DC current measurement mode.

Results

(a) Voltammetry in Dichloromethane Solution. Figure 2a shows a cyclic voltammogram for a mixture of *cis*-Cr(CO)₂(dpe)₂ and *trans*-[Cr(CO)₂(dpe)₂]⁺ obtained over the potential range of -1000 to 1200 mV vs Ag/AgCl at a platinum disk electrode in CH₂Cl₂ (0.1 M Bu₄NClO₄). The three processes labelled I, II,

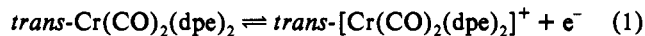
Table I. Voltammetric Data (Scan Rate 200 mV s⁻¹) at a Platinum Disk Electrode for the Cr(CO)₂(dpe)₂ Redox Processes in Dichloromethane (0.1 M Bu₄NClO₄) at 20 °C

	process I ^a	process II ^b	process III ^c	ferrocene ^d
E_p^{ox} e	-0.500	-0.100	0.970	0.380
E_p^{red} e	-0.625	-0.220	0.870	0.480
ΔE_p (mV) ^f	125	120	100	100
E^0 e ^g	-0.565	-0.160 ^h	0.920	430

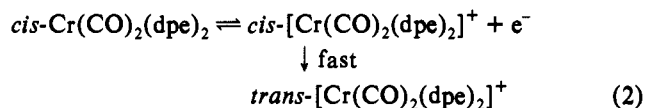
^a *trans*⁰ ⇌ *trans*⁺ + e⁻. ^b *cis*⁰ ⇌ *cis*⁺ (→*trans*⁺) + e⁻. ^c *trans*⁺ ⇌ *trans*²⁺ + e⁻. ^d Oxidation of 5 × 10⁻⁴ M ferrocene; F_c ⇌ F_c⁺ + e⁻. ^e V vs Ag/AgCl. ^f Separation of oxidation (E_p^{ox}) and reduction (E_p^{red}) peak potentials. ^g Calculated as the average value of E_p^{ox} and E_p^{red} . ^h Small error present due to *cis*⁺ → *trans*⁺ isomerization.

and III observed in this potential range in the solution phase in dichloromethane will be used as reference for the studies in aqueous media of the solids attached to carbon electrodes. A fourth irreversible one-electron process observed at very positive potentials in both solution phase and solid studies is not discussed in this paper.

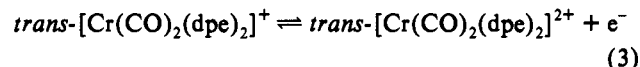
Process I corresponds²⁴ to the reversible one-electron *trans*⁺/*trans*⁰ process



Process II corresponds to the oxidation of *cis*-Cr(CO)₂(dpe)₂ to *cis*-[Cr(CO)₂(dpe)₂]⁺ which rapidly isomerizes by a twist mechanism to *trans*-[Cr(CO)₂(dpe)₂]⁺



Process III represents the reversible *trans*²⁺/*trans*⁺ couple



A dichloromethane solution of *trans*-[Cr(CO)₂(dpe)₂]⁺ exhibits process I (reduction sense) and process III (oxidation sense) only, with process II being absent, whereas a solution of pure *cis*-Cr(CO)₂(dpe)₂ exhibits only processes II and III on the first oxidative scan and all three processes I, II, and III on the reverse and subsequent cyclic scans. On the synthetic time scale the *trans*⁰ compound isomerizes quite rapidly to the *cis*⁰ form in dichloromethane solution. Furthermore *trans*⁰ is readily oxidized to *trans*⁺ by oxygen or light in dichloromethane solution, so that voltammetry of a pure solution of *trans*⁰ is difficult to obtain. Similarly, the voltammetry of pure *cis*⁰ also is difficult to obtain because of slow oxidation to *trans*⁺. Results of the studies in dichloromethane solution are summarized in Table I.

(b) Voltammetry of Solid *trans*-Cr(CO)₂(dpe)₂. Figure 2b shows a cyclic voltammogram (second scan) for the oxidation of solid *trans*-Cr(CO)₂(dpe)₂ attached to a polished pyrolytic basal plane graphite electrode over the potential range of -1000 to +1000 mV vs Ag/AgCl. Two well-defined processes are observed in the potential regions where processes I and III are observed in CH₂Cl₂ solution. However, for the solid, the current for the second oxidation process is significantly larger than that for the first oxidation process and as will be revealed in subsequent discussion there are several other important differences which are indicative of a different electron-transport mechanism. The oxidation and reduction currents, (i_p^{ox})_I and (i_p^{red})_I, associated with process I are well-defined and increase with consecutive cycles (Figure 3a). Process I becomes almost independent of time after 7 cycles (Figure 3b) at which time (E_p^{ox})_I and (E_p^{red})_I have values of -340 and -650 mV vs Ag/AgCl, respectively. Figure 3c shows process III recorded over the potential range +200 to +1200 mV vs Ag/AgCl. In this case, (i_p^{ox})_{III} and (i_p^{red})_{III} decrease gradually with repetitive cycling. However, the peak

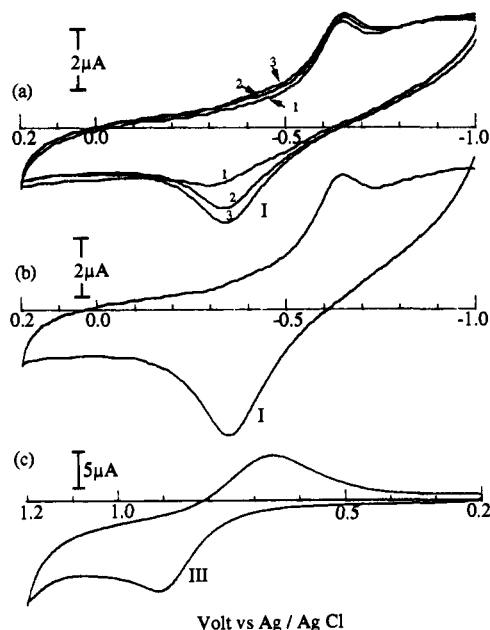


Figure 3. Cyclic voltammograms obtained in aqueous (0.1 M NaClO₄) media at 20 °C for solid *trans*-Cr(CO)₂(dpe)₂ mechanically attached to a polished basal plane pyrolytic graphite electrode (scan rate = 50 mV s⁻¹): (a and b) initial and final potential = -1.0 V and switching potential = 0.2 V, (c) initial and final potential = 0.2 V and switching potential = 1.2 V vs Ag/AgCl; (a) first three cycles, (b) seventh cycle, (c) first cycle.

potential values are constant at 915 and 660 mV vs Ag/AgCl, respectively. Interestingly, if the potential is held between (E_p^{ox})_I and (E_p^{ox})_{III} for a period of time and then scanned, process I is almost absent, whereas process III remains almost unaltered. However, process I could be recovered by reverting to an initial potential of -1000 mV vs Ag/AgCl, and then cycling the potential as in Figure 3a. Voltammograms of *trans*-Cr(CO)₂(dpe)₂ could be obtained for many hours, and after removal of the electrode from the solution it is apparent that the complex remains attached to the surface without detectable dissolution in the water. Further features of the data are summarized in Table II.

(c) Voltammetry of Solid *trans*-[Cr(CO)₂(dpe)₂]⁺. Figure 4a shows a cyclic voltammogram for the oxidation of *trans*-[Cr(CO)₂(dpe)₂]⁺ over the potential range 200–1200 mV vs Ag/AgCl. Process III is observed as a well-defined response as was the case when commencing with *trans*-Cr(CO)₂(dpe)₂. In contrast, if the potential is scanned over the range 200 to -1000 mV vs Ag/AgCl, where process I was expected, no well-defined reduction current was observed (Figure 4b). However, if the potential is switched to -1000 mV vs Ag/AgCl and then scanned over a wide potential range, process I is observed on the first scan as a small response (Figure 4c) and as a well-defined response with further cycling of the potential (Figure 4d). Similarly, if

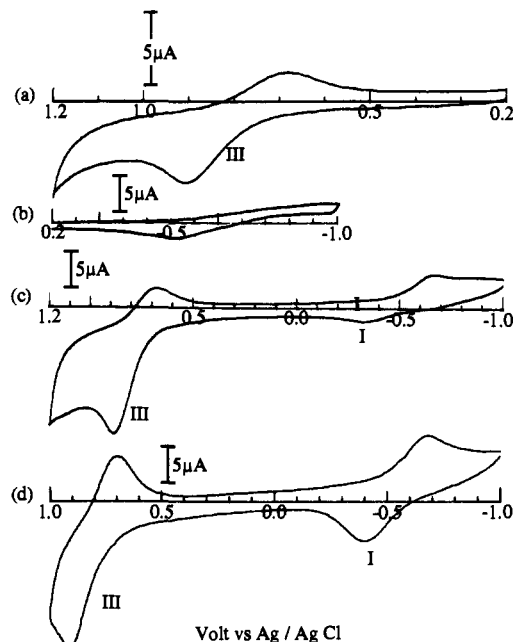


Figure 4. Cyclic voltammograms obtained in aqueous (0.1 M NaClO₄) media at 20 °C for solid *trans*-[Cr(CO)₂(dpe)₂]⁺ mechanically attached to a polished basal plane pyrolytic graphite electrode (scan rate = 50 mV s⁻¹): (a) initial and final potential = 0.2 V, switching potential = 1.2 V; (b) initial and final potential = 0.2 V, switching potential = -1.0 V; (c) first cycle, initial and final potential = -1.0 V, switching potential = 1.2 V vs Ag/AgCl; (d) as for (c) but sixth cycle.

the potential scan is switched to 1200 mV vs Ag/AgCl before cycling, process I is again well-defined. That is, using an initial potential which is intermediate between processes I and III appears to lead to a decrease in the magnitude of process I, whereas holding the potential at either -1000 or 1200 mV vs Ag/AgCl regenerates process I. Clearly, unlike the solution phase data obtained in dichloromethane solution, the initial potential is an important factor in determining the current magnitude observed for process I. Data for the voltammetry of solid *trans*-[Cr(CO)₂(dpe)₂]⁺ are summarized in Table II. As is the case with *trans*-Cr(CO)₂(dpe)₂, no evidence of loss of material from the electrode surface was found over experimental times of several hours. Results on the *trans*⁺ compound were essentially indistinguishable irrespective of whether the BPh₄⁻, BF₄⁻, PF₆⁻, or ClO₄⁻ salts were used.

(d) Voltammetry of Solid *cis*-[Cr(CO)₂(dpe)₂]. Figure 5a shows the first scan of a cyclic voltammogram for oxidation of *cis*-Cr(CO)₂(dpe)₂ over a wide potential range of -1000 to 1000 mV vs Ag/AgCl while Figure 5b shows the response for the first cycle over the potential range -1000 to 200 mV vs Ag/AgCl. Figure 5a exhibits processes I, II, and III and Figure 5b processes I and II, with process II being almost reversible. Second and subsequent scans take on the appearance of those for *trans*-[Cr(CO)₂(dpe)₂]⁺ and *trans*-Cr(CO)₂(dpe)₂ and only show processes

Table II. Voltammetric Data (Scan Rate 50 mV s⁻¹) for Solid Cr(CO)₂(dpe)₂ Compounds Mechanically Attached to Carbon Electrodes Placed in Aqueous 0.1 M Electrolyte Solution (20 °C)

compd	electrode ^a	electrolyte ^b	process I (V vs Ag/AgCl)			process II (V vs Ag/AgCl)			process III (V vs Ag/AgCl)		
			E_p^{ox}	E_p^{red}	E^{0f}	E_p^{ox}	E_p^{red}	E^{0f}	E_p^{ox}	E_p^{red}	E^{0f}
<i>trans</i> ⁰	PGE	NaClO ₄	-0.42	-0.62	-0.52				0.86	0.75	0.81
<i>trans</i> ⁰	GC	NaClO ₄	-0.41	-0.62	-0.52				0.88	0.73	0.81
<i>trans</i> ⁺	PGE	NaClO ₄	-0.36	-0.65	-0.51				0.91	0.70	0.81
<i>trans</i> ⁺	GC	NaClO ₄	-0.37	-0.68	-0.53				0.92	0.70	0.81
<i>trans</i> ⁰	PGE	KClO ₄	-0.39	-0.65	-0.52				0.90	0.68	0.79
<i>trans</i> ⁺	PGE	KClO ₄	-0.39	-0.66	-0.53				0.90	0.68	0.79
<i>cis</i> ^{0 c}	PGE	NaClO ₄		-0.64		-0.04	-0.29	-0.16	0.85	0.73	0.79
<i>cis</i> ^{0 d}	PGE	NaClO ₄	-0.47	-0.57	-0.52				0.86	0.75	0.81

^a PGE = polished basal plane graphite, GC = glassy carbon. ^b Concentration = 0.1 M. ^c First oxidation scan, potentials depend on switching potential (see Figure 5). ^d Second cycle, potentials depend on switching potential. ^e Calculated at the average of the reduction (E_p^{red}) and oxidation (E_p^{ox}) peak potentials.

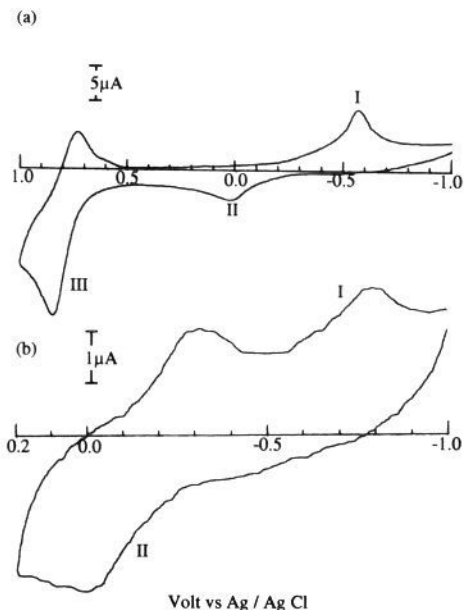


Figure 5. Cyclic voltammograms obtained in aqueous (0.1 M NaClO₄) media at 20 °C for solid *cis*-Cr(CO)₂(dpe)₂ mechanically attached to a polished basal plane pyrolytic graphite electrode (scan rate = 50 mV s⁻¹): (a) first cycle, initial and final potential = -1.0 V, switching potential = 1.0 V; (b) first cycle, initial and final potential = -1.0 V, switching potential = 0.2 V vs Ag/AgCl.

I and III with very little evidence of the *cis*^{+/0} response being obtained after the first cycle. Data are summarized in Table II. The *cis*⁰/*cis*⁺ redox couple observed on the first scan is more reversible than that in CH₂Cl₂ solution at room temperature, although thermodynamic features are similar to those of the solution responses (compare Tables I and II). Once again, the *cis*⁰ compound remained completely adhered to the surface during experimental times of several hours.

(e) Dependence of Peak Height on Scan Rate and Stirring.

The dependence of peak heights for processes I and III was examined over the scan rate (ν) range of 20–1000 mV s⁻¹, with an initial potential of -1000 mV vs Ag/AgCl, corresponding effectively to the oxidation of the *trans*⁰ complex. Plots of peak height versus $\nu^{1/2}$ were linear, as theoretically predicted for a diffusion-controlled process. Since the responses were independent of whether or not the solution was stirred, it would appear that diffusion within the solution is not the rate-determining step.

(f) Voltammetry at Glassy Carbon Electrodes. Data were also obtained for solid *cis*⁰, *trans*⁰, and *trans*⁺ compounds mechanically attached to a glassy carbon electrode. While the voltammograms obtained at the glassy carbon electrode are not as well defined as at the pyrolytic graphite electrode (poorer signal to background ratio), data are essentially the same at both electrode surfaces (Table II).

(g) Resistivity of the Solids. Although an electrochemical process at the electrode–solid–solution boundary does not require conduction through the solid, it is important to confirm the insulating behavior of the materials under investigation. The neutral *cis*⁰ and *trans*⁰ compounds were both found to have resistivities $\geq 10^9 \Omega \text{ cm}$ by the measurement procedures detailed in the Experimental Section. This result is consistent with the carbonyl compounds being nonconducting solids. However, the standard four point probe method of measuring resistivity is required to quantify the extent to which the solids are nonconducting.

(h) X-ray Electron Probe Analysis. Scanning electron microscopy of *cis*-Cr(CO)₂(dpe)₂ mechanically attached to a graphite plate electrode as described in the Experimental Section produced the image shown in Figure 1b, indicating a wide range

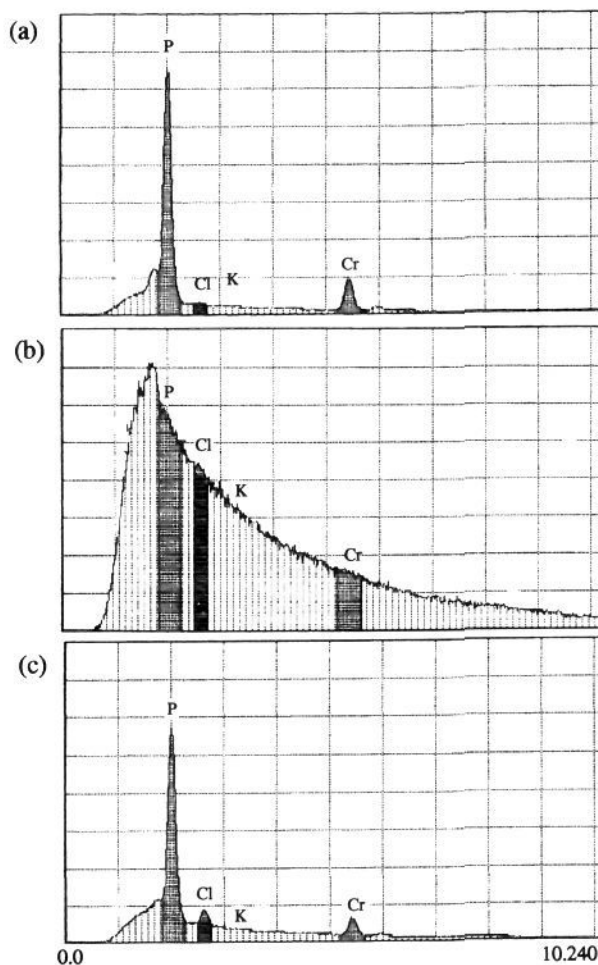


Figure 6. X-ray electron probe microanalysis data obtained at 20 °C for solid *cis*-Cr(CO)₂(dpe)₂ mechanically attached to a polished basal plane pyrolytic graphite electrode (see Figure 1b) (a) before electrolysis showing detection of Cr, P, (b) after oxidative electrolysis in aqueous (0.1 M NaClO₄) media showing detection of Cr, P, and Cl but no K, and (c) as for (b) but for the bare graphite part of the surface showing absence of Cr, P, Cl, and K.

of microcrystalline particle sizes is present. X-ray electron probe analysis of the *cis*-Cr(CO)₂(dpe)₂ prior to application of an oxidizing potential demonstrates the presence of chromium and phosphorus in the theoretically expected 1:4 ratio (Figure 6a). After controlled-potential oxidative electrolysis at 0.0 V vs Ag/AgCl for 120 s with 0.1 M NaClO₄ as the electrolyte, followed by transfer of the electrode to the electron probe analyzer after the treatment described in the Experimental Section, chlorine (arising from the perchlorate) could be detected in addition to chromium and phosphorus. A control experiment without electrolysis did not show any chlorine present. Unfortunately, X-ray electron probe microanalysis is not very sensitive for the detection of light elements such as sodium, so the experiment could not unambiguously reveal whether Na⁺ was present along with perchlorate. The above experiment was therefore repeated with 0.1 M KClO₄ as the electrolyte. Electron probe analysis is sensitive to potassium so this element, if present, would be expected to be readily detected.

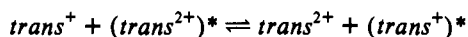
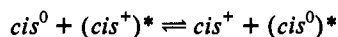
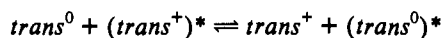
Electron probe analysis of the sample depicted in Figure 1b, after controlled potential oxidative electrolysis with 0.1 M KClO₄ as the electrolyte using a window size of 40 × 60 μm which included several small particles of the micron diameter size as well as areas devoid of compound (i.e., graphite), gave the typical pair of signals expected for Cr and P as well as the Cl signal (Figure 6b) as was the case when NaClO₄ was used as the electrolyte.

However, importantly no K was detected, indicating neither ion paired KClO₄ nor desolvated K⁺ enter the crystal lattice upon oxidation of Cr(CO)₂(dpe)₂ and that neutral aqueous KClO₄ on the surface of the electrode is removed by the washing procedure. Measurements using an analyzer window of 0.25 μm² in some of the black areas of Figure 1b where the amount of cis-Cr(CO)₂(dpe)₂ must be very small yielded extremely weak signals for Cr, P, and Cl, which were consistent with the formation of [Cr(CO)₂(dpe)₂]ClO₄. Additionally, there are also some locations (Figure 6c) that gave zero detectable Cr, P, and Cl, which is indicative of a bare graphite surface. The electron probe data therefore confirm that an electrode–solid array type of model is valid. One problem with using very small window sizes for electron probe analysis is that detection from signals outside the required area may occur because of scattered electrons. However this did not seem to be a significant problem in confirming the existence of an array type model since there were areas where no compound could be detected. In the middle sections of large particles (10 μm) as identified in Figure 1b, there are many locations where almost no Cl was detected, but also a few locations with substantial Cl. These data indicate that oxidation of the solid does not occur uniformly across the entire surface of the solid and that it is dominant at the edges close to the electrode–crystal–solution interface. On applying a potential of –1000 mV vs Ag/AgCl for 120 s and examining the solid by electron probe analysis, Cl always remained detectable at the edges and was never completely eliminated. This is consistent with voltammetric data which imply that oxidation is accompanied by addition of ClO₄[–] and diffusion controlled, but not complete on the time scale of these experiments.

Finally, the fact that voltammetric data for trans-[Cr(CO)₂(dpe)₂]⁺X[–] are independent of the nature of X[–] (X[–] = BF₄[–], BPh₄[–], PF₆[–], ClO₄[–]) suggests that anion exchange is readily achieved with microcrystalline [Cr(CO)₂(dpe)₂]⁺⁰ compounds, at least at the surface, and that effectively it is the voltammetry of the perchlorate form of the complex that occurs irrespective of the nature of X[–] as the counterion in the trans-[Cr(CO)₂(dpe)₂]X compounds.

Discussion

The data presented above demonstrate that extremely well defined voltammograms may be obtained for the nonconducting, solid [Cr(CO)₂(dpe)₂]⁺⁰ compounds when the compounds are mechanically attached to carbon electrodes and placed in water containing NaClO₄ or KClO₄ electrolyte. The results have considerable similarity but also important differences to data obtained when the compounds are dissolved in dichloromethane. In the case of the studies with the solids, the rate determining charge transport mechanism appears to be electron hopping along the phase boundary solid/solution starting from the three-phase electrode–solid–solution boundary that exists at the electrode surface. This electron transfer process may be represented either by the rapid self-exchange electron transfer processes.



and cross redox reactions of the type



or in an equivalent way by a purely solid state electron/hole formalism (see later).

The electron transfer process is accompanied by a rapid uptake of counterions from solution, which leads to overall electroneutrality being achieved during the course of the oxidation reaction.

The important distinguishing features of the voltammetry in the solid state relative to the solution phase are the following: (i) the greater degree of reversibility of the cis⁰/cis⁺ redox couple

as observed on the first scan for oxidation of the cis⁰ compound, (ii) the diminution of the current magnitude for the trans⁺⁰ redox couple by holding the potential between those for the trans⁺⁰ and trans^{2+/+} couples, (iii) the marked decrease of the cis⁰ oxidation process after the initial scan, (iv) the greater peak-to-peak separations of the chemically reversible trans⁺⁰ and trans^{2+/+} couples, (v) the different shapes of the chemically reversible trans⁺⁰ and trans^{2+/+} redox couples, and (vi) the different current magnitudes of the different processes, even though each involves an overall one-electron charge transfer process.

The voltammetry of the microcrystalline solids when considered in conjunction with data obtained from electron probe analysis may be rationalized by proposing that oxidation of neutral cis⁰ or trans⁰ to trans⁺ is accompanied by rapid uptake of perchlorate ions at the solid/solution interface. A true intercalation reaction with diffusion of ions into the host lattice might be possible in longer time scale experiments, but it is not in accord with observed ion exchange and isomerization phenomena. The theory for voltammetry when intercalation occurs has been described.^{28–34} Conductivity along the crystal boundary seems possible when sufficient interaction with the solution phase enables a rapid electron self-exchange mechanism to occur.^{35,36} Factors that govern this conductivity mechanism are still under investigation, but similarities to well-known mechanisms described for redox polymers are obvious.³⁷ A theory for the related case of conduction in Langmuir Blodgett films has also been proposed by Faulkner et al.³⁸

A decrease in rate constants of chemical steps accompanying electron transfer such as isomerization in a surface confined reaction is to be expected. The cis–trans isomerization has been shown to proceed via a twist mechanism,³⁹ and the kinetics in solution are almost independent of solvent. In the solid, a reversible cis⁰/⁺ couple can be observed on the first scan and the trans⁰ species does not isomerize to the energetically favored cis⁰ form on the time scale of our experiments. An interpretation of this result in terms of a slow or hindered isomerization of surface attached species is tempting.

The observed phenomena leads to the need to provide a model which is very similar in complexity to that found in solid-state voltammetry, e.g. of V₂O₅.⁴⁰ According to the solid-state mechanism postulated to be operative with these solids, the rate of the electron hopping mechanism depends on the amount of charged sites already present, or in a microscopic formulation, on the oxidation state of the neighboring sites on the surface. The better defined process III corresponds to a trans⁺²⁺ process which seems to be faster than process I.

In Figure 7 the oxidation processes are considered schematically in a spherical one-dimensional model using the solid state model. In terms of this formalism, the reduction step in process I is likely

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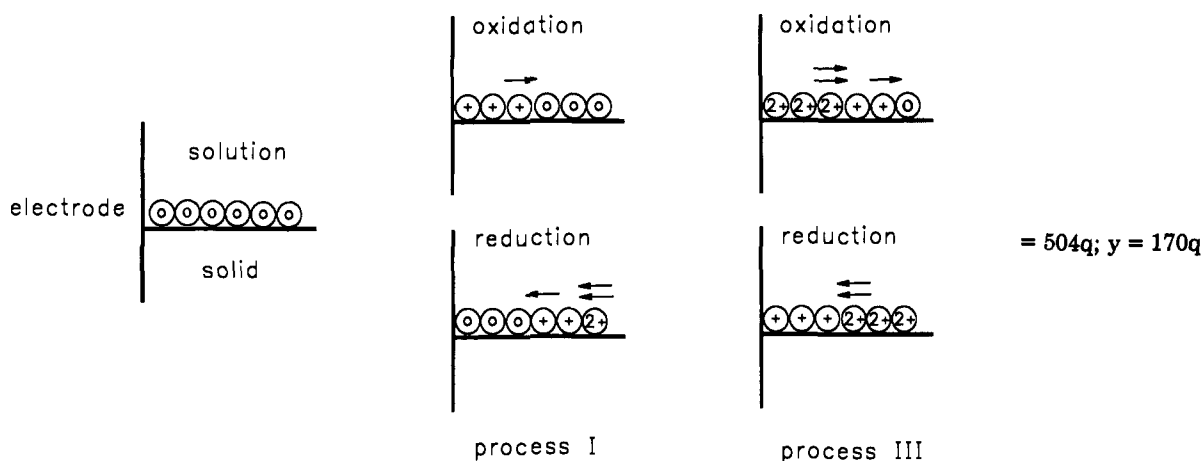


Figure 7. Schematic representation of redox processes in the solid-state model.

to be hindered because an uncharged zone is formed close to the electrode. With this model, it also follows that conduction of holes through this uncharged zone might be the rate-determining factor. The use of the electron/hole formalism therefore also accounts for the fact that oxidation and reduction components of the redox process appear to differ in charge mobility, although this may not be an unambiguous interpretation as mobility also may depend upon partial oxidation of the surface. The equivalent description of this process is to consider results in terms of relative rates of the self-exchange and cross-redox reactions and assign an apparent diffusion coefficient to each step as has been proposed to explain the voltammetry of holes in conducting polymers.⁴¹

The difference in currents for processes I and III shown in Figure 4c also may be explained by a fast comproportionation step. A similar kinetic scheme was described for a redox polymer.⁴¹ Slow $trans^{0/+}$ oxidation and fast $trans^{+/2+}$ oxidation would lead to a situation where the fast process tries to "overtake" the slow process. This will lead to $trans^{2+}$ species in the neighborhood of $trans^0$ sites and they will react to give two $trans^+$ sites. The resulting charge mobility may explain the effective high mobility of process III.

Compared to studies of solids where electrointercalation is observed (e.g. U_3O_8 , C_{60}),^{34,42,43} the compounds used in this study seem to energetically disfavor this bulk reaction presumably because of noncompensated lattice forces or an unfavorable structural type (no layer lattice). However, our experiments cannot exclude this process proceeding at a very slow rate.

The remarkable similarities of the reversible potentials to voltammetry in CH_2Cl_2 solution presumably reflect the fact that in both the solid and solution phases, one-electron charge transfer processes are coupled to diffusion. The reversible potentials obtained from voltammetry of $Cr(CO)_2(dpe)_2$ dissolved in organic

solvents are not highly solvent dependent.⁴⁴ The E^0_f values obtained from a diffusion controlled electron transfer process at the water–solid–electrode interface would be expected to be similar to values expected for diffusion controlled processes in aqueous media since the solid-state and solution structures are probably very similar. Thus it is proposed that the similarity of the thermodynamic data is explained by the closely related nature of the solid and solution structures of the $[Cr(CO)_2(dpe)_2]^{+/0}$ species and the applicability of the diffusion controlled model in all situations irrespective of whether the voltammetry of solid or dissolved forms of the compound is being studied.

Conclusions

The present studies imply that solid compounds will be amenable to voltammetric study via mechanical transfer of microcrystalline forms of solids to carbon electrodes provided transport of ions can take place across the solid–solution interface at a sufficiently fast rate to observe a measurable current. The relatively high edge to total compound area ratio of microcrystalline materials may aid diffusion processes across the solid–solution–electrode boundary. A detailed theoretical understanding of the electron transfer and diffusion process will be difficult to achieve for arrays of microcrystalline solid, although it is clearly related to but possibly more complex than the theory already associated with the voltammetry of intercalation compounds and voltammetry in conducting polymers.

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