

Mechanistic Study of the Voltammetry of Nonconducting Microcrystalline *cis*- and *trans*-Cr(CO)₂(dpe)₂ Complexes (dpe = Ph₂PCH₂CH₂PPh₂) Mechanically Attached to a Graphite Electrode and Immersed in Different Aqueous Electrolyte Media: Identification by Infrared Spectroscopy of *cis*-[Cr(CO)₂(dpe)₂]⁺ Stabilized at the Electrode–Solid–Solution Interface

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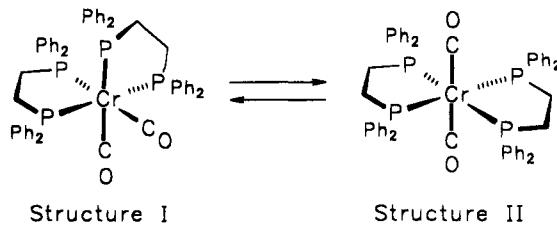
Received August 11, 1994*

Electrochemical oxidation of microcrystalline, but nonconducting, *cis*-Cr(CO)₂(dpe)₂ (dpe = Ph₂PCH₂CH₂PPh₂) mechanically attached to a graphite electrode which has been placed in aqueous electrolyte media enables the thermodynamically unstable *cis*-[Cr(CO)₂(dpe)₂]⁺ to be identified for the first time by specular reflectance infrared spectroscopy. That is, kinetic stabilization of the thermodynamically favored *cis*⁺ → *trans*⁺ isomerization process is achieved at the electrode–solid–electrolyte interface. Detailed studies on the oxidation of microcrystalline *trans*-Cr(CO)₂(dpe)₂ to *trans*-[Cr(CO)₂(dpe)₂]⁺ which involve the variation of temperature, scan rate, and electrolyte reveal that “thick”-layer and “thin”-layer processes are present. A zero current extrapolation process enables potentials to be calculated which are independent of crystal size and spacing. Potential data calculated in this manner show virtually no dependence on electrolyte cation but a variation of potential of almost 500 mV when 0.1 M NaF is used instead of 0.1 M NaClO₄ as the electrolyte. The correlation of oxidation potential data with free energies of partition for anion transport across a water–dichloroethane interface coupled with voltammetric and spectroscopic data indicate that the oxidation reaction may be summarized by eqs 1–5: (1) *trans*_{solid} ⇌ *trans*⁺_{solid} + e⁻; (2) *cis*_{solid} ⇌ *cis*⁺_{solid} + e⁻; (3) A⁻_{solution} ⇌ A⁻_{solid}; (4) *trans*⁺_{solid} + A⁻_{solid} ⇌ (*trans*⁺–A⁻_{solid}); (5) *cis*⁺_{solid} + A⁻_{solid} ⇌ (*cis*⁺–A⁻_{solid}) → (*trans*⁺–A⁻_{solid}). A⁻ denotes the electrolyte anion, and the *cis*⁰⁺ and *trans*⁰⁺ nomenclature represents the relevant isomer of [Cr(CO)₂(dpe)]⁰⁺ in the appropriate oxidation state. The oxidation processes are believed to be accompanied by swelling of crystals, which may aid the transport of ionic species within the solid.

Introduction

The method of mechanically attaching small quantities of solids to graphite and other electrodes and investigating the voltammetric responses when the electrode is placed in aqueous electrolyte media has been shown to broaden the range of methods for studying redox chemistry that occurs at the solid–solution (electrolyte) interface.^{1–5} For example, the analytical method of abrasive stripping voltammetry, developed by Scholz and co-workers,³ in which solid material is oxidized or reduced to a solution-soluble species during the stripping process, can be used to analyze minerals and alloys in nanogram quantities and the voltammetry of substances such as insoluble metal dithiocarbamates, which are oxidized to at least one soluble product in aqueous media, enable stability

constant data to be calculated.⁴ In a theoretical study relevant to the case where the product of electrolysis is soluble, Scholz et al.⁵ proposed a mechanism of ionic species migrating along the solid–solution boundaries to the electrode surface where the electrochemical processes associated with the product dissolution are believed to occur. However, studies on the organometallic complexes *cis*- and *trans*-Cr(CO)₂(dpe)₂ (dpe = Ph₂PCH₂CH₂PPh₂; I and II), which are of interest in



* Abstract published in *Advance ACS Abstracts*, October 15, 1994.
(1) Bond, A. M.; Colton, R.; Daniels, F.; Fernando, D. R.; Marken, F.; Nagaosa, Y.; Van Steveninck, R. F. M.; Walter, J. N. *J. Am. Chem. Soc.* **1993**, *115*, 9556.

(2) Bond, A. M.; Marken, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1994**, *372*, 125.

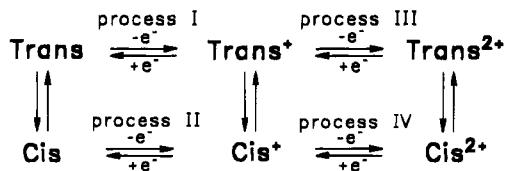
(3) Scholz, F.; Lange, B. *Trends Anal. Chem.* **1992**, *11*, 359 and references cited therein.

(4) Bond, A. M.; Scholz, F. *Langmuir* **1991**, *7*, 3197.

(5) Jaworski, A.; Stojek, Z.; Scholz, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1993**, *354*, 1.

this study, differ in that the compounds are insoluble in water in both the oxidized and reduced forms. For this case, it has been proposed that an interfacial process allows charge transport to proceed along the phase boundary between solid and electrolyte solution, starting from the three-phase boundary at the electrode surface.¹ Coupled to this conduction via electron self-

Scheme 1. Redox and Isomerization Reactions for the $[\text{Cr}(\text{CO})_2(\text{dpe})_2]^{0/+2+}$ System



exchange or an electron-hopping mechanism, ions cross the phase boundary to achieve charge compensation.

Some data related to the voltammetric oxidation of solid *cis*- and *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ at the graphite electrode–aqueous NaClO_4 (0.1 M) boundary have been described in a previous publication.¹ Scheme 1 shows the electrochemical behavior of this system in the solution phase which is known from voltammetric investigations in organic solvents.⁶ Broadly speaking, the same scheme is operative at the electrode–solid–solution interface.¹ All species in Scheme 1 are insoluble in water but soluble in less polar organic solvents, such as dichloromethane. The electron-transfer processes for each isomeric pair (processes I–IV) are coupled to isomerization between the *trans* and the *cis* form in the different oxidation states. However, the conversion of *cis*⁺ to *trans*⁺ species is fast, and the equilibrium position heavily favors the *trans*⁺ isomer. Consequently, *cis*⁺ has not been isolated or even identified spectroscopically in the solution-phase studies.

The present work describes the results of a series of experiments which are aimed at elucidating mechanistic aspects of the physical processes that determine the voltammetric responses of nonconducting insoluble solids mechanically attached in microcrystalline form to graphite electrodes which are then immersed in aqueous media. In particular, the influence of the electrolyte and temperature and changes in spectroscopic data obtained on the solids during the course of the redox change associated with the *trans*^{0/+} and *cis*^{0/+} couples have been probed in some detail. Importantly, stabilization of the *cis*⁺ isomer achieved at the solid–solution interface enables this species to be spectroscopically characterized for the first time and illustrates that the voltammetry of mechanically attached microcrystalline solids can provide a route to characterizing species that are significantly reactive in the solution phase.

Experimental Section

Synthesis. *cis*- and *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$.⁶ $\text{Cr}(\text{CO})_6$ was refluxed with 2 mol equiv of dpe in a small volume of decane under an atmosphere of nitrogen. After 65 h the red crude product was collected by filtration and then washed first with hexane, followed by a small amount of dichloromethane to remove the *cis* isomer to give red crystalline *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$. Addition of methanol to a dichloromethane solution of *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ caused the yellow *cis*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ to separate from solution, as reported previously.⁷ Precipitation and collection by filtration in the dark followed by drying *in vacuo* afford a yellow microcrystalline powder. ¹³C and ¹H NMR studies on samples dissolved in suitable solvents indicate that the microcrystalline solid used for the voltammetric

studies contains no solvent of crystallization. The red microcrystalline powder *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ decomposes at the melting point of 210 °C. The *cis*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ isomer undergoes a solid-state conversion at 185–195 °C in the presence of oxygen to form a white product of the composition $\text{CrO}_2(\text{dpe})_2$.

Reagents and Voltammetric Instrumentation. All reagents were of analytical reagent or electrochemical grade purity. Water from a Millipore system was used for the preparation of electrolyte solution. The reference electrode used was a Ag/AgCl (3 M NaCl) electrode, and the auxiliary electrode was made from a platinum sheet. Voltammetric experiments were performed with a BAS 100 A electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN). Unless otherwise specified, the supporting electrolyte was 0.1 M in aqueous media at stated temperatures. All solutions were deaerated with high-purity nitrogen for 15 min prior to making the measurements.

The carbon-disk electrodes used in this study were made from basal plane pyrolytic graphite (5 mm diameter) fitted into a Teflon holder, and the solid organometallic compound was transferred to the surface of the carbon electrode as follows. Sample amounts of 1–3 mg of the microcrystalline complex were placed on a coarse grade filter paper. The carbon electrode was pressed onto the substance and rubbed over the material, causing some of the compound to adhere to the electrode surface as an array of microcrystalline particles of 0.1–10 μm size.¹ For electrochemical measurements, the electrode was transferred into the electrochemical cell containing aqueous electrolyte solution. The electrode surface could be renewed after the measurement by dipping into dichloromethane and allowing the compound to dissolve into this solvent. Alternatively, a clean surface can be obtained by cutting the electrode surface with a razor blade.

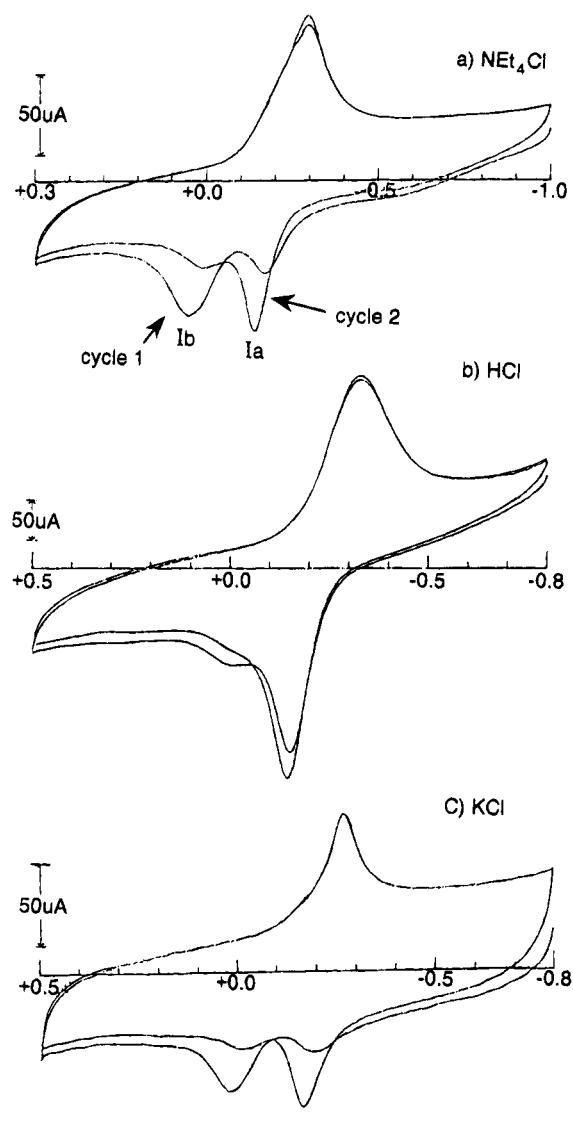
Specular Reflectance FTIR Spectroscopy. Basal plane pyrolytic graphite modified with solid microcrystalline material exhibits a shiny graphite surface which is an excellent reflector of light. Attempts to use diffuse reflectance FTIR spectroscopy to characterize the microcrystalline particles gave only very weak, unsatisfactory signals. However, a specular reflectance system (angle of incidence 30°) mounted in a Perkin-Elmer FTIR 1720X gave intense and reproducible reflection signals which correspond to the expected IR bands in the carbonyl region. Electrodes were rinsed with Millipore water after the electrochemical experiment and dried in air before positioning them into the IR beam to maximize the detector energy. A total of 10–20 scans was appropriate to obtain good-quality spectra when good background subtraction could be achieved.

Results

(a) Voltammetry of Microcrystalline *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$. Effect of Varying the Electrolyte Cation. Previous studies were undertaken solely with aqueous 0.1 M NaClO_4 electrolyte media.¹ However, chloride is more suitable than perchlorate as the common anion for experiments aimed at understanding the role of the cation, because a much wider range of cations are available as water-soluble chloride salts. Only process I, the first oxidation of *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$, is used to evaluate the effect of varying the cation, since the charge-transfer step occurs without the complication of a structural change. Elevated temperatures are employed to obtain well-defined responses, since the response in some electrolytes at ambient temperatures of about 20 °C is fairly small. With 0.1 M HCl , KCl , and NEt_4Cl as electrolytes, well-defined but related voltammetric responses are observed (Figure 1). The single process reported¹ in NaClO_4 electrolyte at 22 °C is now readily recognized as being split into two

(6) Wimmer, F. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* 1974, 13, 1617 and references cited therein.

(7) Chatt, J.; Watson, H. R. *J. Chem. Soc.* 1961, 4980.

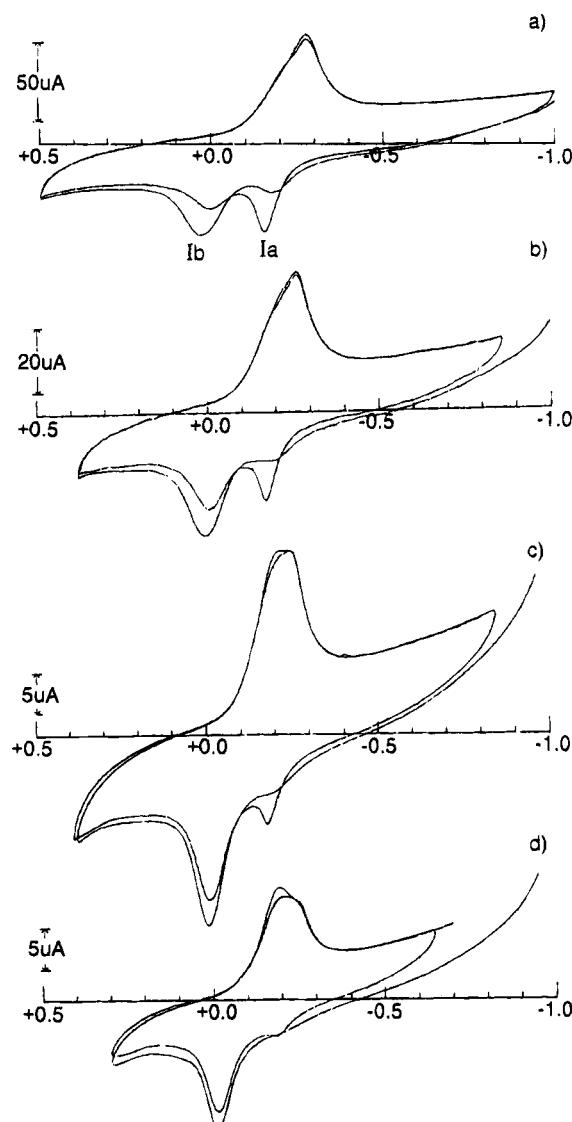


E in Volt vs. Ag / Ag Cl

Figure 1. Cyclic voltammograms obtained for oxidation of *trans*-Cr(CO)₂(dpe)₂ mechanically attached to a basal plane pyrolytic graphite electrode and placed in different aqueous electrolytes at 50 °C using a scan rate of 200 mV s⁻¹: (a) 0.1 M NEt₄Cl; (b) 0.1 M HCl; (c) 0.1 M KCl.

processes at elevated temperatures. It will be shown later that both the change of electrolyte anion and the increased temperature are responsible for this change. The split processes are now labeled Ia and Ib. With all cations, the second and subsequent cycles deviate from the first cycle as shown in Figure 1. Change after the first cycle consists of a potential shift toward more positive values as well as changes in relative peak currents of the oxidation component of processes Ia and Ib. Furthermore, the time between two cycles determines what may be described as a relaxation effect. The splitting of the oxidation component of the process is much larger than that of the reduction component, which consists of two almost completely superimposed signals. Reversing the scan direction between the peaks corresponding to processes Ia and Ib leads to a smaller reduction response and no increase of Ia in the second cycle.

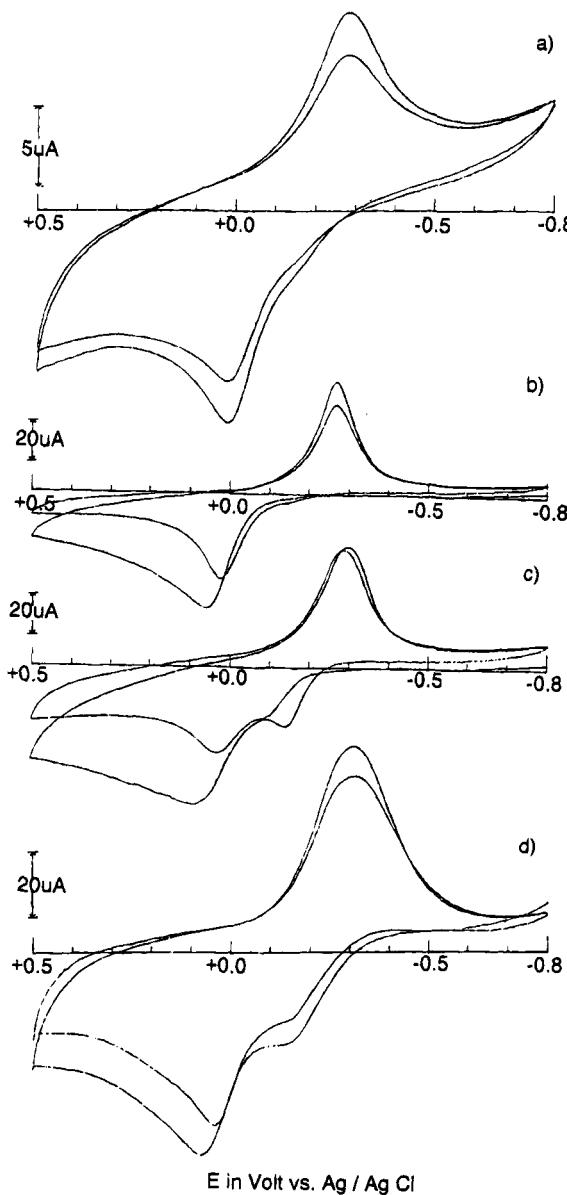
Effect of Scan Rate. In Figure 2, in which KCl is the electrolyte, the dependence on scan rate is shown to be considerable and follows different laws for different



E in Volt vs. Ag / Ag Cl

Figure 2. Cyclic voltammograms obtained for oxidation of *trans*-Cr(CO)₂(dpe)₂ mechanically attached to a basal plane pyrolytic graphite electrode and placed in aqueous 0.1 M KCl electrolyte at 50 °C using scan rates of (a) 100 mV s⁻¹, (b) 50 mV s⁻¹, (c) 20 mV s⁻¹, and (d) 10 mV s⁻¹.

processes. The peak height for oxidation process Ia in the first cycle can be seen to vary linearly with scan rate, as expected for oxidation of a thin film; however, process Ib exhibits a square root dependence which is theoretically expected for diffusion-controlled mechanisms and for the reduction signal a $v^{0.7}$ law is observed, which could be due to the presence of two overlapping processes. Similar observations have been reported for oxidation of decamethylferrocene,² and the proposed mechanism of a surface confined process (Ia) followed by a second diffusion-controlled process (Ib), in which anions penetrate into the solid, also seems to apply to the compound *trans*-Cr(CO)₂(dpe)₂. From this argument it follows that the enhanced signal for process Ia in the second cycle may be attributed to an expanded crystal surface area, which can be understood in terms of a process involving swelling of the solid. At low scan rates this swelling process approaches reversibility and does not interfere with the second oxidation cycle, whereas at high scan rates, where insufficient time is available



E in Volt vs. Ag / AgCl

Figure 3. Cyclic voltammograms obtained for oxidation of *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ mechanically attached to a basal plane pyrolytic graphite electrode and placed in aqueous 0.1 M HCl electrolyte at 50 °C using a scan rate of 200 mV s⁻¹ and variable amounts of material attached to the surface.

to achieve reversibility, a strong relaxation effect is found.

Effect of Surface Coverage and Particle Size. Voltammograms vary considerably with surface coverage of the graphite electrode and particle size of the electroactive solid. Unfortunately, accurate control of the surface coverage and particle size parameters is difficult to achieve. Examples of the variations that may be observed are summarized in Figure 3. Peak currents as well as peak potentials and the relative magnitude of processes Ia and Ib are all dependent on both factors. However, the problem of comparison between experiments with different electrode coverages and particle sizes can be addressed by a method involving extrapolation to zero current. The measured peak potentials and peak currents obtained as a function of scan rate from different experiments can be combined in a potential-current plot (Figure 4) to reveal some details of the oxidation process. In this diagram the

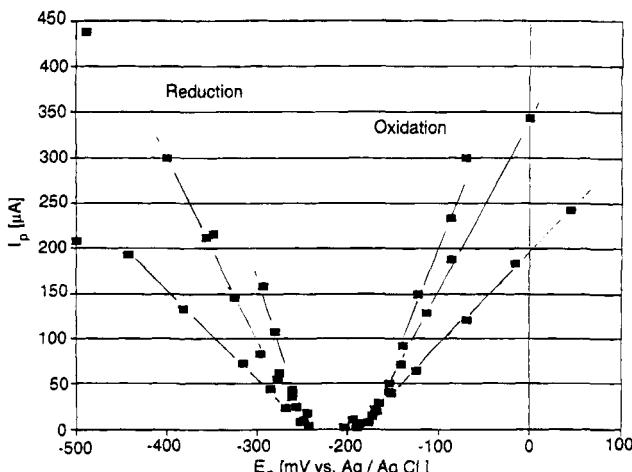


Figure 4. Plots of peak current *vs* peak potential for oxidation of *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ and reduction of *trans*- $[\text{Cr}(\text{CO})_2(\text{dpe})_2]^+$ mechanically attached to a basal plane pyrolytic graphite electrode and placed in aqueous 0.1 M KCl electrolyte at 50 °C using scan rates of 10–2000 mV s⁻¹.

dominant signal pair for an experiment in chloride electrolyte (0.1 M KCl) at 50 °C is used to provide data under conditions in which a plot of $\log(\text{scan rate})$ *versus* $\log(\text{peak current})$ is linear with a slope of approximately 0.5. At very high peak currents corresponding to high scan rates or high coverages, peak potentials are not very reproducible. This explains the scatter of peak potentials observed at high current values in Figure 4. The linear (ohmic) dependency of the plot in Figure 4 allows extrapolation of peak potential data to zero current and thus the derivation of reliable potentials that are independent of surface coverage or spacing and crystal size at the ± 10 mV level. The slope theoretically is associated with the uncompensated resistance and with the amount of electroactive material, which again correlates to the particle number and size. The same linear E_p *vs* I_p behavior, although with smaller slopes and smaller currents, can be found for the second signal pair to give two “zero current” oxidation potentials at -30 and -181 mV *vs* Ag/AgCl and two zero current reduction potentials at -150 and -242 mV *vs* Ag/AgCl when 0.1 M KCl is the electrolyte. These zero current potentials are found to be independent of the electrolyte cation (H^+ , K^+ , $\text{N}(\text{Et}_4)^+$) at the ± 10 mV level. It is therefore concluded *via* data obtained from extrapolation to zero current that the influence of cations on the voltammetric response for oxidation of microcrystalline solid *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ attached to graphite electrodes is not detectable within experimental error.

Effect of Varying the Temperature. The remarkable effect of increasing the temperature on peak currents of materials mechanically attached to electrodes has been noted previously in studies on the oxidation of decamethylferrocene.² In Figure 5 a series of voltammograms obtained over a temperature range of 20–80 °C is shown for oxidation of solid *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$. Peak currents can be seen to double for a 20 °C change in temperature. The effect of temperature is therefore much more pronounced than in comparable solution phase voltammetry. In the case of solids there also are dramatic changes in the characteristics of the voltammograms, as the major oxidation response at 20 °C cannot be detected at elevated temperature and the reduction process clearly splits into two distinct com-

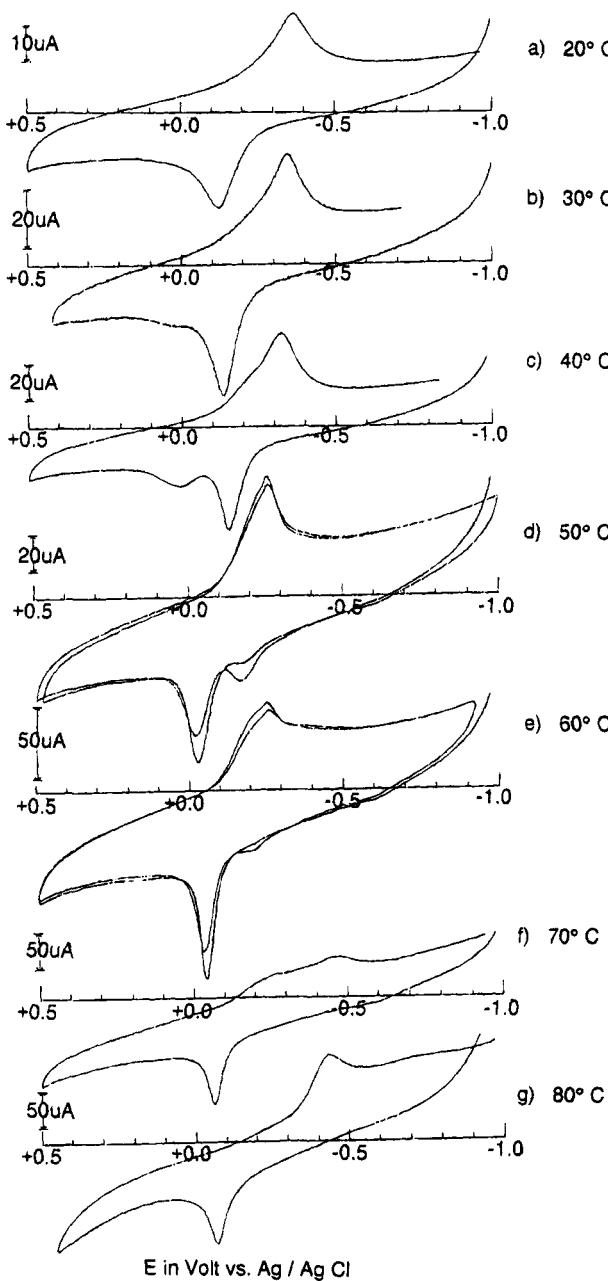


Figure 5. Cyclic voltammograms obtained for oxidation of *trans*-Cr(CO)₂(dpe)₂ mechanically attached to a basal plane pyrolytic graphite electrode and placed in aqueous 0.1 M NaCl electrolyte at various temperatures using a scan rate of 20 mV s⁻¹.

ponents with the second (more negative) one dominating the voltammogram at higher temperature. The effects related to temperature variation are comparable with changes due to variation in scan rate. The changes with temperature are reversible, although the experiment at 80 °C appears to lead to a loss of electroactive material. A plot of peak current *versus* peak potential (Figure 6) illustrates the pronounced temperature dependence of the extrapolated zero current peak potentials and shows that increasing the temperature leads to a narrower gap between oxidation and reduction processes.

Effect of Varying the Electrolyte Concentration. The oxidation of *trans*-Cr(CO)₂(dpe)₂ requires anion uptake into the solid in order to achieve charge neutralization. This implies that the electrolyte anion concentration could be important in determining the nature of the voltammetric response. A series of vol-

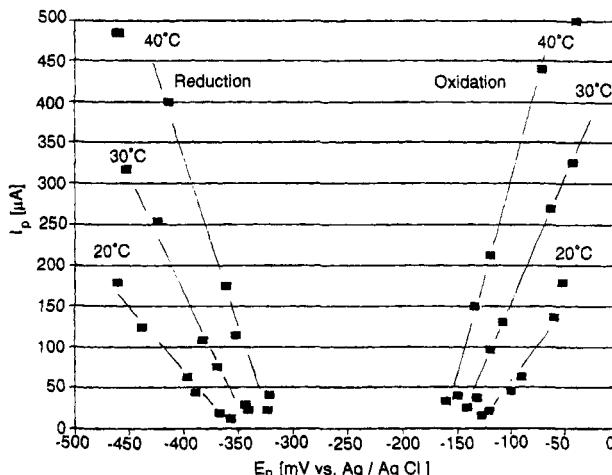
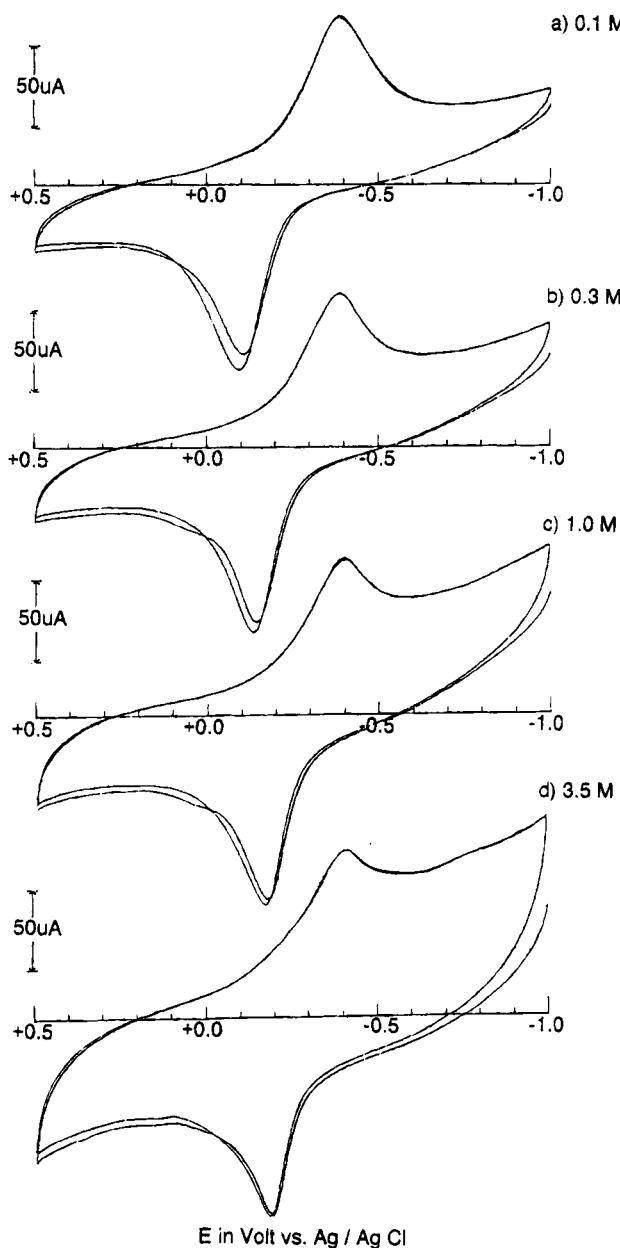


Figure 6. Plots of peak current *vs* peak potential for oxidation of *trans*-Cr(CO)₂(dpe)₂ and reduction of *trans*-[Cr(CO)₂(dpe)₂]⁺ mechanically attached to a basal plane pyrolytic graphite electrode and placed in aqueous 0.1 M NaCl electrolyte at various temperatures using scan rates of 10–2000 mV s⁻¹.

tammograms obtained with microcrystalline *trans*-Cr(CO)₂(dpe)₂ attached to a basal plane graphite electrode and placed in aqueous NaCl solution at 30 °C is shown as a function of NaCl concentration in Figure 7. Although a change in background current occurs, the peak currents are essentially independent of concentration over the range of 0.1–3.5 M. A plot of peak currents *vs* peak potentials (Figure 8) reveals a small but similar shift of oxidation and reduction signals toward more negative potentials and an increase in slope with increasing chloride concentration. Extrapolating the peak potentials to zero current and plotting these values against concentration give the data that are summarized in Figure 9. In summary, the anion concentration, while not strongly influencing the current magnitude, does have a small influence on the potentials which approximates a Nernstian shift of 2.303RT/nF (volt per decade) change in concentration and is slightly different for the oxidation and the reduction responses.

Effect of Varying the Electrolyte Anion. The oxidation of *trans*-Cr(CO)₂(dpe)₂ (process I) as a function of different electrolyte anions was studied at 50 °C (Figure 10). The more hydrophobic anions (perchlorate and iodide) tend to give lower peak currents and broader signals, whereas the more hydrophilic anions (hydroxide, fluoride, and sulfate) show complicated splitting of signals at low scan rates. Changing the anion from perchlorate to hydroxide produces a potential shift of almost 500 mV, which is comparable to results described previously² for oxidation of decamethylferrocene. In order to obtain more accurate potential values, voltammograms were obtained in different electrolytes at various scan rates and the extrapolation method described earlier has been employed to yield zero current potentials. Results of the experiments are compiled in Table 1. The anions are listed in order of decreasing oxidation peak potential. The peak potentials cited in the first column correspond to the dominant signal pair, which in some cases is a somewhat arbitrary choice. The comparison of oxidation peak potentials with the Gibbs energies for partition of anions at a 1,2-dichloroethane–water interface⁸ exhibits an interesting correlation, which suggests that the free energy of transfer of the



E in Volt vs. Ag / Ag Cl

Figure 7. Cyclic voltammograms obtained for oxidation of $\text{trans-}\text{Cr}(\text{CO})_2(\text{dpe})_2$ mechanically attached to a basal plane pyrolytic graphite electrode and placed in aqueous NaCl electrolyte at 30°C using a scan rate of 200 mV s^{-1} and concentrations of (a) 0.1 M , (b) 0.3 M , (c) 1.0 M , and (d) 3.5 M .

particular anion from solution into the solid phase is an important term in determining the observed peak potential. A further interesting parameter is the observed peak to peak separation, which is large for rather hydrophobic anions such as perchlorate and iodide.

(b) Voltammetry of Microcrystalline $\text{cis-}\text{Cr}(\text{CO})_2(\text{dpe})_2$. The metal complex $\text{cis-}\text{Cr}(\text{CO})_2(\text{dpe})_2$ is known to be in equilibrium with its trans isomer when dissolved in organic solvents.⁹ Oxidation leads to a large shift in the equilibrium position so that the trans^+ species is very dominant, unlike the case in the reduced form, where the cis form is slightly favored. The situation with respect to isomerization after oxidation

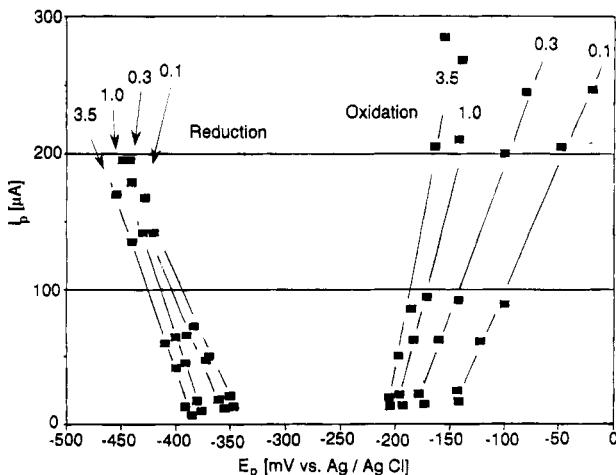


Figure 8. Plots of peak current *vs* peak potential for oxidation of $\text{trans-}\text{Cr}(\text{CO})_2(\text{dpe})_2$ and reduction of $[\text{Cr}(\text{CO})_2(\text{dpe})_2]^+$ mechanically attached to a basal plane pyrolytic graphite electrode and placed in aqueous NaCl electrolyte at 30°C using scan rates of $10\text{--}2000 \text{ mV s}^{-1}$ and concentrations of $0.1, 0.3, 1.0$, and 3.5 M .

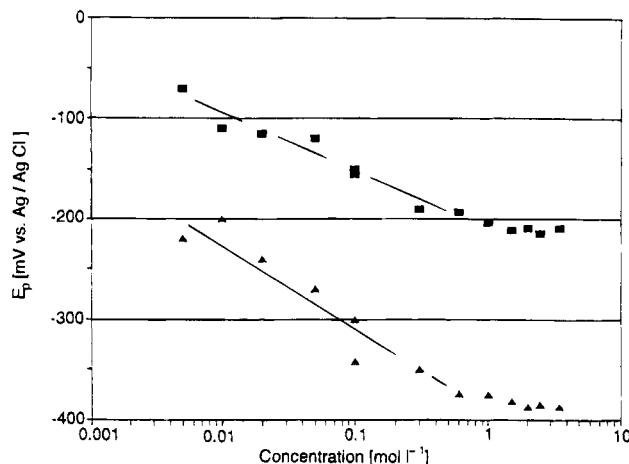


Figure 9. Plots of peak potential *vs* concentration for oxidation of $\text{trans-}\text{Cr}(\text{CO})_2(\text{dpe})_2$ and reduction of $[\text{Cr}(\text{CO})_2(\text{dpe})_2]^+$ mechanically attached to a basal plane pyrolytic graphite electrode and placed in aqueous NaCl electrolyte at 30°C using data obtained from extrapolation to "zero current".

becomes more complicated when the voltammetry of microcrystalline $\text{cis-}\text{Cr}(\text{CO})_2(\text{dpe})_2$ attached to a basal plane graphite electrode in aqueous electrolyte is investigated. In Figure 11 the voltammetric responses obtained at 50°C with aqueous NaCl (0.1 M) are shown and the development from a response corresponding to the oxidation of the cis isomer to that for oxidation of the $\text{trans-}\text{Cr}(\text{CO})_2(\text{dpe})_2$ complex can be followed. The cyclic voltammogram of the trans species, obtained by isomerization of the cis^+ compound, is evident after 20 cycles, and at this time the change upon varying the scan rate can be investigated. Peak potential values for zero current can be obtained by interpolation and are included in Table 1. With 0.1 M perchlorate electrolyte, the data obtained after 10 cycles is indistinguishable from the same result obtained with pure $\text{trans-}\text{Cr}(\text{CO})_2(\text{dpe})_2$. However, in chloride electrolyte, a shift in potential and a larger peak to peak separation are found and the results differ slightly from those for pure $\text{trans-}\text{Cr}(\text{CO})_2(\text{dpe})_2$. It can be concluded that, although isomerization of electroactive material does

(8) Girault, H. H. J.; Schiffrian, D. J. *Electroanal. Chem.* **1989**, *15*, 1.

(9) Bond, A. M.; Colton, R.; Cooper, J. B.; Traeger, J. C.; Walter, J. N.; Way, D. *Organometallics* **1994**, *13*, 3434.

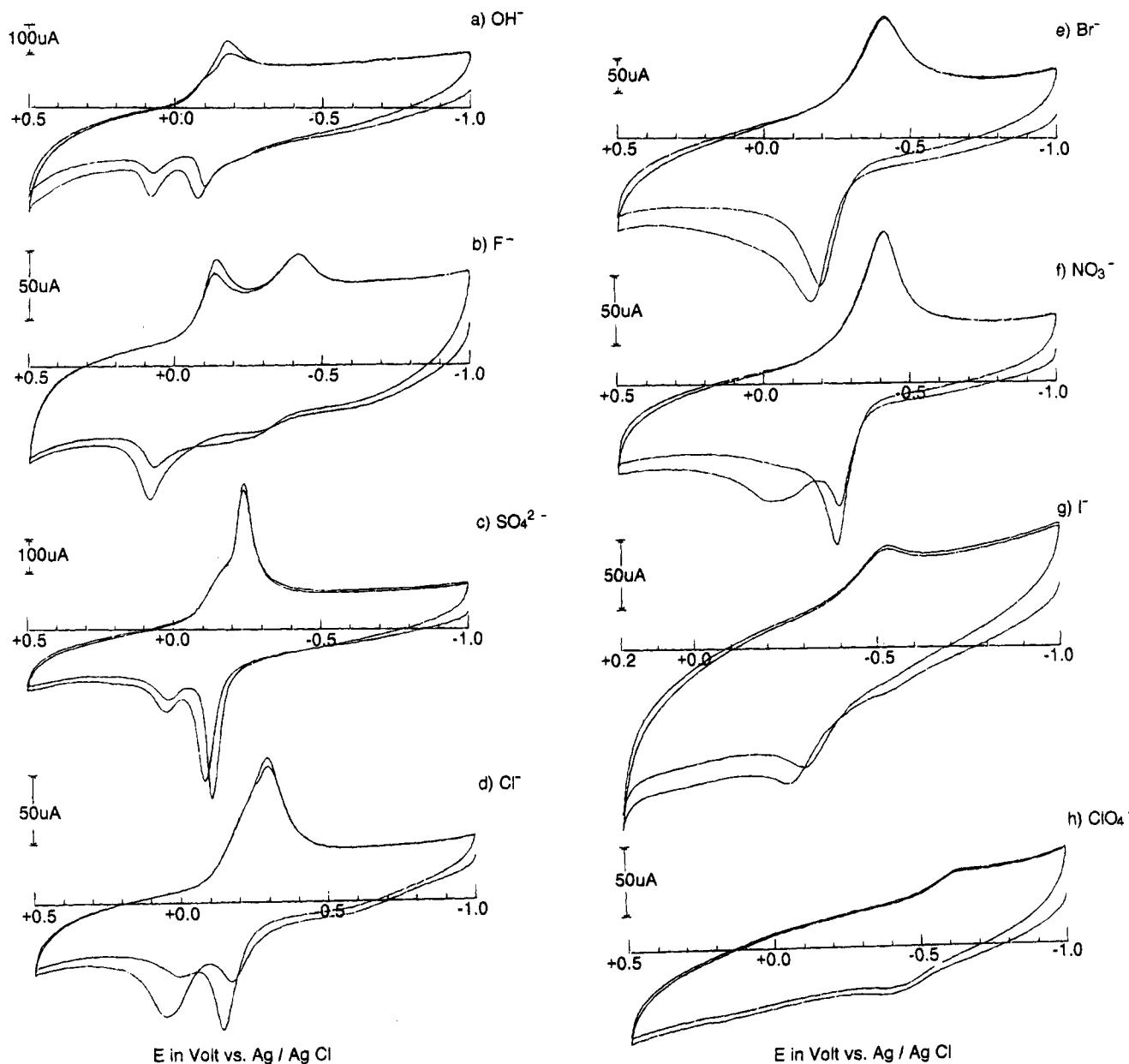


Figure 10. Cyclic voltammograms obtained for oxidation of *trans*-Cr(CO)₂(dpe)₂ mechanically attached to a basal plane pyrolytic graphite electrode and placed in aqueous 0.1 M electrolytes at 50 °C using scan rates of 200 mV s⁻¹: (a) NaOH; (b) NaF; (c) Na₂SO₄; (d) NEt₄Cl; (e) KBr; (f) NaNO₃; (g) KI; (h) NaClO₄.

occur at the surface, some influence of the underlying solid *cis*-Cr(CO)₂(dpe)₂ remains on voltammetric responses which are believed to occur at the solid–solution boundary. The fact that the response for the *cis* isomer disappears more rapidly in the presence of perchlorate anions than for chloride ions suggests that there is a direct influence of the anion on the environment in which the isomerization (twist mechanism¹⁰) occurs.

(c) Characterization of the Electrode Processes by Specular Reflectance IR Spectroscopy. A useful technique to monitor electrochemical processes on the solid surfaces and to characterize generated surface species is IR spectroscopy.¹¹ Specular reflectance FTIR spectroscopy is used in this work because the modified graphite surface reflects sufficient light intensity. Good signal to noise ratios are possible after only 5–40 scans. Perhaps surprisingly, the obtained signals show reflec-

tion rather than absorption characteristics which could be related to the smooth surface obtained by the mechanical attachment of solids to pyrolytic graphite and the fact that nontransparent solid particles rather than a monolayer of material are investigated. A very effective background subtraction is possible when spectra obtained for the starting material attached to the graphite electrode are used and only the relative change in intensity after electrochemical treatment is measured. IR spectra of surface species generated in the presence of aqueous NaCl (0.1 M) are shown in Figure 12. The *trans* isomer with an IR band at 1796 cm⁻¹ (compare diffuse reflectance on KBr powder, 1783 cm⁻¹, Table 2) is shown to be converted into *trans*⁺ with a signal at 1846 cm⁻¹ (compare diffuse reflectance on

(11) (a) Nichols, R. J. In *Adsorption of Molecules at Metal Electrodes*; Lipkowski, J., Ross, P. N., Eds.; VCH Publishers: New York, 1992; p 347, and references therein. (b) Christensen, P. A.; Hamnett, A.; Trevellick, P. R. *J. Electroanal. Chem. Interfacial Electrochem.* 1988, 242, 23.

Table 1. Voltammetric Data^a Obtained for Oxidation of Microcrystalline *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ Mechanically Attached to a Basal Plane Pyrolytic Graphite Electrode at 50 °C as a Function of Supporting Electrolyte Anion

anion ^c	process Ia			process Ib		
	E_p^{ox} (mV)	E_p^{red} (mV)	$E_p^{\text{os}} - E_p^{\text{red}}$ (mV)	E_p^{ox} (mV)	E_p^{red} (mV)	ΔG_p^b (kJ mol ⁻¹)
OH^-	35	-100	135	-115	-200	
F^-	41	-100	141	-108	-400	56.1
SO_4^{2-}	-160	-200	40	10	-160	
Cl^- ^d	-166	-290	124			
Cl^-	-181	-242	61	-30	-150	46.4
Br^-	-235	-381	146	-50		38.5
NO_3^-	-270	-400	130	-90		33.9
I^-	-335	-500	165	-590	-760	26.4
ClO_4^- ^d	-424	-600	176			
ClO_4^-	-428	-610	182			17.2

^a E_p values are peak potentials obtained by extrapolation to zero current at very low scan rates. ^b ΔG_p = Gibbs energy of partition for a water-1,2-dichloroethane system.⁸ ^c The aqueous electrolytes used were 0.1 M NaOH, NaF, NaCl, KBr, KI, Na_2SO_4 , NaNO_3 , and NaClO_4 . ^d Generated after 20 cycles by oxidation of *cis*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$.

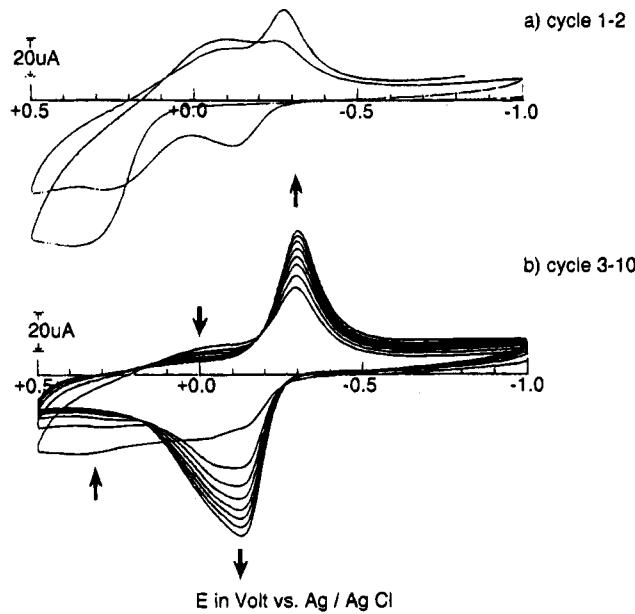


Figure 11. Cyclic voltammograms obtained for oxidation of *cis*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ mechanically attached to a basal plane pyrolytic graphite electrode and placed in aqueous 0.1 M NaCl electrolyte at 50 °C using a scan rate of 200 mV s⁻¹ over 10 potential cycles.

KBr powder, 1845 cm⁻¹) when oxidation is undertaken at 500 mV vs Ag/AgCl (Figure 12a).

The spectroscopic identification of the *cis*-[$\text{Cr}(\text{CO})_2(\text{dpe})_2$]⁺ isomer and the isomerization process producing *trans*⁺ also is possible by specular reflectance FTIR spectroscopy (Figure 12b,c). After oxidation at 500 mV vs Ag/AgCl the IR bands detected at 1846 (*trans*⁺) and 1933 (*cis*⁺) cm⁻¹ show that some of the *cis* starting material has been oxidized (compare diffuse reflectance IR signal at 1764 and 1830 cm⁻¹). The 1780 cm⁻¹ region response is broad because overlap of unoxidized *cis*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ occurs with the signal for the *trans*⁺ oxidation product. The IR band at 1933 cm⁻¹ is attributable to the formation of the *cis*⁺ form of the molecule, which is too unstable to be detected in solution. The second IR band expected for *cis*⁺ is unresolved from the *trans*⁺ band. The shift of +89 cm⁻¹ for comparable IR bands of the *cis*⁺ species relative to the *cis* species (Table 2) is of the order expected for formation of *cis*⁺ and cor-

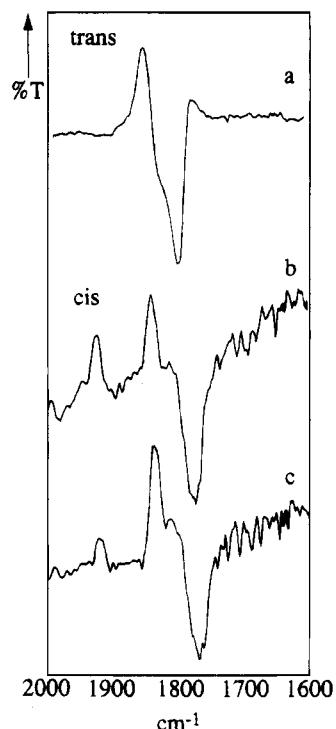


Figure 12. Specular reflectance FTIR spectra obtained for *cis*- and *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ mechanically attached to a basal plane pyrolytic graphite electrode, after being placed in aqueous 0.1 M NaCl electrolyte, electrochemically oxidized at ambient temperature, and then dried in air after removal of the electrolyte solution: (a) *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ after the potential was held at 500 mV vs Ag/AgCl for 2 min; (b) *cis*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ after the potential was held at 500 mV vs Ag/AgCl for 5 s; (c) the same system as in (b) after 2 min. The spectra were background-corrected by subtraction of the response prior to electrolysis.

Table 2. FTIR Data Obtained in the Carbonyl Region ($\nu(\text{CO})$ in cm⁻¹) for *cis*-[$\text{Cr}(\text{CO})_2(\text{dpe})_2$]^{0/+} and *trans*-[$\text{Cr}(\text{CO})_2(\text{dpe})_2$]^{0/+} Species in Solution (CH_2Cl_2) and the Solid State by the Diffuse Reflectance Method on KBr and the Specular Reflectance Method (Mechanically Attached to a Basal Plane Pyrolytic Graphite Electrode)

	<i>trans</i>	<i>trans</i> ⁺	<i>cis</i>	<i>cis</i> ⁺
in CH_2Cl_2 soln		1792	1850	1846 s 1772 m
diffuse reflectance KBr powder		1783	1845	1830 s 1764 m
specular reflectance graphite electrode	1796	1846	1844 1780	1933 b

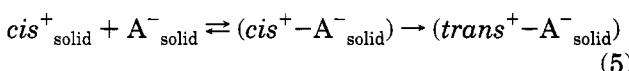
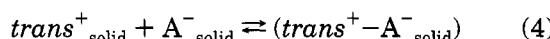
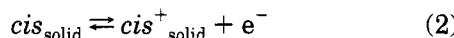
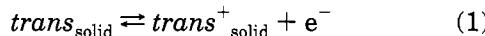
^a Isomerization to *trans*⁺ too rapid for detection or isolation. ^b Second band not resolved from *trans*⁺ band.

responds to the increased positive charge on the metal center. The IR band at 1933 cm⁻¹ decays slowly (50% after 60 min) when monitored at room temperature. Evidently, constraints posed by the solid matrix allow the achievement of kinetic stabilization of a thermodynamically unstable isomer. The IR detection of the *trans*⁺ isomer after a potential of 500 mV vs Ag/AgCl is applied for 2 min is observed with considerably reduced spectral overlap with the converted *cis* compound (Figure 12c). A summary of IR spectra of surface-attached and solution-phase spectra is collected in Table 2.

Discussion

A detailed voltammetric investigation of the one-electron oxidation of *trans*- and *cis*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ as

microcrystalline solids attached to pyrolytic graphite electrodes has allowed the elucidation of additional details concerning the processes occurring at the solid-solution (electrolyte) boundary. The reactions of interest in this study are described by eqs 1-5, where the



subscript "solid" is used to describe the solid compound at an electrode-solid-solution interface, A^- represents the electrolyte anion, and $\text{cis}^{0/+}$ and $\text{trans}^{0/+}$ are introduced as a shorthand form of notation to represent the $[\text{Cr}(\text{CO})_2(\text{dpe})_2]^{0/+}$ compound in its appropriate isomeric form and oxidation state. The surface reactions occur in the thin-film mode when diffusion of electrolyte anions within the solid is not rate-determining.

From experiments described in this study, the following points may be deduced for oxidation of *cis*- and *trans*- $[\text{Cr}(\text{CO})_2(\text{dpe})_2]$ at the electrode-solid-solution interface. (i) The electrolyte cation does not significantly influence the voltammetric responses. (ii) An increase of scan rate leads to larger peak currents and a shift in peak potentials. A plot of these peak potentials *vs* peak currents exhibits linear (ohmic) behavior. The slope of this plot, which is related to a resistance term, varies with particle size and surface coverage. However, the zero current intercept is essentially independent of these variables. (iii) The use of different anions in the aqueous electrolyte system leads to a potential shift which correlates approximately to Gibbs energies of partition of the anions in a water-1,2-dichloroethane system. In the change from the relatively hydrophobic anion ClO_4^- to the relatively hydrophilic F^- there is a trend to higher peak currents, sharper signals, and an increased tendency to peak-splitting phenomena. (iv) Peak currents as well as potentials are strongly dependent on temperature. (v) Variation in the concentration of the aqueous supporting electrolyte influences the peak positions and peak separation of oxidation and reduction components of the process. (vi) Stabilization of *cis*- $[\text{Cr}(\text{CO})_2(\text{dpe})_2]^+$ is achieved relative to the solution-phase species *via* a matrix effect. (vii) Several aspects of the model of the surface processes shown in eqs 1-5 are supported by specular reflectance FTIR measurements. (viii) Two distinctly different processes are available for the electrochemical process, as is evident from the peak splitting that is detected with hydrophilic electrolyte anions at elevated temperatures. In a system where many parameters may determine the observed response, methods have to be found to reduce the number of these parameters in order to derive readily usable relationships. The empirical observation that a linear dependence of peak currents and potentials exists over a range of scan rates, surface coverages, and crystal sizes represents an example of such an approach which considerably simplifies the description of the

electrochemical processes on the solid surfaces. The magnitude of the "resistance" derived from the slope of this plot and the fact that it depends on the amount of electroactive material on the electrode surface lead to the conclusion that this slope is a parameter determined by the conduction process. Furthermore, the interpolation of peak potentials at zero current leads to values that are not influenced by parameters, which are difficult to evaluate, such as the electrode surface coverage or the particle size of the solid attached to the graphite electrode. A mechanism and a theoretical treatment to explain the ohmic behavior are not available at this time. However, the occurrence of a resistance term, as is the case with redox polymer modified electrodes,¹² is not surprising. The change of the resistance with the electrolyte concentration in solution suggests that, at least partly, solution resistance plays a role.

The presence of two processes obeying different scan rate and temperature dependencies suggests that both "thick"-layer diffusion-controlled and "thin"-layer (interface-confined) processes occur. The former process shows a square root dependence on scan rate and the latter a linear dependence on scan rate. Equation 3 is not rate-determining for the latter process but is of fundamental importance to understanding of the thick-layer or intercalation process. To achieve the oxidation of the solid, electron transport and ion transport are necessary and the ions have to diffuse to sites within the solid. The occurrence of a swelling process, used to explain the relaxation effect, may allow solvent molecules to enter the solid and thereby assists the ion transport process through the solid. As a consequence of the unfavorable interaction between hydrophobic anions and water molecules, the swelling process is observed only for hydrophilic anions. It may be proposed that "intercalation" occurs, although this cannot be proved without relevant structural information.¹³

An increase in temperature leads to two effects. Peak separations between oxidation and reduction couples become smaller (Figure 8), but other processes are enhanced which may lead to an apparently wider separation (Figure 7). Consistent with our discussion given above, we propose a change in mechanism from a surface to a thick-layer process followed by a swelling process to account for the behavior at elevated temperature. The interesting change in voltammetric characteristics between the first and the following cycles, described as a relaxation effect, has a parallel in the voltammetry of conducting polymer films at fast scan rates, as recently reported by Andrieux *et al.*¹⁴ However, the mechanism for relaxation may be different.

Conclusions

This work demonstrates that complex interfacial processes which occur at the microcrystal-electrode-solution (electrolyte) interface between organometallic complexes and aqueous electrolyte solutions are coupled to ion transport across the solution-solid interface or

(12) Inzelt, G. *Electroanal. Chem.* **1994**, *18*, 89.

(13) Murphy, D. W.; Rosseinsky, M. J. In *Chemical Physics of Intercalation II*; Bernier, P., Fischer, J. E., Roth, S., Solin, S. A., Eds.; Plenum Press: New York, 1993; p 73.

(14) (a) Andrieux, C. P.; Audebert, P.; Hapiot, P.; Nechtschein, M.; Odin, C. *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *305*, 153.

(b) Odin, C.; Nechtschein, M.; Hapiot, P. *Synth. Met.* **1992**, *47*, 329.

adsorption and desorption of ionic species at the surface. Since the reactions occur in constrained media, unusual species can be stabilized. In the study presented, *cis*- $[\text{Cr}(\text{CO})_2(\text{dpe})_2]^+$ is sufficiently stabilized so that it has been possible to spectroscopically identify this thermodynamically unstable (with respect to the *trans*⁺ species) isomer for the first time.

Acknowledgment. Grateful acknowledgment is

made to the following organizations: (a) the Alexander von Humboldt Foundation for the award of a Feodor-Lynen Fellowship to F.M., (b) the Australian Research Council, and (c) the Australian Government for an Australian Postgraduate Research Award granted to J.N.W. Jeff Pura and Bruce James are acknowledged for providing the additional equipment necessary for measurement of the specular reflectance FTIR spectra.

OM9406411