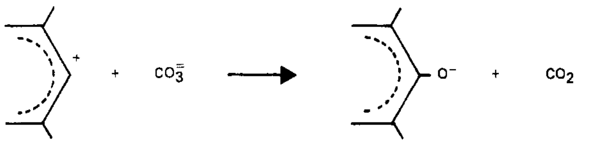
(32)

to a phenoxide-type intermediate. Such intermediates have been shown to exist in potassium carbonate impregnated samples of Spherocarb that had been maintained at 704 °C for 33 min in inert atmosphere.[20] A similar mechanism was reported recently for steam gasification of coal char[21] and probably also operates in the aqueous Fe(III) oxidation of carbon.[22] A number of successive steps are possible to account for the ultimate decomposition of the phenoxide analogue to produce carbon monoxide. An example is the transfer of the negative charge on the bound oxygen atom to another positive center in the carbon matrix, allowing desorption of carbon monoxide from the locally "neutral" carbon matrix.

The proposed sequences of reactions are clearly oversimplified. At least in air-sparged melts, all of the reactions represented in Table III probably participate in the overall oxidation process (e.g., give rise to the overall half-order dependence of the rate on oxygen pressure). Thus, in eq 25, peroxydicarbonate is shown as the active anionic species (as the data suggest); however, the other oxyanions present in air-sparged melts, including carbonate ion, probably also participate. The overall rate of the carbon oxidation process catalyzed by a given alkali-metal carbonate is probably primarily governed by the concentrations of the anions present. However, the fact that the overall rate is dependent on the graphite surface area throughout the process and that the dependence approaches first order as the graphite is nearly consumed indicates that the initial step (eq 23) is also important, and clearly this step is important in determining the overall rates of oxidation processes in which different alkali-metal carbonate catalysts are compared (e.g., sodium vs. potassium).

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Registry No. Na_2CO_3, 497-19-8; O_2^-, 11062-77-4; O_2^{2-}, 14915-07-2; CO_4^{2-}, 34099-49-5; $C_2O_6^{2-}$, 34099-48-4; CO_2, 124-38-9; CO_2^{2-}, 12709-62-5; CO, 630-08-0; N_2, 7727-37-9; Na, 7440-23-5; graphite, 7782-42-5.

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Electron Exchange between Cu(phen)$_2^+$ Adsorbed on Graphite and Cu(phen)$_2^{2+}$ in Solution

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The bis(1,10-phenanthroline) complexes of Cu(I) and Cu(II) are both adsorbed on pyrolytic graphite electrodes from aqueous chloride electrolytes. The adsorption of the Cu(II) complex reaches a full monolayer at a concentration of ca. 0.1 mM. The Cu(I) complex appears to oligomerize both in solution and in the adsorbed layer. As a result, much larger quantities of the Cu(I) complex can be deposited on the electrode surface. Rotating-disk voltammetric measurements of the reduction of Cu(phen)$_2^{2+}$ at electrodes coated with a deposit of the Cu(I) complex were utilized to measure the rate of electron transfer between the two complexes. This rate was independent of the quantity of Cu(I) deposited on the electrode, indicating that only the outermost layer of relatively impervious deposit participated in the electron exchange. An estimate of ca. 10^5 M^{-1} s^{-1} was obtained for the rate constant governing the self-exchange reaction.

One of the simplest methods for attaching metal complexes to the surfaces of graphite electrodes takes advantage of the high affinity for graphite of molecules having multiple aromatic centers.[1] Coordination of polypyridine ligands to metal centers creates complexes that show affinity for graphite surfaces, and we have exploited this fact to bind the bis(1,10-phenanthroline) (1,10-phenanthroline = phen) complexes of Cu(II) and Cu(I) to pyrolytic graphite electrodes from aqueous media. In addition, the Cu(I) complex appears to oligomerize in solution. This enhances its tendency to accumulate at the graphite solution interface and causes large quantities of the complex to deposit on the electrode surface. The rate of electron transfer between the deposited Cu(phen)$_2^+$ complex and Cu(phen)$_2^{2+}$ ions dissolved in solution was measured by means of rotating-disk electrode voltammetry.[2,3] This electron-transfer rate is of interest in assessing the potential of deposited Cu(phen)$_2^+$ as an electrocatalyst for the reduction of dioxygen.[4] In addition, there is disagreement in the literature regarding the rate of homogeneous electron exchange between Cu(phen)$_2^+$ and Cu(phen)$_2^{2+}$,[5] and we expected that an electrochemical estimate of the same rate could help to resolve the disagreement.

Experimental Section

Materials. Cu(phen)$_2$Cl$_2$·3H$_2$O was prepared by dissolving a slight excess of 1,10-phenanthroline hydrate (J. T. Baker Co.) in warm ethanol and adding it to a solution of $CuCl_2 \cdot 2H_2O$ dissolved in an equal volume of warm water. The crystals that formed after the solution stood overnight were collected, washed with ethanol, and dried under vacuum. Anal. Calcd: C, 52.51; H, 4.04; Cl, 12.92. Found: C, 53.30; H, 4.03; Cl, 13.03.

All other chemicals were reagent grade and were used as received. Solutions were prepared from laboratory deionized water that was passed through a purification train (Barnsted Nanopure) before use. Solutions were deoxygenated with prepurified argon and buffered at

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pH 5.6 with 0.02 M acetate buffer. Electrodes were prepared from basal-plane pyrolytic graphite (Union Carbide Co., Chicago, IL) and were mounted as stationary or rotating disk electrodes as previously described.[3] The electrodes had an exposed area of 0.17 cm^2. The reference electrode was a saturated calomel electrode (SCE) except when the solvent was dimethylformamide where a silver–silver chloride reference electrode was used. Quoted potentials are with respect to the SCE. Experiments were conducted at the laboratory temperature, 22 ± 2 °C.

Apparatus and Techniques. Cyclic voltammetry and rotating disk voltammetry were conducted with apparatus and procedures described previously.[3,4] Absorption spectra were recorded with a Hewlett-Packard Model 8450 spectrophotometer. Controlled-potential reductions of $Cu(phen)_2^{2+}$ were conducted inside a glovebag (to exclude dioxygen rigorously) with a pyrolytic graphite plate as working electrode. Chronocoulometric measurements[7] were performed with a computer-based apparatus similar to one previously described.[8]

The application of chronocoulometry to the measurement of adsorption at rotating disk electrodes has not previously been described. The following procedure was employed: The quantity of $Cu(phen)_2^+$ deposited on rotating graphite disk electrodes by the reduction of $Cu(phen)_2^{2+}$ was measured by stepping the potential of the continuously rotating electrode from the value where the reductive deposition of $Cu(phen)_2^+$ was proceeding to a value where the $Cu(phen)_2^+$ was rapidly reoxidized to $Cu(phen)_2^{2+}$. The total charge consumed during the oxidation was monitored as a function of time. The only significant sources of $Cu(phen)_2^+$ are the deposit itself and the "Levich layer" at the electrode surface[9] because the rest of the electrogenerated $Cu(phen)_2^+$ is stirred into the large volume of the solution of $Cu(phen)_2^{2+}$ and is thus diluted to a negligibly small concentration. As a result, the charge–time transient during the oxidation step consists of a rapid rise followed by an essentially flat plateau that can be linearily extrapolated to zero time, $t = 0$, to obtain, from Faraday's law, an estimate of the quantity of $Cu(phen)_2^+$ that had been deposited. First, there must be subtracted from the charge at $t = 0$ the charge measured in a blank experiment in the absence of the $Cu(phen)_2^{2+}$ plus the charge associated with the $Cu(phen)_2^+$ in the Levich layer. The contribution from the latter source was estimated as $FC^b\delta/2$ where F is the Faraday constant, C^b is the concentration of $Cu(phen)_2^{2+}$ in the bulk solution, and δ is the thickness of the Levich layer (cm). In aqueous solutions for a species with diffusion coefficient 5×10^{-6} cm^2 s^{-1}, $\delta = 1.28 \times 10^{-2}\omega^{-1/2}$ (cm) where ω is the angular frequency of rotation of the electrode. At a rotation rate of 1000 rpm and a concentration of 1 mM, the maximum contribution from the Levich layer amounts to 6×10^{-10} mol cm^{-2} and it becomes proportionately smaller at lower concentrations or higher rotation rates. The reliability of this technique was tested with solutions of $Ru(NH_3)_6^{3+}$, which is not adsorbed on graphite. A sharply stepped charge–time transient resulted when the potential was stepped from a value where $Ru(NH_3)_6^{3+}$ was being reduced to $Ru(NH_3)_6^{2+}$ to a value where the opposite was true and the charge on the plateau of the transient matched the sum of the charge measured in the blank experiment plus the contribution from the Levich layer as calculated from the formula given above.

Results

Cyclic Voltammetry. Most of our measurements on $Cu(phen)_2^{2+}$ were conducted in chloride rather than perchlorate supporting electrolytes to increase the solubility of $Cu(phen)_2^+$ produced at the electrode. The possibility that mixed chloride complexes might interfere in the experiments was ruled out by substituting 0.05 and 0.1 M trifluoromethanesulfonate for the corresponding chloride electrolytes in several cases and observing essentially no change in the resulting electrochemical responses, including the kinetic studies (vide infra). The test solutions were buffered at pH 5.6 to ensure the coordinative stability of the complexes. Cyclic voltammograms for solutions of $Cu(phen)_2^{2+}$, shown in Figure 1, contain two current peaks at potentials where $Cu(phen)_2^{2+}$ is reduced to $Cu(phen)_2^+$. A second irreversible wave corresponding to the reduction of $Cu(phen)_2^+$ to Cu appears at potentials more negative than −1 V and was not examined in this study. The reported dissociation constant for $Cu(phen)_2^+$, $K_d = 1.6 \times 10^{-16}$ M^{-2},[10] combined with the standard potential of the $Cu^+(aq)/Cu$ couple, $E° = 0.28$ V vs. SCE,[11] gives a calculated potential of −0.65 V for the half-reaction $Cu(phen)_2^+ + e^- = Cu + 2phen$ at [phen] = 1 M. In the absence of excess phen, a 1 mM solution of $Cu(phen)_2^+$ would therefore be expected to undergo reversible reduction to Cu near −0.3 V vs. SCE. The much more negative potentials that are required before the reaction actually occurs show it to be highly irreversible.

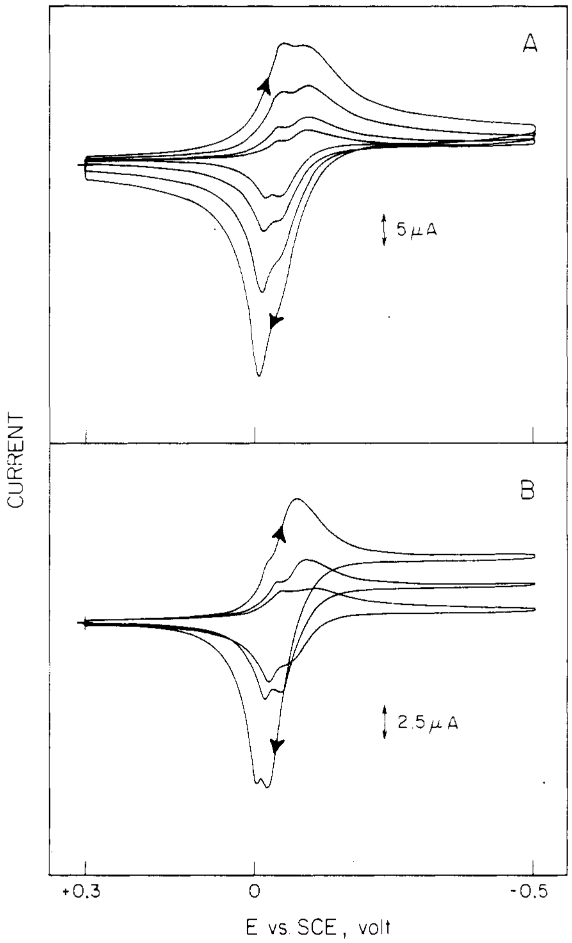

Figure 1. Cyclic voltammograms of $Cu(phen)_2^{2+}$ at a pyrolytic graphite electrode (supporting electrolyte 0.1 M NaCl buffered at pH 5.6 with acetate (0.02 M)): A ($[Cu(phen)_2^{2+}] = 0.4$ mM), scan rates 10, 20, 50, 100 mV s^{-1}; B (scan rate 10 mV s^{-1}); $[Cu(phen)_2^{2+}] = 2 \times 10^{-4}, 4 \times 10^{-4}, 8 \times 10^{-4}$ M.

The two peaks in the voltammograms in Figure 1 show different dependences on the rate of potential scan and the bulk concentration of $Cu(phen)_2^{2+}$: The first cathodic peak current is smaller than the second at low scan rate, but the converse is true at higher scan rates (Figure 1A). The first peak is also more prominent at lower concentrations and becomes less so as the concentration increases (Figure 1B). These features correspond to those expected when a reactant is reduced to a product that is strongly adsorbed on the electrode surface,[12] an interpretation that is also supported by anodic peak currents that are much larger than their cathodic counterparts. However, the Cu(II) complex is also strongly adsorbed. This is evident in Figure 2A where cyclic voltammograms for a very dilute solution (5 μM) of $Cu(phen)_2^{2+}$ are

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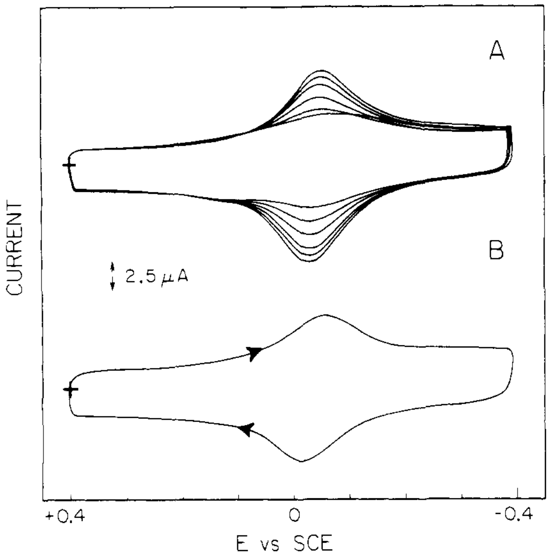

Figure 2. (A) Successive cyclic voltammograms recorded in a 5 μM solution of $Cu(phen)_2^{2+}$. The potential was maintained at 0.4 V between scans. The curves shown were recorded 0.2, 1, 2, 5, 10, and 20 min after the freshly cleaved electrode was immersed in the solution. (B) Cyclic voltammogram recorded after the electrode was removed, washed, and transferred to pure supporting electrolyte solution (0.1 M NaCl; pH 5.6; scan rate 200 mV s^{-1}).

shown. The magnitude of the wave increases with time as the $Cu(phen)_2^{2+}$ complex diffuses to the electrode surface and adsorbs.[1b] Only a single current peak is evident in this dilute solution because the adsorbed reactant dominates the overall response. After the voltammetric response became steady, the electrode was removed with the adsorbed complex in the Cu(II) state, washed, and transferred to a pure supporting electrolyte solution to record the curve shown in Figure 2B. The wave persisted for 30 min without significant diminishment, showing that both the Cu(I) and Cu(II) complexes are adsorbed irreversibly on the electrode surface.

The first ligand dissociation constant of $Cu(phen)_2^{2+}$ is $10^{-6.6}$ M[10] so that about 20% of the complex in a 5 μM solution is present as $Cu(phen)^{2+}$. This complex is adsorbed less strongly than $Cu(phen)_2^{2+}$ because similar solutions prepared by adding 1 mol of phen/mol of Cu(II) yield considerably smaller peak currents. However, at concentrations of 20 μM or greater (where ligand dissociation is <10%), the electrochemical behavior of solutions of $Cu(phen)_2^{2+}$ is not altered significantly by additions of small excesses (1–5 μM) of phen. Further increase in the concentration of free ligand causes decreases in peak currents probably because of competitive adsorption of the ligand. For this reason we usually avoided the presence of excess ligand except in spectral measurement where it was desirable to suppress dissociation of the complex.

The peak potentials of the waves in Figure 2 are very close to those of the first peak in Figure 1A, which confirms our assignment of the first wave to the adsorbed reactant and/or product. The peak current in Figure 2B increases linearly with scan rate as expected for an attached reactant.[13]

Measurement of Adsorption of $Cu(phen)_2^{2+}$ by Chronocoulometry. The extent of the adsorption of $Cu(phen)_2^{2+}$ was estimated from single-step chronocoulometric measurements[7] in which the potential of the electrode was stepped from +0.3 to −0.4 V. The intercepts of the resulting charge–$(time)^{1/2}$ plots were corrected for background and double-layer charging effects by subtracting the charge obtained when the same potential step was applied in the absence of $Cu(phen)_2^{2+}$. The background corrections were relatively large with pyrolytic graphite electrodes, ca. 40 μC cm^{-2}, and experiments were repeated with several electrodes to obtain representative average values of the adsorption. The dependence of the adsorption of the complex on its bulk concentration is shown in Figure 3. Full coverage is apparently reached at concentration of ca. 0.1 mM. The maximum adsorption of ca. 4×10^{-10} mol cm^{-2} corresponds to a monolayer of close-packed $Cu(phen)_2^{2+}$ taking the diameter of the complex as 14 Å[5a,14] and the microscopic area of the electrode as ca. 3 times larger than its geometric area.

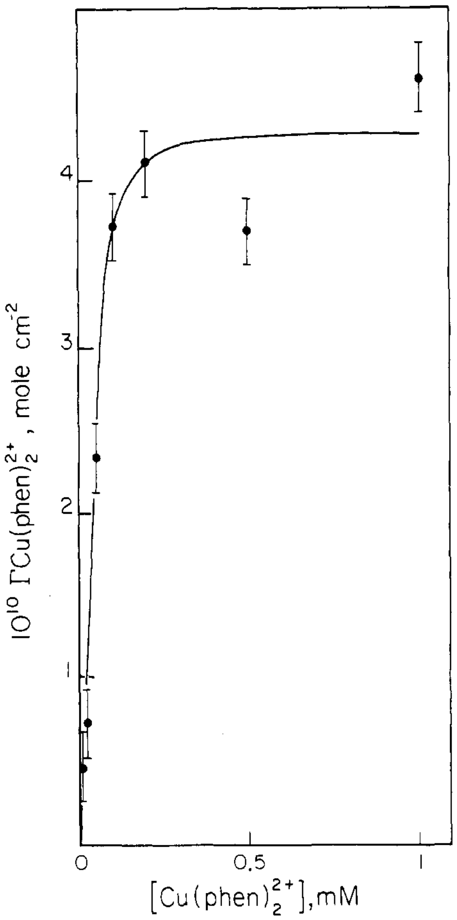

Figure 3. Adsorption of $Cu(phen)_2^{2+}$ at pyrolytic graphite electrodes (supporting electrolyte 0.1 M NaCl (pH 5.6)).

Spectral Properties of Solutions of $Cu(phen)_2^+$. The few previous spectral studies of solutions of $Cu(phen)_2^+$[5a,15,16] contain evidence of concentration-dependent speciation in the form of shifting values of λ_{max} and molar absorbances. For example, the color of aqueous solutions of the complex changes from purple to yellow as the concentration of complex is decreased from ca. 1 mM to 50 μM.[15] To examine this phenomenon in our 0.1 M NaCl supporting electrolyte, a series of solutions of $Cu(phen)_2^+$ were prepared by electrolytic reduction (at −0.5 V) of $Cu(phen)_2^{2+}$ solutions that also contained 2 mM excess ligand to suppress dissociation of the complex. The electrolysis was carried out inside a controlled-atmosphere box where dioxygen was rigorously excluded. After completion of the electrolysis, portions of the solution were transferred to cuvettes and sealed and spectra recorded. The three representative spectra shown in Figure 4 were recorded with different cuvettes chosen so that the

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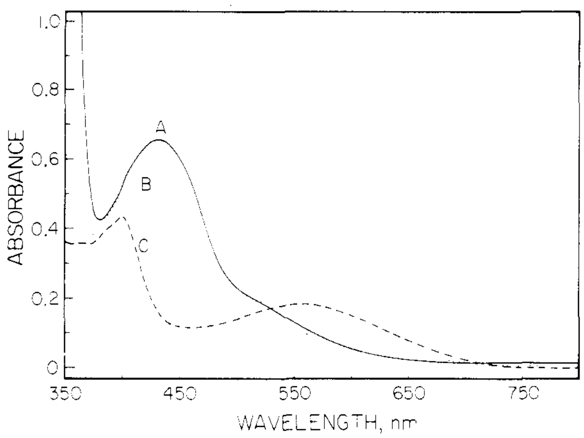

Figure 4. Representative electronic absorption spectra of solutions of $Cu(phen)_2^+$ that exhibit a concentration dependence (supporting electrolyte 0.1 M NaCl (pH 5.6, acetate buffer)). $[Cu(phen)_2^+]$: A, 0.01 mM; B, 0.10 mM; C, 1.0 mM. Optical path length of cuvette: A, 10 cm; B, 1 cm; C, 0.1 cm.

product of the optical path length and the concentration of complex remained constant. At lower concentrations the spectrum is dominated by the band at 434 nm. As the concentration increases, two new bands appear, first at 402 nm and later at 554 nm, as the intensity of the band at 434 nm diminishes. The same qualitative behavior was also obtained when solutions containing only $Cu(phen)_2(CF_3SO_3)_2$ were treated with ascorbic acid to obtain the $Cu(phen)_2^+$ complex in the absence of chloride so that the behavior does not appear to be a function of the anion present.

The behavior observed could result from oligomerization of the $Cu(phen)_2^+$ complexes as their concentration is increased. The spectra of dilute solutions (<ca. 15 μM) correspond to a molar absorbance, ϵ_{434}, of 6700 M^{-1} cm^{-1}. This is larger than a previous reported value,[16a] ϵ_{410} = 4100 M^{-1} cm^{-1}, but the concentration dependence of the spectra in Figure 4 reveals the origin of the apparent discrepancy. The molar absorbance between 400 and 500 nm is a strong function of the concentration of Cu(I). The concentration dependence of the spectra may result from association of the Cu(I) complexes because of attractive interactions between the phenanthroline ligands. Similar "stacking interactions" have been invoked to explain the observation that a second bipyridine or terpyridine ligand adds to metal–ligand complexes more rapidly than did the first ligand.[17-19] The stacking interactions are attributed to a combination of "hydrophobic bonding and polarization effects".[19] Examples in which such π–π intermolecular stacking interactions lead to oligomerization of metal complexes that contain aromatic ligands have also been described recently.[20] Attractive interactions between the metal centers might also contribute to the proposed association as "soft, attractive Cu(I)–Cu(I) interactions" have been calculated to exist in some instances.[21] Whatever its origin, the apparent oligomerization of $Cu(phen)_2^+$ produces striking effects in the electrochemistry of the complex.

Electrochemical Behavior of $Cu(phen)_2^+$. Even very dilute solutions of $Cu(phen)_2^+$ exhibit extensive adsorption on the surface of graphite electrodes. For example, a solution 5 × 10^{-5} M in $Cu(phen)_2^+$ produced chronocoulometric intercepts corresponding to many monolayers of attached complex. This extensive adsorption of $Cu(phen)_2^+$ means that it is continuously deposited on the surface of electrodes where $Cu(phen)_2^{2+}$ is being reduced. This process was monitored at a rotating disk electrode in solutions of $Cu(phen)_2^{2+}$ by holding the electrode potential at −0.5 V for various times and then stepping the potential to +0.8 V where $Cu(phen)_2^+$ that had been depositing on the electrode was very rapidly oxidized. The electrogenerated $Cu(phen)_2^+$ that did not remain on the surface was stirred into the bulk of the solution by the rotating electrode and contributed negligibly to the oxidation current. The charge–time responses that resulted when the electrode was stepped to +0.8 V were recorded and utilized to estimate the quantity of $Cu(phen)_2^+$ that had been deposited. Figure 5 contains a set of charge–time curves obtained in this way. The curves become relatively flat at times greater than ca. 0.5 s although, with thicker coatings, charge continues to accumulate at a low rate for longer times. This may result from $Cu(phen)_2^+$ in the outer portions of the coating disengaging from the electrode surface when the intervening complex is oxidized to $Cu(phen)_2^{2+}$, which is adsorbed much less strongly. Any $Cu(phen)_2^{2+}$ that is detached from the surface would have to diffuse back to the electrode to be oxidized. In any case, the value of charge accumulated after 1 s (corrected for background and Levich layer contributions as explained in the Experimental Section) was used to estimate the quantity of $Cu(phen)_2^+$ deposited on the electrode during the time it was held at −0.5 V. The quantities of $Cu(phen)_2^+$ that can be

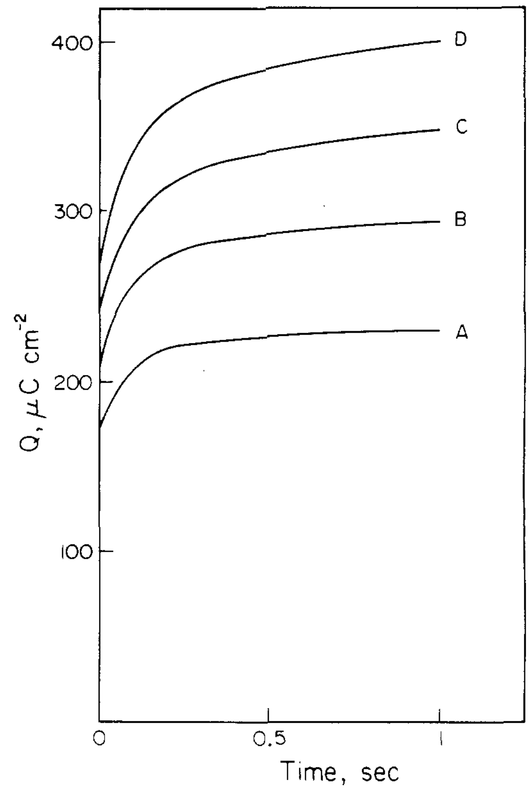

Figure 5. Chronocoulometric charge–time data at a rotating graphite disk electrode in a 1 mM solution of $Cu(phen)_2^{2+}$. The electrode potential was held at −0.5 V for time τ and then stepped to +0.8 V where the charge–time responses were recorded (supporting electrolyte 0.1 M NaCl (pH 5.6); electrode rotation rate 1600 rpm). τ values: A, 5 s; B, 50 s; C, 100 s; D, 200 s. Plotted charges are the total measured charge less the sum of the charge consumed when the experiment was repeated in the absence of $Cu(phen)_2^{2+}$ and the charge corresponding to the $Cu(phen)_2^+$ in the Levich layer (see Experimental Section).

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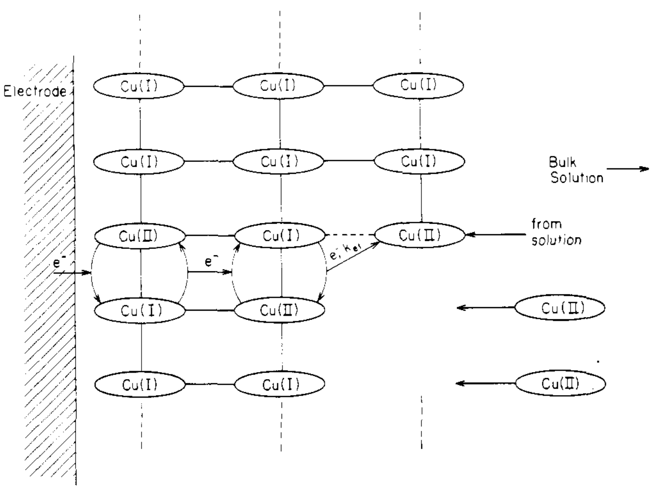

Figure 6. Schematic model of the mechanism of electron transport through a growing deposit of $Cu(phen)_2^+$ on a graphite electrode. The anions that must also be incorporated in the deposit are not shown.

deposited on the electrode in a state adherent enough to withstand the stirring resulting from the rotation of the electrode correspond to multiple layers of the complex. Prolonging the deposition times or increasing the electrode rotation rate or concentration of $Cu(phen)_2^{2+}$ all produce increasingly thick deposits. Nevertheless, the reduction currents at rotating disk electrodes stabilize within a few seconds when the potential is stepped to the limiting current plateau and remain steady for hundreds of seconds as the $Cu(phen)_2^+$ coating continues to deposit on the electrode. These features of the rotating disk responses indicate that the thickening film on the electrode introduces no impediment to the flow of current. It therefore seems likely that as the film grows by reductive deposition of additional $Cu(phen)_2^+$ at the film/electrolyte interface, the electrons necessary for the reduction are transported from the underlying electrode across the deposit by electron hopping between Cu(I) and Cu(II) centers in the coating.

A schematic model of a possible electron-transport process is sketched in Figure 6. Anions must be incorporated in the deposit as it forms to maintain electroneutrality so that the composition of the deposit is assumed to be $Cu(phen)_2Cl$. The rates of electron transfer from the electrode to nearby Cu(II) sites and between Cu(I) and Cu(II) sites in the interior of the deposit are assumed to be rapid. The deposit grows by reduction of $Cu(phen)_2^{2+}$ molecules arriving at the deposit/solution interface at a rate governed by the second-order constant k_{et}. An estimate of the magnitude of k_{et} was obtained from measurements with a rotating disk electrode.

Koutecky–Levich Analysis of the Reduction of $Cu(phen)_2^{2+}$ at the Rotating Disk. Current–potential curves recorded with a rotating disk electrode in a solution of $Cu(phen)_2^{2+}$ are shown in Figure 7. The persistence on the electrode of the deposit of $Cu(phen)_2^+$ is evident from the anodic peak currents observed during the reverse potential scans. Levich plots[2,3] of the plateau currents of such curves vs. (rotation rate)$^{1/2}$ were nonlinear (Figure 8A), but linear Koutecky–Levich plots[2,3] of (plateau current)$^{-1}$ vs. (rotation rate)$^{-1/2}$ were obtained with positive intercepts (Figure 8B). This is the expected behavior when the plateau currents are limited by a process other than the rate of supply of the reactant to the electrode surface.[22] The intercepts of these plots provide a means for the evaluation of k_{et} as explained below.

The behavior of the $Cu(phen)_2^{2+/+}$ couple is much different in solvents where both oxidation states of the complex are more soluble. For example, Figure 9 shows cyclic voltammograms and rotating disk current–potential curves for $Cu(phen)_2^{2+}$ in dimethylformamide. There is no evidence of adsorption or deposition of either oxidation state, and the rotating-disk plateau currents yield a linear Levich plot (Figure 9C). Thus, the contrasting behavior observed in Figures 8A and 9C seems

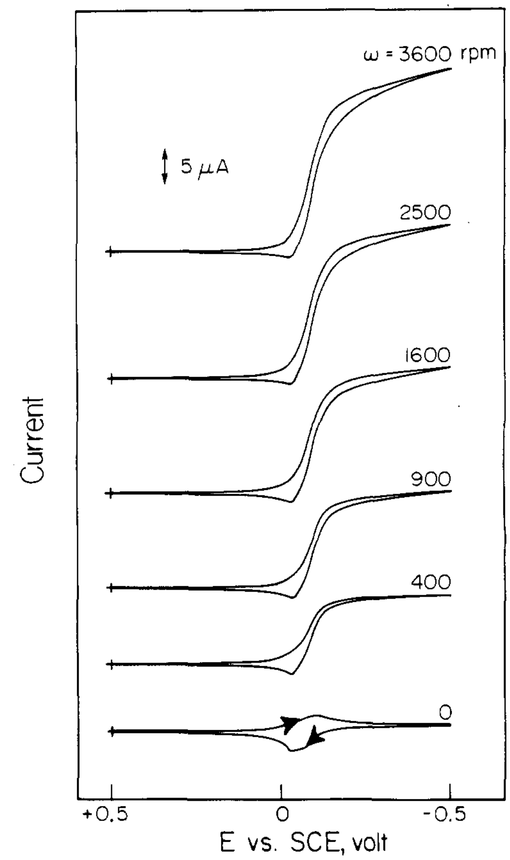

Figure 7. Current–potential curves for the reduction of 0.2 mM $Cu(phen)_2^{2+}$ at a rotating graphite disk electrode (supporting electrolyte 0.1 M NaCl (pH 5.6); potential scan rate 5 mV s^{-1}).

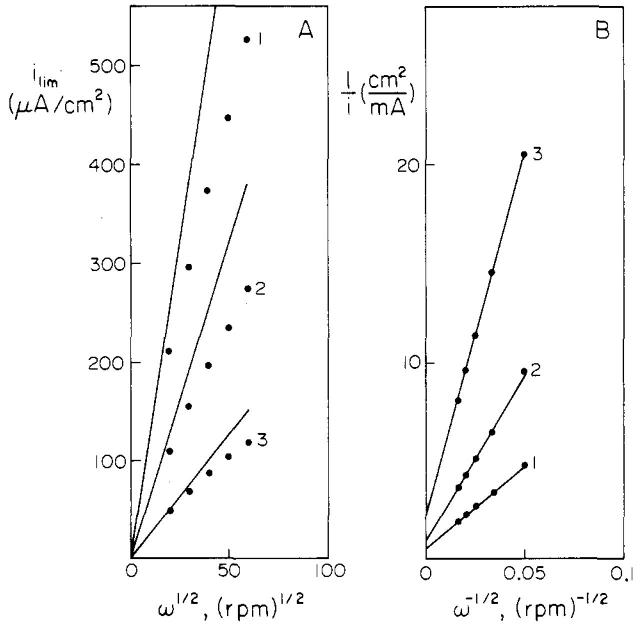

Figure 8. Levich (A) and Koutecky–Levich (B) plots for the reduction of $Cu(phen)_2^{2+}$ at rotating graphite disk electrodes. [$Cu(phen)_2^{2+}$]: 1, 1 mM; 2, 0.5 mM; 3, 0.2 mM. Other conditions are as in Figure 7. The lines drawn in A give the calculated responses for the mass-transfer limited reduction.

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[22] Reference 7, p 280 ff.

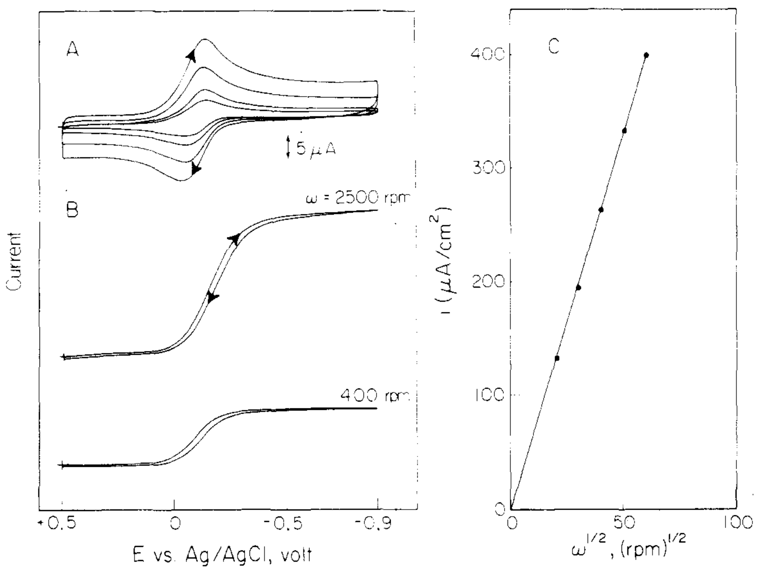

Figure 9. Cyclic voltammetric and rotating disk electrode responses of 0.5 mM $Cu(phen)_2^{2+}$ in dimethylformamide: (A) cyclic voltammograms, Scan rates 10, 20, 50, 100 mV s^{-1}; (B) rotating disk voltammograms; (C) Levich plots of the disk plateau currents vs. (rotation rate)$^{1/2}$ (supporting electrolyte 0.1 M tetraethylammonium perchlorate).

clearly to be associated with the coating of the electrode surface when the electrochemistry is examined in aqueous media.

Since the thickness of the deposited layer of $Cu(phen)_2^+$ increases continuously during the recording of curves such as those in Figure 7, and more so at higher concentrations and rotation rates, the linearity of the Koutecky–Levich plots in Figure 8B indicates that the current-limiting process cannot depend on the thickness of the coating. It follows that the propagation rate of electrons across the coating must be much greater than the current-limiting process. This leaves the rate of electron-exchange reaction between the $Cu(phen)_2^{2+}$ ions arriving at the surface of the growing deposit and the $Cu(phen)_2^+$ ions in the outermost layer of the deposit as the most likely current-limiting process.

To check that the $Cu(phen)_2^{2+}$ centers produced in the outermost layer of the coating could be electrochemically reduced to $Cu(phen)_2^+$ much more rapidly than they are formed by the reaction between $Cu(phen)_2^+$ in the coating and $Cu(phen)_2^{2+}$ in the solution, the characteristic current density, i_E, that measures the maximum rate of electron transport across the coating[23] was evaluated from the slopes of chronocoulometric charge–(time)$^{1/2}$ plots. These plots were recorded by depositing a measured amount of $Cu(phen)_2^+$ on a rotating-disk electrode at −0.4 V and then stepping its potential to +0.5 V to oxidize the Cu(I) centers in the deposit. The slopes, S, of the linear portions of the charge–(time)$^{1/2}$ plots obtained at times sufficiently short to obtain a diffusion-like response[24] were used to calculate i_E according to eq 1, where F is the Faraday constant and Γ_{tot} is the total quantity

$$i_E = \pi S^2/4F\Gamma_{tot} \qquad (1)$$

of $Cu(phen)_2^+$ deposited. Since the measured values of S were essentially independent of Γ_{tot}, the value of i_E decreases as Γ_{tot} was increased (Table I) and the deposit thickened. However, even with 1 mM solutions of $Cu(phen)_2^{2+}$ that produced the thickest deposits examined, i_E was always more than 1 order of magnitude greater than the maximum kinetically limited currents corresponding to the intercepts of the Koutecky–Levich plots. Thus, the propagation of electrons through the deposits of $Cu(phen)_2^+$ was clearly not a current-limiting process.

Table I. Chronocoulometric Slopes for the Oxidation of $Cu(phen)_2^+$ Deposited on Graphite Electrodes[a]

equil time,[b] s	$10\Gamma_{tot}$,[c] mol cm^{-2}	$10^{-3}S$,[d] μC cm^{-2} s$^{-1/2}$	i_E,[e] mA cm^{-2}
30	2.7	4.0	48
60		3.9	
100	3.7	4.0	35
200		4.0	

[a] $Cu(phen)_2^+$ was deposited from a 1 mM solution of $Cu(phen)_2^{2+}$ with the electrode held at −0.4 V. [b] Length of time that the electrode was held at −0.4 V to deposit $Cu(phen)_2^+$. [c] Measured by coulometric assay after transfer of the coated electrode to pure supporting electrolyte solution. [d] Slope of plot of charge vs. (time)$^{1/2}$ when electrode potential was stepped to +0.5 V. The slope was evaluated at times short enough to obtain semiinfinite diffusion-like responses. [e] Calculated from eq 1.

Table II. Evaluation of k_{et} from Rotating Disk Voltammetric Data[a]

$[Cu(phen)_2^{2+}]$, M	int,[b] cm^2 mA^{-1}	$10^5 k_{et}\Gamma_m$,[c] L cm^{-2} s^{-1}	$10^{-4}k_{et}$,[d] M^{-1} s^{-1}
1.0×10^{-3}	0.53	2.0	6.1
5.0×10^{-4}	0.96	2.2	6.7
2.0×10^{-4}	2.3	2.3	7.0
1.0×10^{-4}	4.3	2.4	7.3
1.0×10^{-4} [e]	4.2[e]	2.5[e]	7.5[e]
5.0×10^{-5}	11	1.9	5.8
2.0×10^{-5}	15	3.5	11
			7.3 (av)

[a] Supporting electrolyte 0.1 M NaCl (pH 5.6). [b] Intercept of Koutecky–Levich plot (Figure 8B); int = i_k^{-1}. [c] From eq 3. [d] Calculated by taking $\Gamma_m = 3.3 \times 10^{-10}$ mol cm^{-2} in every case. [e] Supporting electrolyte 0.1 M CF_3SO_3Na (pH 5.6).

Koutecky–Levich plots such as those in Figure 8B were analyzed by means of eq 2 and 3,[24] where i_{lim} is the plateau

$$1/i_{lim} = 1/i_L + 1/i_k \qquad (2)$$

current of current–potential curves such as those in Figure 7, i_L is the corresponding Levich current,[2] which is proportional to $\omega^{1/2}$, and i_k, the kinetic current density, is given by eq 3,

$$i_k = k_{et}FC_A\Gamma_m \qquad (3)$$

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[23] (a) Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *134*, 163. (b) Anson, F. C.; Saveant, J. M.; Shigehara, K. *J. Phys. Chem.* **1983**, *87*, 214.

[24] Anson, F. C.; Saveant, J. M.; Shigehara, K. *J. Am. Chem. Soc.* **1983**, *105*, 1096.

where k_{et} is the rate constant governing the reaction between the $Cu(phen)_2^+$ in the outermost layer of the coating and $Cu(phen)_2^{2+}$ in solution (M^{-1} s^{-1}), C_A is the concentration of $Cu(phen)_2^{2+}$ in the bulk of the solution (M), and Γ_m is the quantity of $Cu(phen)_2^+$ in the outermost layer (mol cm^{-2}). The intercepts of lines such as those in Figure 8B were used with eq 2 and 3 to evaluate i_k and the rate constant, k_{et}.

Table II contains a set of rate constants evaluated for a range of concentrations of $Cu(phen)_2^{2+}$. Γ_m was taken as 3.3×10^{-10} mol cm^{-2} at all concentrations of $Cu(phen)_2^{2+}$. This value was calculated from the dimensions of a molecule of $Cu(phen)_2Cl$ and the electrode roughness factor of 3 estimated from the saturation adsorption measured for $Cu(phen)_2^{2+}$ (vide supra). Substitution of trifluoromethanesulfonate for the chloride supporting electrolyte (fifth entry in Table II) produced no change in the kinetic response, indicating that chloride anions do not play an important role in the electron-transfer process. The values of k_{et} obtained are reasonably constant despite the large differences in the total quantities of $Cu(phen)_2^+$ present in the coatings that were used to obtain the data in Table II. This supports the assumption that only the outermost layer of the $Cu(phen)_2^+$ deposit participates in the reaction with $Cu(phen)_2^{2+}$. The average value of k_{et} is ca. 10^5 M^{-1} s^{-1}.

Oxidation of $Cu(phen)_2^+$ at the Rotating Disk Electrode. The experiments of Figures 7 and 8 were repeated with a solution of $Cu(phen)_2^+$ prepared by exhaustive electrolytic reduction of $Cu(phen)_2^{2+}$. The experiments were carried out with the apparatus inside a controlled-atmosphere box to avoid air oxidation of the $Cu(phen)_2^+$. The current–potential curves obtained are shown in Figure 10. The peak preceding the current plateau at the lower rotation rates results from the oxidation of the initially adsorbed complex. In contrast with the analogous curves in Figure 7, a Levich plot of the plateau currents for the curves in Figure 10 remains linear up to the highest accessible rotation rate.

We expected to obtain results in these experiments that resembled those in Figures 7 and 8 because the same self-exchange reaction between $Cu(phen)_2^{2+}$ and $Cu(phen)_2^+$ could limit the current. Instead, the currents were limited only by the supply of $Cu(phen)_2^+$ to the electrode. The difference in behavior seems most likely to be the result of the much thinner coating of adsorbed complex that is present on the electrode surface when $Cu(phen)_2^+$ is oxidized to $Cu(phen)_2^{2+}$. Adsorption of the latter complex amounts to no more than a single monolayer through which electrons can pass directly without the necessary intervention of the self-exchange reactions. The kinetics of the latter only begin to limit the flow of current when the thicker coatings resulting from the deposition of $Cu(phen)_2Cl$ prevent direct electron transfer between the graphite electrode and the reactant.

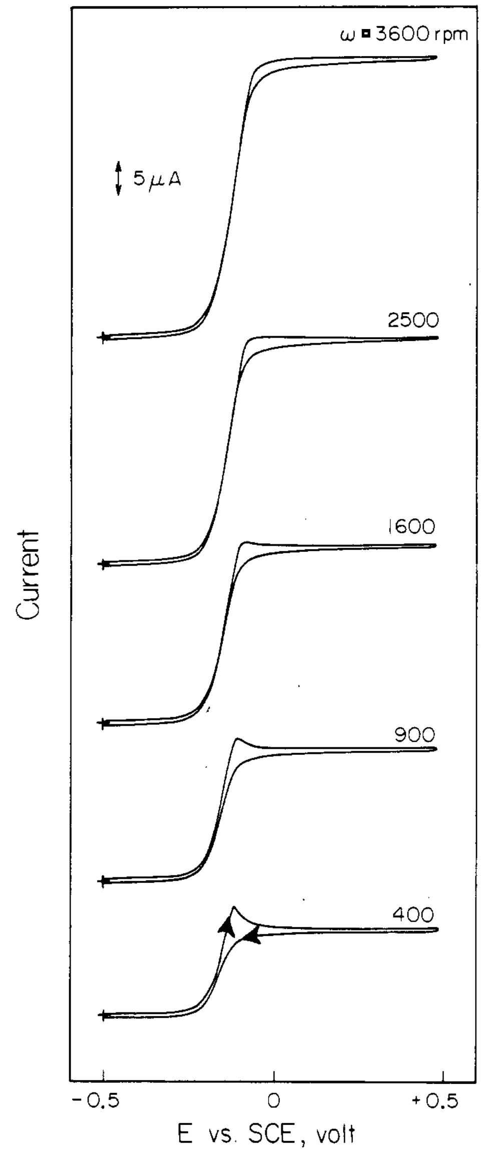

Figure 10. Current–potential curves for the oxidation of 0.4 mM $Cu(phen)_2^+$ at a rotating graphite disk electrode. Experimental conditions are as in Figure 7.

Discussion

The adsorption of the 1,10-phenanthroline complexes of Cu(I) and Cu(II) on graphite surfaces is not surprising. Qualitative polarographic evidence of such adsorption on mercury electrodes was reported many years ago,[25] and in numerous subsequent studies adsorption has complicated the cyclic voltammetry of metal ions coordinated to phenanthroline, terpyridine, or bipyridine ligands. Molecules bearing aromatic centers have recently been shown to be strongly adsorbed on graphite surfaces from aqueous media.[1] Thus, the 1,10-phenanthroline ligands are certainly responsible for the adsorption of both $Cu(phen)_2^{2+}$ and $Cu(phen)_2^+$ observed in this study. However, the adsorption of multiple layers of $Cu(phen)_2^+$ indicates that some additional factors act to enhance its adsorption. Solid $Cu(phen)_2Cl$ could be dissolved in the supporting electrolytes employed to produce concentrations of Cu(I) well above 0.01 M so that the deposition of complex on the electrode is not the result of a simple precipitation reaction. Instead, we believe that the tendency of this complex to oligomerize as its concentration is increased (Figure 3) is the important factor in its extensive adsorption. The ligand-induced adsorption of the complex on graphite yields cross-sectional concentrations that correspond to solution concentrations of ca. 1 M so that oligomerization as suggested by the spectra in Figure 3 would be even more favored in the adsorbed state. We believe that this is the reason that large quantities of the $Cu(phen)_2^+$ complex accumulate on the electrode surface when $Cu(phen)_2^{2+}$ is reduced at graphite electrodes. The large value of i_E measured for the layer of oligomerized $Cu(phen)_2^+$ indicates good "electronic conductivity" in the vicinity of the $Cu(phen)_2^{2+/+}$ redox potential so that the layer of oligomerized complex is able to grow continuously as $Cu(phen)_2^{2+}$ is reduced to $Cu(phen)_2^+$ at the outer edge of the layer.

Rate Constant for Self-Exchange. The average value of k_{et} listed in Table II does not agree with either of the mutually discrepant previous estimates of the rate constant for self-exchange between $Cu(phen)_2^{2+}$ and $Cu(phen)_2^+$ in homogeneous solution: $k_{ex} = 5 \times 10^7$ M^{-1} s^{-1} [5a] and $k_{ex} = 50$ M^{-1} s^{-1}.[5b]

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[25] Onstott, E. I.; Laitinen, H. A. *J. Am. Chem. Soc.* **1950**, *72*, 4724.

It is not difficult to find reasons for expecting the rate of electron self-exchange between two reactants to be governed by a different rate constant when the reaction proceeds in homogeneous solution than when one of the coreactants is bound to a surface in an oligomerized state. Steric factors that decrease the rate of collision between the coreactants when one is confined to a surface as well as differences in the activation energies for the two reaction conditions could act to decrease the rate constant for the surface reaction.

The previously reported values for the homogeneous self-exchange reaction,[5] were both obtained from the measured rates of cross-reactions (rather than the self-exchange reaction itself) combined with the Marcus correlation of rate constants for the two types of reactions.[26] However, there is good reason for doubting the applicability of the unmodified Marcus correlation between cross-reactions and self-exchange reactions that involve structural changes as significant as those that both halves of the $Cu(phen)_2^{2+/+}$ couple undergo upon electron transfer.[27] Indeed, the previous discrepant estimates of k_{ex} for the $Cu(phen)_2^{2+/+}$ couple have been shown to be mutually compatible with a value of k_{ex} near 10^5 M^{-1} s^{-1} if the Marcus correlation is appropriately modified to take account to the possible effects of large structural changes.[27] The resulting agreement between the values of k_{ex} obtained from (recalculated) homogeneous and heterogeneous experiments suggests that, despite the adsorption and oligomerization of $Cu(phen)_2^+$ on the surface of graphite electrodes, its reactivity in undergoing electron exchange with $Cu(phen)_2^{2+}$ in solution is not significantly diminished.

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Registry No. $Cu(phen)_2^+$, 17378-82-4; $Cu(phen)_2^{2+}$, 15823-71-9; $Cu(phen)_2Cl_2$, 83043-11-2; graphite, 7782-42-5.

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Solution Equilibria and Redox Properties of Schiff Base Complexes of Oxomolybdenum(V) in Dimethylformamide Solution

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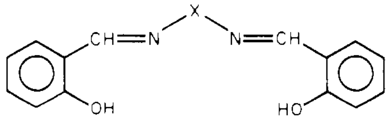
Measurement of spin and free halide concentrations in solutions of *trans*-[MoOL(MeOH)]Br (H_2L = H_2SALOPHEN, H_2SALPN, H_2SALEN) and [MoO(SALPN)Cl] in DMF (1-5 mM Mo; 0.1 M Et_4NX; X = PF_6, Cl, Br) indicates the presence of equilibria between mononuclear and polynuclear species. For [MoO(SALOPHEN)(MeOH)]Br in the presence of 0.1 M PF_6^-, the mononuclear cation *trans*-$[MoO(SALOPHEN)(DMF)]^+$ is present at a concentration of about 100 mol % but equivalent solutions of [MoOL(MeOH)]Br (H_2L = H_2SALPN, H_2SALEN) contain low concentrations (ca. 10 mol %) of ESR-silent polynuclear species containing bound bromide. For [MoO(SALPN)Cl] solutions, the concentration of polynuclear species is much higher, being >50 mol % Mo in PF_6^- media and >85 mol% in Cl^- media. The dominant mononuclear species appears to be [MoO(SALPN)Cl]. The electrochemistry of these systems is complicated by the equilibria and an unequivocal interpretation is not possible from the present (quite extensive) data. Examination of the first reduction process for each system suggests that the halide-bound complexes are electroactive, even for [MoO(SALOPHEN)(MeOH)]Br in 0.1 M PF_6^- media where the free bromide concentration is about 100 mol %. For [MoO(SALPN)Cl], reduction of both mononuclear and polynuclear species is observed. The total data appear to reflect the tendency of mononuclear oxomolybdenum(V) species ($4d^1$) to associate in solution to form binuclear or polynuclear products that are stabilized by spin–spin interactions, whereas the oxomolybdenum(IV) analogues tend to thermodynamically favor mononuclear (low-spin d^2) forms.

Introduction

In view of the presence of mononuclear oxomolybdenum centers in certain redox enzymes,[2] detailed study of the redox properties of such centers in low molecular weight species is desirable and several systems featuring [Mo^VO] and [$Mo^{VI}O_2$] centers have been examined in some detail.[3] The four crystalline compounds *trans*-[MoOL(MeOH)]Br (H_2L = H_2SALPN, H_2SALEN, H_2SALOPHEN) and [MoO(SALPN)Cl] have been isolated in *recrystallizable, soluble* form.[4] The synthetic aspects of this system are somewhat complicated, with polynuclear species of low solubility tending to contaminate the isolated, soluble mononuclear species under certain conditions.[4] This is a particular problem for the chloride complexes. Synthetic,[5,6] ESR,[5-7] and reactivity[8]



H_2SALEN, X = $(CH_2)_2$
H_2SALPN, X = $(CH_2)_3$
H_2SALOPHEN, X = *o*-phenylene

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