and group charges over the course of the reaction, which depend on the electronic character of the olefin substituent.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation (No. CHE-77-19899). G.D.G. also thanks the National Science Foundation for a Predoctoral Fellowship. In addition, W.N.L. wishes to thank the Humboldt Foundation for an award which aided this research. We acknowledge NSF grant PCM 77-11398 for the computational laboratory.

Electrochemical Responses of Electrodes Coated with Redox Polymers. Evidence for Control of Charge-Transfer Rates across Polymeric Layers by Electron Exchange between Incorporated Redox Sites

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Abstract: Redox polymers prepared by the reaction of $Fe(CN)_5OH_2^{3-}$ with poly(4-vinylpyridine) were used to coat pyrolytic graphite electrodes. The number of redox groups within the polymer was varied systematically while monitoring the resulting changes in the electrochemical responses of the electrode coatings. Coatings composed of the preformed redox polymer yielded responses close to that expected for an ideal nernstian reactant confined to the electrode surface, while coatings prepared by coordinating redox centers to PVP films that were already attached to the electrode gave less ideal responses. Effective diffusion coefficients for the transfer of charge through the polymer films were estimated. Decreasing the number of redox sites in the films caused no change in the rates of charge transfer at high concentrations of sites, but a drop in rate occurred when the number of redox sites was decreased sufficiently. The effect is believed to reflect the composition of the polymer–redox center mixture where electron transfer between adjacent pairs of redox centers begins to limit the rate of charge transfer through the polymer.

Previous studies of electrodes with polymeric coatings attached to their surfaces[1,2] have usually employed coating techniques that result in films with properties that are determined by the particular coating procedure. Consequently, systematic studies of the variations in electrochemical responses produced by changes in the physical characteristics and, especially, the chemical compositions of the deposited films have only rarely been reported.[3] In our own previous work on this topic various approaches were used to attach metal complexes to polymer coatings on electrode surfaces[4] but in every case the polymeric ligands were applied to the electrode surface before the metal complexes had been incorporated in the polymers because of difficulties in preparing solutions in which both the polymers and metal complexes were soluble. This obstacle has now been overcome by the combination of poly(4-vinylpyridine) (PVP) and $Fe(CN)_5OH_2^{3-}$. Both of these reactants are soluble over a reasonable range of mole ratios in a mixed methanol–water solvent (50 vol % of each). By taking advantage of the well-documented coordination chemistry of $Fe(CN)_5OH_2^{3-}$ with heterocyclic nitrogen ligands such as pyridine,[5] it was possible to prepare homogeneous solutions containing $Fe(CN)_5^{3-}$ centers coordinated to pyridine groups in PVP at levels as high as one $Fe(CN)_5^{3-}$ complex for every third pyridine group (precipitates form at higher ratios). Films cast on graphite electrode surfaces by evaporation of aliquots of these solutions proved to be quite stable in perchlorate or trifluoroacetate supporting electrolytes where their electrochemical responses were examined. Of particular interest was a comparison of the behavior of films formed from the homogeneous solutions of polymer–metal complexes with that of similar films formed by coating electrodes with pure PVP followed by coordination of $Fe(CN)_5^{3-}$ to the films from aqueous solutions of $Fe(CN)_5OH_2^{3-}$ in which the polymer is not soluble. The considerable differences that were encountered in the morphology of current–potential and current–time curves for these two types of films are described in this report. The effects of film thickness and composition on the apparent diffusion coefficients of the attached complexes and on the fraction of them that are electroactive are also discussed.

Experimental Section

Materials. Poly(4-vinylpyridine) (PVP) (Borden Co.) was purified and its average molecular weight (7.4×10^5) was measured as described previously.[4d] $Na_3Fe(CN)_5NH_3{\cdot}3H_2O$ (Eastern Chem. Co., Hauppauge, N.Y.) was purified by repeated recrystallization from saturated ammonia.[5b] Solutions of $Fe(CN)_5OH_2^{3-}$ were prepared by dissolving this salt in aqueous solutions under conditions where substitution of the NH_3 group by H_2O proceeds rapidly.[5] Solutions of $Fe(CN)_5py^{3-}$(py = pyridine) were prepared by mixing $Fe(CN)_5OH_2^{3-}$ and pyridine in situ.[5b] Solutions containing PVP to which various quantities of $Fe(CN)_5^{3-}$ groups were coordinated were prepared by mixing aqueous solutions of $Fe(CN)_5OH_2^{3-}$ and methanolic solutions of PVP having appropriate concentrations to produce a final mixture with the desired stoichiometric ratio of PVP to $Fe(CN)_5OH_2^{3-}$ in a 50/50 vol % methanol–water mixture. Neither PVP nor $Na_3Fe(CN)_5OH_2$ precipitated from the mixed solvent when both reagents were present although precipitates did form if either one was absent. The mixture was neutralized to pH 6–7 by

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(1) The literature on this topic has become extensive and is growing rapidly. A review has recently appeared: K. D. Snell and A. G. Keenan, *Chem. Soc. Rev.*, **8**, 259 (1979), and an up-to-date listing of relevant references is given in ref 2.

(2) P. Peerce and A. J. Bard, *J. Electroanal. Chem.*, **112**, 97 (1980).

(3) M. C. Pham, G. Tourillon, P. C. Lacaze, and J. E. Dubois, *J. Electroanal. Chem.*, **111**, 385 (1980).

(4) (a) N. Oyama and F. C. Anson, *J. Am. Chem. Soc.*, **101**, 739 (1979); (b) *ibid.*, **101**, 3450 (1979); (c) N. Oyama and F. C. Anson, *J. Electrochem. Soc.*, **127**, 247 (1980); (d) *ibid.*, **127**, 640 (1980); (e) N. Oyama and F. C. Anson, *Anal. Chem.*, **52**, 1192 (1980); (f) N. Oyama, T. Shimomura, K. Shigehara, and F. C. Anson, *J. Electroanal. Chem.*, **112**, 271 (1980).

(5) (a) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973); (b) *ibid.*, **12**, 2080 (1973).

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careful addition of trifluoroacetic acid. It was important to keep the pH above 5 in order to avoid the formation of a gel thought to result from intermacromolecular bridging between protonated pyridine and $Fe(CN)_5py^{3-}$ groups. The coordination of $Fe(CN)_5^{3-}$ to the PVP proceeds rapidly and essentially quantitatively at molar ratios of pyridine units to $Fe(CN)_5OH_2^{3-}$ ions greater than ca.3 as established by the absence of an immediate color change upon addition of *N*-methylpyrazinium cation to aliquots of the mixtures.[5] The absence of uncoordinated $Fe(CN)_5OH_2^{3-}$ in the mixtures with PVP was also confirmed by another test. Films of the polymer–$Fe(CN)_5$ combination were cast on glass slides or transparent graphite electrodes[6] by evaporating aliquots of the solution to dryness. The quantity of $Fe(CN)_5^{3-}$ groups present in such films was then monitored spectrophotometrically[6] both before and after the films were washed with water in which uncoordinated $Fe(CN)_5OH_2^{3-}$ is readily soluble. The absorbance of such films was not changed by copious washing or immersion in solutions of supporting electrolytes (sodium perchlorate or sodium trifluoroacetate).

Coatings of PVP or $PVP[Fe(CN)_5]_n$ were prepared by micropipeting aliquots of solutions of the polymer onto pyrolytic graphite electrodes and allowing the solvent to evaporate.

Apparatus and Procedures. Cyclic voltammetry and chronoamperometry were conducted with PAR (E G & G Instrument Co., Princeton, N.J.) instruments and a Houston Instruments x–y recorder or Tektronix storage oscilloscope. Spectra were recorded with a Varian 219 spectrophotometer. Electrochemical measurements were conducted at ambient temperatures (22 ± 2 °C) in solutions deaerated by bubbling with prepurified argon. Potentials were measured with respect to a sodium chloride saturated calomel reference electrode (SSCE).

The quantities of electroactive $Fe(CN)_5^{3-}$ groups present in polymer films were measured coulometrically by integration of the current–time responses obtained in solutions of pure supporting electrolyte when the electrode potential was stepped to values well beyond the peak potential for oxidation of the bound reactant. Integration was continued until the currents had decayed to background levels.

To provide some estimate of the degree of swelling of the PVP and $PVP[Fe(CN)_5]_n$ polymers induced by exposure to aqueous electrolytes, small samples of each polymer in the form of 30-mesh powders were packed in calibrated cylindrical tubes closed at one end with a membrane permeable to the supporting electrolyte. The volume of the samples was monitored for several weeks as they were bathed in pure supporting electrolyte or solutions containing $Fe(CN)_5OH_2^{3-}$. The swelling, which amounted to 10–20% of the initial polymer volume, provided a rough idea of the degree of swelling likely to occur with coatings of the corresponding polymers. However, application of such data to the thin films cast on graphite electrodes is highly approximate because of the great disparity in the surface-to-volume ratios of the polymers in the two cases.

Results and Discussion

Electrochemical Responses of Electrodes Coated with Films of $PVP[Fe(CN)_5]_n$ Having Homogeneous or Inhomogeneous Distributions of $Fe(CN)_5^{3-}$ Groups. Coatings of $PVP[Fe(CN)_5]_n$ were applied to graphite electrodes by two alternative methods. Procedure I, a two-step method, involved application of the pure ligand, PVP, to the electrode in an initial step that was followed by coordination of $Fe(CN)_5^{3-}$ to the pyridine groups in the attached polymer coating in a second step. It is convenient to monitor the progress of the incorporation of the metal complex by the polymer film by recording cyclic voltammograms with the polymer-coated electrodes in the solutions of metal complex as the pick-up of the complex proceeds.[4a] Procedure II, a one-step method, involved dipping the electrode into solutions of preprepared $PVP[Fe(CN)_5]_n$ or, to obtain coatings with known quantities of $PVP[Fe(CN)_5]_n$, evaporation of measured aliquots of preprepared solutions on the electrode surface. The preparation of homogeneous solutions of PVP to which varying quantities of $Fe(CN)_5^{3-}$ were coordinated is described in the Experimental Section.

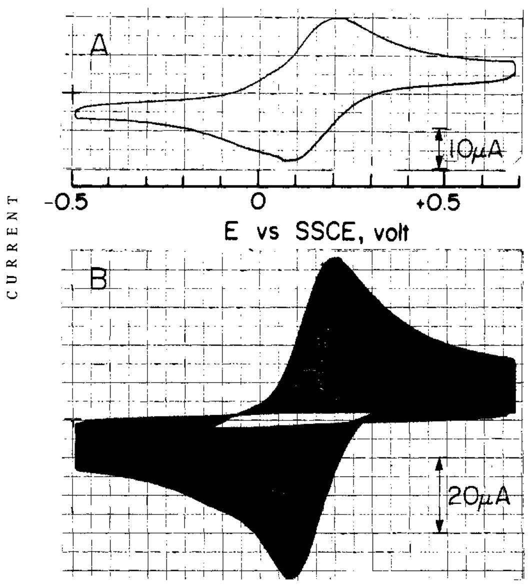

Figure 1. (A) Steady-state cyclic voltammogram of 0.5 mM $Fe(CN)_5OH_2^{3-}$ at an uncoated graphite electrode. Supporting electrolyte: 0.2 M CF_3COONa adjusted to pH 3 with CF_3COOH. Scan rate: 500 mV s^{-1}. (B) Voltammograms resulting when a graphite electrode coated with 5×10^{-7} mol cm^{-2} of pyridine units as PVP was cycled for ca. 5 min in 0.5 mM $Fe(CN)_5OH_2^{3-}$. Supporting electrolyte and scan rate as in A. A discrete voltammogram resulted from each cycle but they are too closely spaced to be distinguished in this photographic reproduction.

A primary goal of this work was to compare the electrochemical responses obtained from electrodes coated by procedures I and II. Figure 1A shows a cyclic voltammogram for the $Fe(CN)_5OH_2^{2-/3-}$ couple at a bare graphite electrode and Figure 1B presents the voltammetric responses obtained when procedure I was used to prepare the electrode coating. Transfer of an electrode coated only with PVP to a solution of $Fe(CN)_5OH_2^{3-}$ at pH 3 results in almost no current flow during the first few potential scans, but large peaks gradually develop as the polycationic film of partially protonated PVP incorporates $Fe(CN)_5^{3-}$ groups. Electrostatic (anion-exchange) binding[4c] as well as coordinative attachment of the complex anions occurs, but the electrostatically held complex can be rapidly removed by washing the electrode with dilute base (pH 11) to neutralize the cationic pyridinium sites.[4c] A washed, neutralized electrode that is transferred to pure supporting electrolyte gives a voltammogram that persists for several hours without further change.

Figure 2 shows the voltammetric responses obtained in a supporting electrolyte at pH 3 from an electrode coated by procedure II. The initial potential scan produces a pair of broad waves centered at ca. +0.12 V (Figure 2A), but on continued cycling of the potential a new pair of peaks at +0.23 V appears and continues to grow at the expense of the original wave (Figure 2B). After about 10 min of cycling, only the second, larger and narrow pair of peaks remains (Figure 2C). The final voltammogram persists without further change for several hours of continued cycling in acidic trifluoroacetate or perchlorate supporting electrolytes in which the polyelectrolyte films appear completely insoluble. The area under the final voltammogram is about half again as large as that under the initial voltammogram, indicating that the number of electroactive $Fe(CN)_5py^{3-}$ groups in the coating increases during the transformations shown in Figure 2B. If the electrode of Figure 2C is removed, washed with dilute base (pH 11) to neutralize the acid in the film, washed with water, dried, and returned to the supporting electrolyte at pH 3, the slowly changing pattern of Figure 2B is repeated.

If the supporting electrolyte used to record the voltammograms is neutral or alkaline, the coated electrode yields essentially no current no matter how long its potential is cycled, indicating that the film formed by evaporation from the mixed water–methanol solvent is impervious to the aqueous supporting electrolytes in the absence of acid. However, if PVP that is half-quaternized with benzyl groups,[4f] QPVP, is employed to prepare coatings of $QPVP[Fe(CN)_5]_n$ by procedure I, large voltammetric responses are obtained at pH values where unprotonated $PVP[Fe(CN)_5]_n$ coatings exhibit almost no response. The initial coatings with QPVP contain both coordinated $Fe(CN)_5py^{3-}$ and electrostatically bound[4c] $Fe(CN)_5OH_2^{3-}$. The latter complex departs from the coating during the first 10 min of cycling in pure supporting

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(6) N. S. Scott, N. Oyama, and F. C. Anson, *J. Electroanal. Chem.*, **110**, 303 (1980).

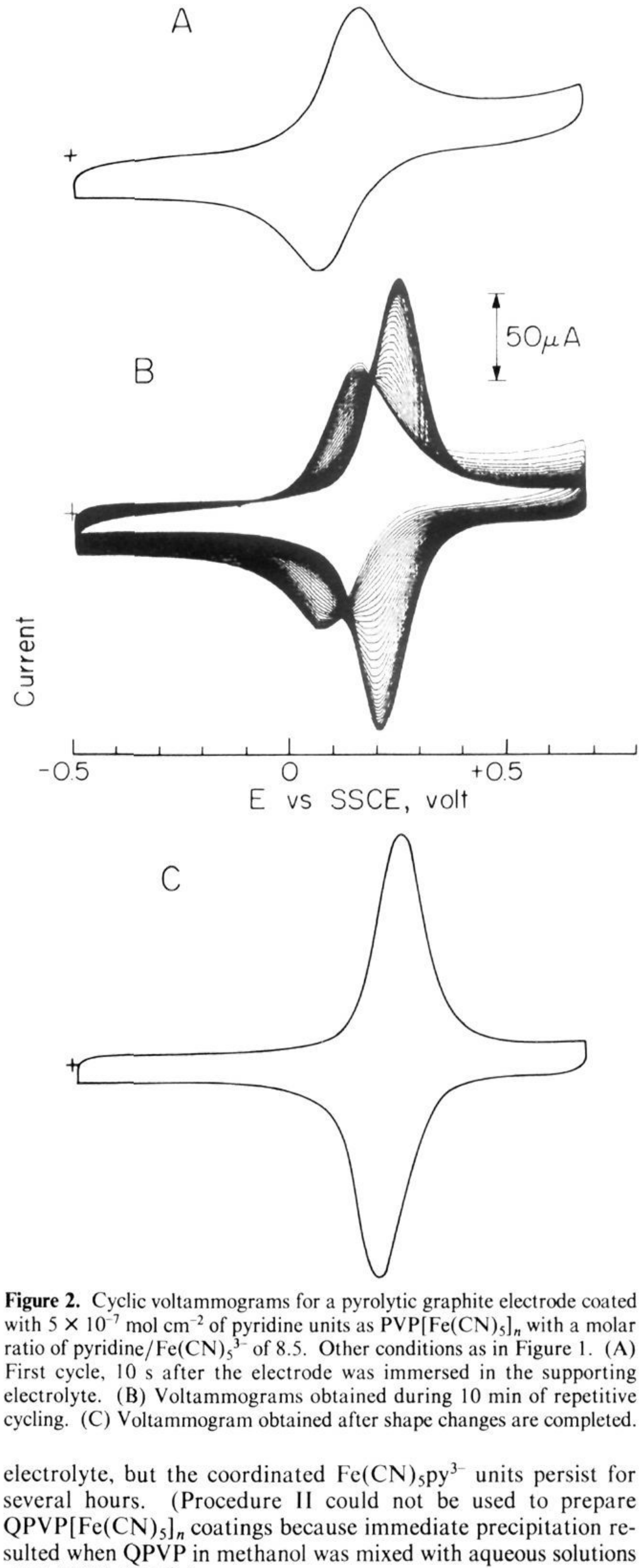

Figure 2. Cyclic voltammograms for a pyrolytic graphite electrode coated with 5×10^{-7} mol cm^{-2} of pyridine units as PVP[Fe(CN)$_5$]$_n$ with a molar ratio of pyridine/Fe(CN)$_5^{3-}$ of 8.5. Other conditions as in Figure 1. (A) First cycle, 10 s after the electrode was immersed in the supporting electrolyte. (B) Voltammograms obtained during 10 min of repetitive cycling. (C) Voltammogram obtained after shape changes are completed.

electrolyte, but the coordinated Fe(CN)$_5$py^{3-} units persist for several hours. (Procedure II could not be used to prepare QPVP[Fe(CN)$_5$]$_n$ coatings because immediate precipitation resulted when QPVP in methanol was mixed with aqueous solutions of Fe(CN)$_5$OH$_2^{3-}$.)

The large difference in the electrochemical responses of coatings prepared from PVP and QPVP is probably the result of greater swelling of the less hydrophobic QPVP films whose high density of fixed and pH-independent charges produce intrapolymer interactions that facilitate both the counterion migration and segmental motion of polymer strands that are essential for rapid oxidation and reduction of the metal complexes within the coating. These comparisons of the responses of PVP and QPVP coatings support our conclusion that the changes in the voltammograms recorded in Figure 2B reflect the gradual introduction of charged groups into the polymer by protonation of the free pyridine groups accompanied by a charge-induced swelling of the film.

The clear isopotential points present in Figure 2B show that the Fe(CN)$_5^{3-}$ groups bound to the PVP film apparently experience just two different environments as the polymer film is converted from its neutral to its protonated form. The formal potential of the Fe(CN)$_5$py$^{2-/3-}$ couple in 0.2 M CF$_3$COONa is ca. +0.20 V vs. SSCE and essentially independent of pH between pH 3 and 7 so that the shift in peak potentials of Figure 2B is not attributable to changes in the pH experienced by the Fe(CN)$_5^{3-}$ centers bound to the PVP film. The shift in peak potential is more likely to result from differential ion pairing of Fe(CN)$_5$py^{3-} and Fe(CN)$_5$py^{2-} with the pyH$^+$ groups in the protonated polymer. The shift is in the direction expected for stronger ion pairing by the reduced form of the redox couple that carries the higher negative charge. Thus, the changing voltammetric response shown in Figure 2B is believed to reflect an acid-induced alteration of the structure of the film as depicted schematically in Figure 3. With only Fe(CN)$_5^{3-}$ groups bound to the PVP, the film is likely to be composed of a random tangle of polymer chains (Figure 3A). However, at pH values where the available pyridine groups in the polymer are protonated, a strong tendency for rearrangement might be expected with untangling of the chains to produce the more open, ladder-like structures depicted in Figure 3B.[7] The interior of such a structure might be more accessible to counterions from the supporting electrolyte which could account for the greater area and more symmetrical shape of the voltammogram in Figure 2C.

This interpretation is strengthened by the observation that the behavior shown in Figure 2B is influenced strongly by the ratio of pyridine units to Fe(CN)$_5^{3-}$ ions in the PVP[Fe(CN)$_5$]$_n$ films. At ratios greater than ca. 10 the voltammograms undergo almost no change on repeated cycling. They retain a shape very similar to that of the voltammogram in Figure 2A. This is to be expected when the anchored Fe(CN)$_5^{3-}$ groups are separated by large segments of the positively charged polymer chain so that strong coulombic interactions between adjacent chains (as in Figure 3B) is prevented.

Additional supporting evidence is provided by the behavior of the water–methanol solutions of PVP[Fe(CN)$_5$]$_n$ (py/Fe(CN)$_5$ = 3.5) when they are acidified to pH values below 5. The initially fluid solution gradually develops a high viscosity and eventually gels into a solid that cannot be poured from the beaker. Similar behavior has been reported with other polyelectrolytes that can form interpolymer association complexes by electrostatic interactions.[7,8]

It is instructive to compare the final, stable voltammograms for the Fe(CN)$_5$py$^{2-/3-}$ centers when the electrode coatings are applied by procedures I and II. This is done in Figure 4 for a series of potential scan rates. The coating resulting from procedure II yields more symmetrical voltammograms with peak potentials separated by only 30 mV at a scan rate of 50 mV s^{-1} and very little "tailing" of the current on either side of the peaks. The peak currents are directly proportional to scan rate. By contrast, procedure I, which might be expected to produce films with higher concentrations of the attached reactant near the film–solution interface than close to the electrode surface, yields voltammograms with much greater peak separations and extensive "tailing" of the current. The peak currents increase less rapidly with scan rate than those in Figure 4A. These characteristics are typical of coatings through which charge transfer is limited by small effective diffusion coefficients corresponding to the coupled motions of counterions, polymer chain segments, and anchored reactants that are required for charge to move through the films.[4d,9] Figure 4 suggests that charge can be transported through coatings with a homogeneous distribution of redox centers considerably more rapidly than through those resulting from procedure I with an inhomogeneous distribution of Fe(CN)$_5^{3-}$ groups. Quantitative estimates of the difference in apparent diffusion coefficients for

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[7] E. Tsuchida, K. Abe, and M. Honma, *Macromolecules*, **9**, 112 (1976).

[8] E. Tsuchida, Y. Osada, and K. Abe, *J. Polym. Sci., Polym. Chem. Educ.*, **14**, 767 (1976).

[9] F. B. Kaufman and E. M. Engler, *J. Am. Chem. Soc.*, **101**, 547 (1979).

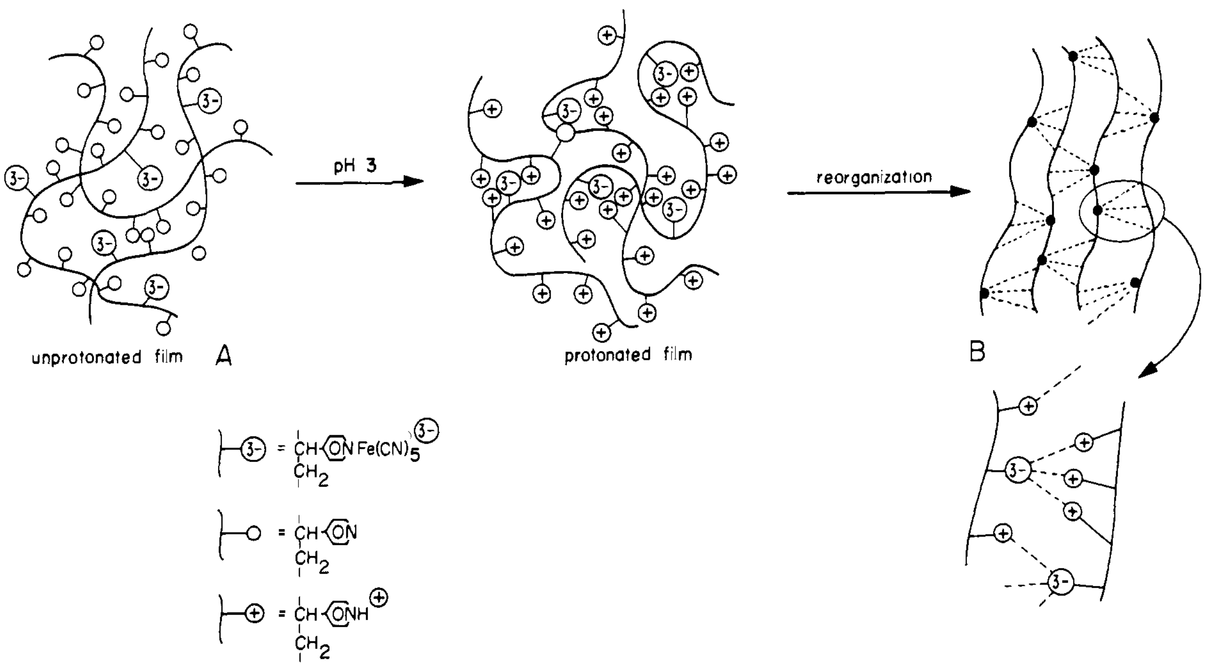

Figure 3. Schematic picture of proposed structural changes in polymer films to account for the changes in the cyclic voltammograms in Figure 2.

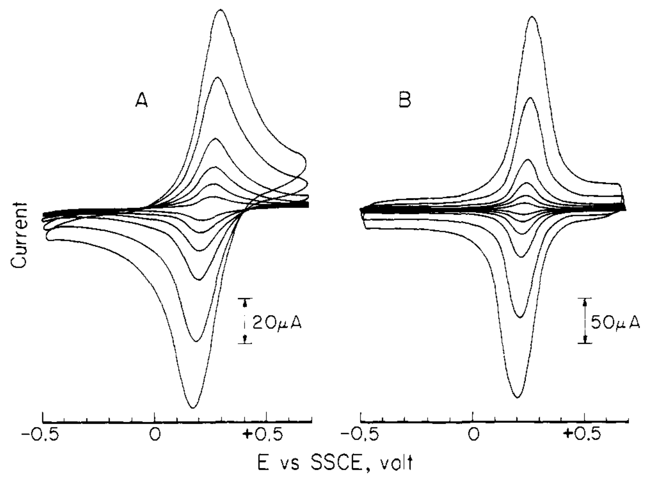

Figure 4. Cyclic voltammograms for graphite electrodes coated with PVP[$Fe(CN)_5$]$_n$. (A) The electrode was coated by procedure I, washed, and transferred to a solution of pure supporting electrolyte. (B) Electrode coated by procedure II. The coatings on both electrodes contained 5×10^{-7} mol cm^{-2} of pyridine units as PVP and ca. 1.3×10^{-9} mol cm^{-2} of electroactive $Fe(CN)_5py^{3-}$ groups. (The total quantity of $Fe(CN)_5^{3-}$ on the electrode used to record B was 5.8×10^{-8} mol cm^{-2}.) Scan rates from inner-to-outermost curves: 20, 50, 100, 200, 500, 1000 mV s^{-1}; supporting electrolyte as in Figure 1.

the two coatings are given in a later section.

The shapes of current–potential curves obtained with thin films of PVP[$Fe(CN)_5$]$_n$ prepared by procedure II match that expected for an ideal reactant confined to the electrode surface.[10] Figure 5 compares the calculated and observed responses for three coatings of increasing thickness. Even with films containing as much as 5×10^{-7} mol cm^{-2} of PVP, the current–potential response does not deviate extensively from that calculated assuming nernstian control of the electrode reaction.

Effect of pH on the Electroactivity of Bound $Fe(CN)_5^{3-}$ Groups. In supporting electrolytes at pH 3 the fraction of the $Fe(CN)_5^{3-}$ groups that are electroactive in the homogeneous coatings applied by procedure II depends on the thickness of the coatings; full electroactivity is obtained only with relatively thin films. However, if the pH of the supporting electrolyte is lowered to 1, much larger fractions of the complexes become electroactive. Figure 6 shows

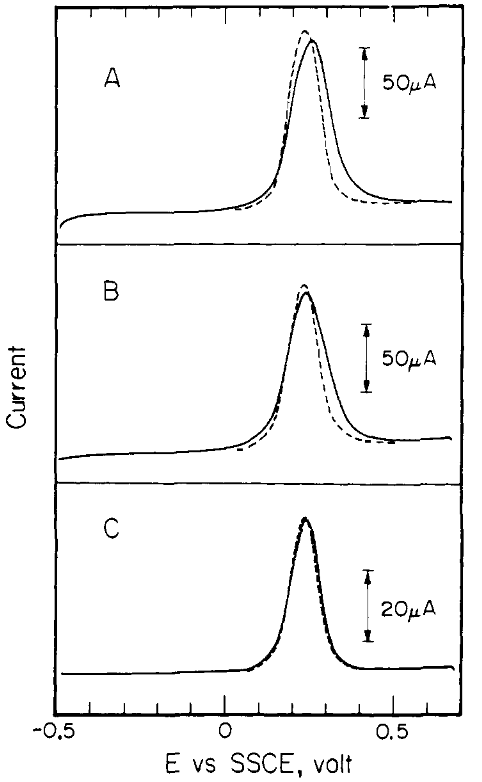

Figure 5. Comparison of the shapes of experimental cyclic voltammograms (solid lines) with those calculated (dashed lines) for a surface-confined reactant couple governed by the Nernst equation.[10] Electrodes were coated by procedure II with PVP[$Fe(CN)_5$]$_n$ having a molar ratio of pyridine to $Fe(CN)_5^{3-}$ of 8.5. The total pyridine units and electroactive $Fe(CN)_5^{3-}$ groups in the coatings were, respectively, (A) 4.9×10^{-7} and 1.3×10^{-9}, (B) 9.8×10^{-8} and 1.2×10^{-9}, (C) 9.8×10^{-9} and 4.7×10^{-10} mol cm^{-2}; other conditions as in Figure 1.

how the electroactive fraction of $Fe(CN)_5^{3-}$ groups (measured coulometrically as described in the Experimental Section) varies as the total quantity of $Fe(CN)_5^{3-}$ contained in the films applied to the electrode is increased. The latter was calculated from the known composition and volume of the solutions of PVP[$Fe(CN)_5$]$_n$ that were evaporated on the electrode surface to form the films. The stability of the $Fe(CN)_5^{3-}$ groups in the thicker films was

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(10) E. Laviron, *J. Electroanal. Chem.*, **39**, 1 (1972); **100**, 263 (1979).

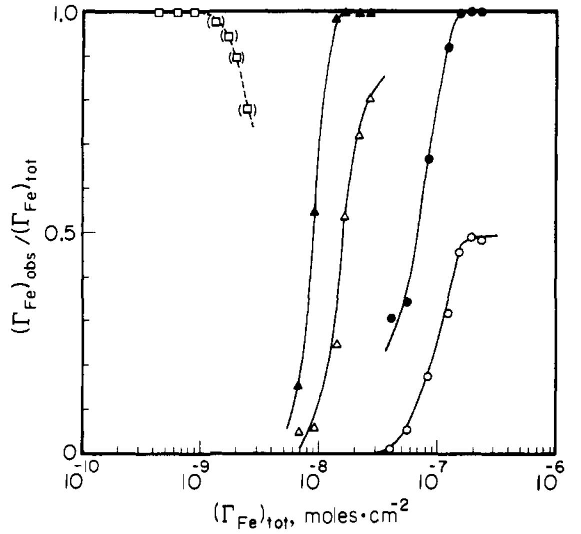

Figure 6. Electroactive fraction of $Fe(CN)_5^{3-}$ groups in films of PVP-$[Fe(CN)_5]_n$ as a function of the total quantity of $Fe(CN)_5^{3-}$ groups contained in the films (prepared by procedure II). The pyridine units in the films were: (○, ●) 4.9×10^{-7}; (△, ▲) 9.7×10^{-8}; (□) 4.9×10^{-9} mol cm^{-2}. Supporting electrolytes: open points, 0.2 M CF_3COONa + 0.001 M CF_3COOH; closed points, 0.2 M CF_3COONa + 0.1 M CF_3C-OOH. Points in parentheses are less reliable because of film instability.

demonstrated by showing that full electroactivity could be obtained by performing the electrochemical assay of electroactive groups in a supporting electrolyte at pH 1 (Figure 6).

With higher densities of $Fe(CN)_5^{3-}$ groups in the film the chances that any one group is electronically insulated from its neighbors and, therefore, from the electrode surface, is smaller, and this probably accounts for the increase in the fractional electroactivity with the ratio of $Fe(CN)_5^{3-}$ to pyridine groups in the polymers. With thicker films a breakdown in electronic continuity at various points within the film becomes statistically more likely and this would account for the decrease in the fraction of electroactive centers in thicker films. Figure 7 portrays one possible picture of the cross-section of polymer films that exhibit incomplete electroactivity of the incorporated $Fe(CN)_5py^{3-}$ groups. The portions of the film that remain unswollen prevent the entry or exit of counterions required for the oxidation of the groups and block the underlying electrode surface for charge transfer to $Fe(CN)_5py^{3-}$ groups in the swollen portions of the film.

Swelling experiments with small bulk samples of PVP laden with $Fe(CN)_5py^{3-}$ groups showed that the polymer swelled almost twice as much when treated with electrolyte at pH 1 than at pH 3. This greater swelling, with the associated increase in flexibility of the polymer chains, and a more open polymer texture that could facilitate counterion entry into the films are possible reasons for the significant pH effects on the electroactivity of $Fe(CN)_5py^{3-}$ groups coordinated to PVP films.

Effective Diffusion Coefficient for Transfer of Charge through Films of PVP$[Fe(CN)_5]_n$. Effective diffusion coefficients within polymeric coatings on electrodes can be estimated from plots of voltammetric peak currents vs. scan rate,[4d,11] chronoamperometric current vs. (time)$^{-1/2}$,[11] or chronocoulometric charge vs. (time)$^{1/2}$ [4d] if the concentration of the "diffusing reactant" within coatings of known composition is evaluated by measuring or guessing the film thickness.[11,12]

We performed chronoamperometric experiments with films of PVP$[Fe(CN)_5]_n$ prepared by procedures I and II in pure supporting electrolyte to compare the effective diffusion coefficients they exhibited. Figure 8 shows the resulting plots of current vs. (time)$^{-1/2}$ whose slopes at the shortest times are proportional to the product $(D_{eff}^{1/2}C)$ where D_{eff} is the effective diffusion coefficient and C is the concentration (mol cm^{-3}) of $Fe(CN)_5py^{3-}$ within the film. As pointed out by Daum et al.,[11] one expects chronoamperometric plots for reactants confined within thin polymer films to exhibit slopes corresponding to semiinfinite diffusion at sufficiently short times and corresponding to finite diffusion within a thin layer for longer times. The deviations of the data points from the extrapolation of the lines in Figure 8 mark the time range where the transition from semiinfinite to finite diffusion occurs. If the polymer film had a uniform thickness, the short-time slope could be used to calculate the point at which deviations from linearity are expected in the chronoamperometric

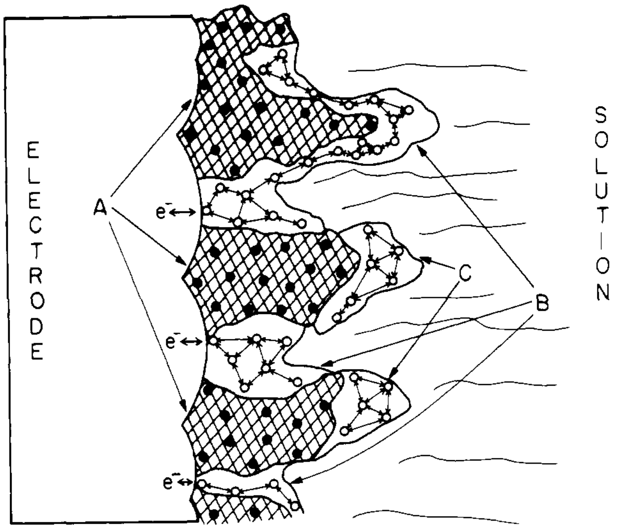

Figure 7. Schematic picture of electron-transfer pathways within partially swollen films of PVP$[Fe(CN)_5]_n$ introduced onto graphite electrodes by procedure II. Open circles represent $Fe(CN)_5^{3-}$ groups in swollen portions of the film where electron exchange between neighboring groups, indicated by the small arrows, is facile. Closed circles represent $Fe(CN)_5^{3-}$ groups in unswollen portions of the film that are impervious to the supporting electrolyte so that rapid electron exchange is prevented. Note that $Fe(CN)_5^{3-}$ groups in swollen portions of the film that are separated from the electrode surface by unswollen portions will remain unoxidizable despite their ability to exchange electrons with their immediate neighbors: (A) unswollen film, (B) swollen film in direct contact with the electrode, (C) swollen film out of contact with the electrode.

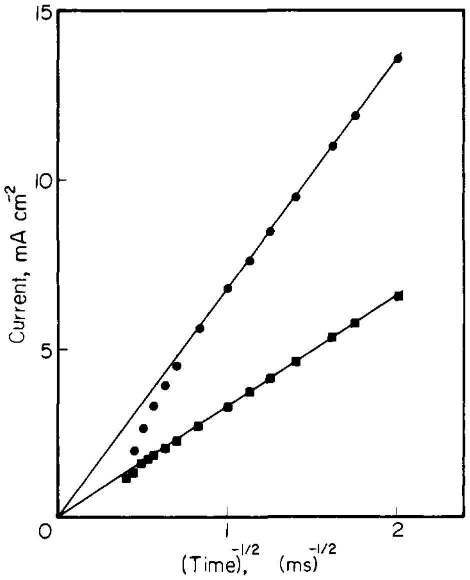

Figure 8. Chronoamperometric plots for films of PVP$[Fe(CN)_5]_n$ prepared by procedures I (■) and II (●). Both films contained 4.9×10^{-7} mol cm^{-2} of pyridine units and 1.3×10^{-9} mol cm^{-2} of electroactive $Fe(CN)_5py^{3-}$ groups. The total quantity of $Fe(CN)_5py^{3-}$ present in the film prepared by procedure II was 5.5×10^{-8} mol cm^{-2}. The potential was stepped from −0.2 to 0.6 V; supporting electrolyte as in Figure 1.

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(11) P. Daum, J. R. Lenhard, D. Roleson, and R. W. Murray, *J. Am. Chem. Soc.*, **102**, 4649 (1980).

(12) C. P. Andrieux and J. M. Saveant, *J. Electroanal. Chem.*, **111**, 377 (1980).

Table I. Estimates of D_{eff} for Films of Different Thickness

procedure[a]	$10^9 \Gamma_{PVP}$, mol cm^{-2}	$10^4 d$,[b] cm	$10^9 (\Gamma_{Fe})_{tot}$,[c] mol cm^{-3}	$10^9 (\Gamma_{Fe})_{obsd}$,[d] mol cm^{-2}	10^4 slope,[e] cm^{-2} s$^{-1/2}$	$10^8 D_{eff}$,[f] cm^2 s^{-1}
II	490	0.54	0			
II	490	0.80	57.6	1.27	2.1	6.3
I	490	0.65		1.30	1.1	0.95
II	97	0.16	11.4	1.22	12.1	8.5
I	97	0.13		1.25	9.1	3.0
II	9.7	0.016	1.14	0.47	52.3	11

[a] Procedures I and II are described in the text. [b] Estimated from the densities of swollen samples of the polymers determined as described in the Experimental Section. [c] The total quantity of $Fe(CN)_5py^{3-}$ present in the coatings prepared by procedure II. [d] The quantity of electroactive $Fe(CN)_5py^{3-}$ groups as measured coulometrically. [e] Chronoamperometric slope evaluated at times short enough to obtain linear plots. With the thinnest coating, times shorter than ~2 ms were required. [f] Calculated from eq 1.

plots.[11] Analysis of the data in Figure 8 in this way leads to the prediction that the deviations should occur at longer times than is observed. We believe this disagreement may result from nonuniformities in the effective thickness of incompletely swollen polymer films. As is suggested in Figure 7 the distance between the electrode surface and the more remote electroactive $Fe(CN)_5py^{3-}$ groups might vary considerably depending on the patterns of film swelling, especially with thicker films. We believe it is the thinner portions of such nonuniformly swollen films that cause the nonlinearity in the chronoamperometric plots in Figure 8 to appear at shorter times than would be observed with more uniformly swollen films.

Note that a considerably smaller slope is obtained in Figure 8 for the coating obtained by procedure I even though it consists of the same amount of PVP containing the same total quantity of electroactive $Fe(CN)_5py^{3-}$ centers. The smaller slope most likely reflects the lower concentration of $Fe(CN)_5py^{3-}$ groups believed to be present in the portion of the film nearest the electrode surface because of the two-step procedure used to prepare the film. If the diffusion-controlled transfer of charge through the film is governed by differing effective diffusion coefficients at different depths within the film, the smallest diffusion coefficient would be expected to control the response observed in measurements such as those of Figure 8. This line of reasoning also leads to the prediction that films containing a homogeneous distribution of redox centers should begin to show a dependence of the effective diffusion coefficient on the number of $Fe(CN)_5py^{3-}$ groups present in the film as this number is decreased toward zero. To test this prediction chronoamperometric plots such as those in Figure 8 were prepared for a series of homogeneous films containing decreasing numbers of $Fe(CN)_5py^{3-}$ groups. Figure 9 gives the observed chronoamperometric slopes, normalized by dividing by the measured quantities of electroactive $Fe(CN)_5py^{3-}$ groups in each film, as a function of the electroactive $Fe(CN)_5py^{3-}$ groups present. In each case there is a significant decrease in the normalized slopes when the total $Fe(CN)_5py^{3-}$ present in the films is decreased to 10^{-9} to 10^{-10} mol cm^{-2}. Since the normalized slope is proportional to $d^{-1}D_{eff}^{1/2}$,[11] where d is the (assumed uniform) thickness of the film, the decline in slope can be ascribed either to decreases in D_{eff} or to increases in d as the number of $Fe(CN)_5py^{3-}$ groups in a film is decreased. Independent measurements of polymer swelling as a function of the quantity of $Fe(CN)_5^{3-}$ incorporated in it showed that the swelling diminished with the quantity of $Fe(CN)_5py^{3-}$ groups so that the effect shown in Figure 9 seems most likely to reflect a real decrease in D_{eff} as the number of redox centers present in the film diminishes.

These data constitute one of the few cases in which such an effect has been reported with polymer-coated electrodes. Pham et al.[3] reported increases in the conductance of dry films of polymerized 2-methyl-8-hydroxyquinoline as the concentration of $CuCl_2$ was increased in solutions to which the polymers had been exposed. With sufficiently high concentrations the conductance became constant, but the quantities of Cu^{2+} incorporated by the films were not determined. Peerce and Bard[13] noted a higher effective diffusion coefficient in films of polyvinylferrocene than in similar films prepared from a copolymer of vinylferrocene and acrylonitrile where the concentration of ferrocene groups within the copolymer film was decreased about twofold. However, the concentration of redox sites in such a copolymer is still much greater than that of the electroactive $Fe(CN)_5py^{3-}$ groups in our $PVP[Fe(CN)_5]_n$ films that exhibit values of D_{eff} insensitive to further increases in the concentration of $Fe(CN)_5py^{3-}$ groups (Figure 9). Thus, the nature of the polymer film appears to influence strongly the rate at which charge can be transferred through it by electron exchange between pairs of redox centers incorporated in the films. Measurements similar to those in Figure 9 with films in which essentially all of the redox centers are electroactive may provide an estimate of the minimum encounter distances required for efficient electron transfer between redox centers in polymer films. However, complications resulting from nonuniformities induced in the film because of its interactions with the surface[14] may be difficult to avoid.

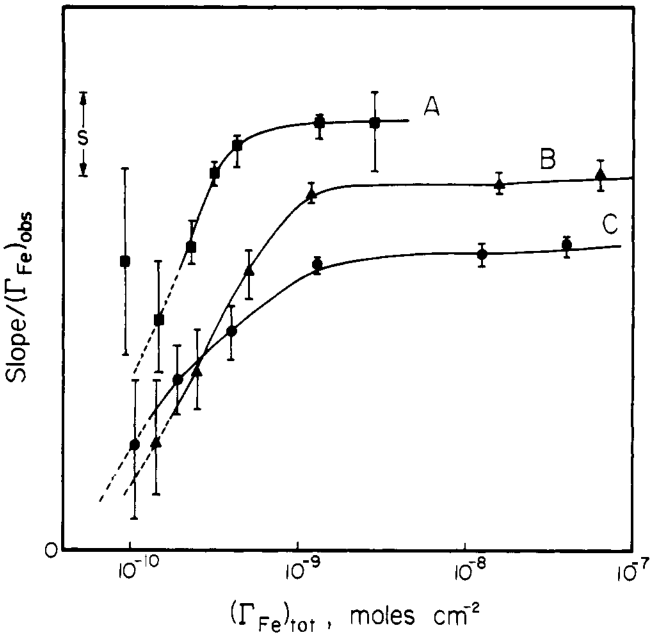

Figure 9. Normalized slopes of chronoamperometric plots for films of $PVP[Fe(CN)_5]_n$ prepared by procedure II as a function of the quantity of electroactive $Fe(CN)_5^{3-}$ groups in the films. The pyridine units contained in the films were (A) 5 × 10^{-8}, (B) 10^{-7}, (C) 5 × 10^{-7} mol cm^{-2}. The scale factor, S: (A) 0.5 × 10^{-5}; (B) 0.25 × 10^{-6}; (C) 0.25 × 10^{-7} A mol^{-1} s$^{-1/2}$.

Values of D_{eff} can be obtained from eq 1 if the thickness of the

$$D_{eff} = \pi \left(\frac{Sd}{(\Gamma_{Fe})_{obsd} F} \right)^2 \qquad (1)$$

films on the electrode is assumed to be uniform (despite the evidence to the contrary cited in connection with Figure 8) and calculated from the polymer densities (0.6–0.7 g cm^{-3}) estimated

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(13) P. J. Peerce and A. J. Bard, *J. Electroanal. Chem.*, **114**, 89 (1980).

(14) C. A. J. Hoeve, *J. Chem. Phys.*, **43**, 3007 (1965).

from the solvent-swelling measurements described in the Experimental Section. S is the chronoamperometric slope (A cm^{-2} $s^{-1/2}$), d is the film thickness (cm), $(\Gamma_{Fe})_{obsd}$ is the quantity of electroactive complex in the film (mol cm^{-2}), and F is the faraday. Values of D_{eff} obtained in this way for several coatings are given in Table I. The uniformly smaller values observed with the coatings resulting from procedure I are in accord with the smaller voltammetric peak currents obtained with these films. The systematic increase in D_{eff} with thinner films formed by procedure II is in the direction expected from the increase in the fraction of $Fe(CN)_5py^{3-}$ groups that are electroactive in thinner films. However, the correlation is not a straightforward one; a 20-fold increase in the concentration of electroactive centers produces only a twofold increase in the measured value of D_{eff}. The large uncertainties associated with the estimated values of d for these films discourages us from attempting more detailed analysis of the trends. The approximate values of D_{eff} estimated in this study fall within the range of previously reported values.[11-13,15] However, this range encompasses several orders of magnitude and it seems clear that the rates of diffusive charge transport through polymer films containing redox centers vary much more extensively than do the rates of diffusion of small molecules in liquid solutions.

Conclusions

By exploiting the coordination chemistry and solubility properties of mixtures of PVP and $Fe(CN)_5OH_2^{3-}$ it proved possible to incorporate redox active $Fe(CN)_5^{3-}$ groups into PVP either before or after films of the polymer were cast on electrode surfaces. The markedly different electrochemical responses of the two types of films, even when their nominal compositions and dimensions are the same, shows that the spatial distribution as well as the total number of redox centers within such films determines the rate at which charge can be transported through them. The now generally accepted proposal[9] that the mechanism of charge transport involves electron exchange between adjacent pairs of (oxidized and reduced) redox centers is supported by our observation of a sharp decrease in this rate when the concentration of redox centers falls below a critical value.

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(15) R. J. Nowack, F. A. Schultz, M. Umana, R. Lam, and R. W. Murray, *Anal. Chem.*, **52**, 315 (1980).

Theoretical Study of Concerted vs. Stepwise Fragmentation of 2-Carbena-1,3-dioxolane

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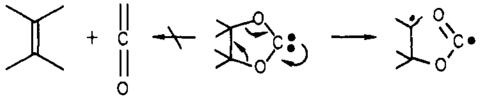
Abstract: The transition state for concerted fragmentation of the lowest singlet state of 2-carbena-1,3-dioxolane to ethylene plus carbon dioxide has been located at the restricted Hartree–Fock (RHF) level of ab initio theory, using a 4-31G basis set. The transition state is calculated to lie 30.4 kcal/mol above the optimized geometry for the reactant at this level of theory. This energy difference is rather insensitive to expansion of the basis set or to reaction, of CI. The STO-3G basis set is shown, however, to be very unsatisfactory for treating this reaction, since STO-3G gives the correct magnitude but the wrong sign for the energy difference between the reactants and products. The energy of the diradical formed by cleavage of just one C–O bond in carbenadioxolane is computed to lie at least 8.8 kcal/mol below the transition state for concerted fragmentation. Since a previous theoretical study of dihydroxycarbene suggests that the energy of the transition state for formation of the diradical should not be significantly higher than the energy of the diradical itself, it is concluded that cleavage of one C–O bond in carbenadioxolane is a lower energy process than concerted fragmentation. This theoretical finding rationalizes the experimental results in the pyrolysis of carbonate tosylhydrazone salts.

Pyrolysis of carbonate tosylhydrazone salts gives products whose formation can be most easily rationalized as involving one-bond cleavage in presumed 2-carbena-1,3-dioxolane intermediates.[1] That such intermediates do not decompose to alkene plus CO_2 in a concerted ${}_\sigma 2_2 + {}_\sigma 2_s + {}_\omega 2_s$ process is somewhat surprising, since in the lowest singlet state of the carbene this reaction pathway is "allowed" by orbital symmetry.[2] However, a computational study of an analogous reaction, fragmentation of singlet dihydroxycarbene [$C(OH)_2$] to H_2 plus CO_2, showed that, although a transition state for concerted fragmentation exists, cleavage of just one OH is energetically preferable.[3]



The high energy of the transition state for concerted fragmentation of $C(OH)_2$ was attributed principally to the fact that at the transition state the incipient CO_2 fragment remains highly bent (OCO bond angle = 121.8°). This small angle is necessary for decreasing the H–H distance from that in $C(OH)_2$ toward that in H_2 while maintaining a modicum of OH bonding. Since the force constant for bending CO_2 is large, a high-energy transition state results.

The 1.33-Å C–C bond in ethylene is considerably longer than the 0.74-Å H–H bond in H_2. We speculated, therefore, that at the transition state for concerted fragmentation of carbenadioxolane the incipient CO_2 molecule might be less bent than at the transition state for concerted decomposition of $C(OH)_2$. Consequently, we suggested that the calculated barrier height for concerted carbenadioxolane fragmentation might be lower than that for the analogous process in $C(OH)_2$. In order to test these

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(1) Borden, W. T.; Hoo, L. H. *J. Am. Chem. Soc.* **1978**, *100*, 6274.

(2) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(3) Feller, D.; Borden, W. T.; Davidson, E. R. *J. Comput. Chem.* **1980**, *1*, 158.

0002-7863/81/1503-2558$01.25/0