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Hydration of the Carbonyl Groups in 1,10-Phenanthroline-5,6-dione Induced by Binding Protons or Metal Cations to the Pyridine Nitrogen Sites

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Abstract: In acidic solutions, the chemical or slow electrochemical reduction of the organic ligand−oxidant 1,10-phenanthroline-5,6-dione consumes two electrons and two protons. However, when the electrochemical reduction is examined on shorter time scales using cyclic or rotating disk voltammetry, fewer than two electrons are consumed in the reduction. The magnitude of the electron deficit depends upon pH and the deficit is eliminated at pH values where the pyridine nitrogen sites on the molecule are not protonated. Complexation of metal cations, e.g., Os(II) or Ni(II), to the 1,10-phenanthroline portion of the molecule also produces an electron deficit in electrochemical reductions of the dione. A proton- or metal ion-induced addition of H_2O to the quinone carbonyl groups is shown to be responsible for the observed behavior. Rate and equilibrium constants for the hydration−dehydration equilibrium were evaluated by fitting experimental and calculated parameters in a digital simulation. The possible consequences of the results to studies in which the dione is used to oxidize amines and other organic reductants are pointed out.

The action of 1,10-phenanthroline-5,6-dione (Figure 1) and its complexes with metal cations as oxidizing agents for organic amines and inorganic reducing agents and for biological reductants such as NADH has attracted considerable interest and several experimental studies have appeared.[1−5] The electrochemical behavior of a variety of metal complexes of the ligand has also been described.[6,7] Our interest in the molecule stems from its strong spontaneous adsorption on graphite electrodes. The electroactivity of the ortho quinone allows the number of molecules present in adsorbed layers to be determined easily by coulometric assays. In addition, the stoichiometric composition of metal complexes that are formed on the surfaces of graphite electrodes when electrodes coated with the ligand are exposed to solutions of metal cations can be established. Some of the resulting complexes exhibit electrocatalytic activity that is under investigation in separate studies.[8]

Although previous reports of the electrochemistry of 1,10-phenanthroline-5,6-dione (pdon) in aqueous[7] or semiaqueous solutions[6] indicated that a reasonably well-behaved, two-electron, two-proton reversible electrode process is involved, we observed large deviations from this pattern when the reaction was inspected on time scales of a few seconds or less at pH values where the pyridine nitrogen sites were protonated. Under these conditions, the cathodic currents observed for the reduction of pdon were much smaller than the currents obtained at higher pH values where the nitrogen sites are not protonated. Coordination of metal cations to the pyridine nitrogens also diminished the reduction current of the metal−pdon complex, even at pH values where the uncoordinated pdon ligand undergoes a diffusion-limited, two-electron reduction.

1,10-phenanthroline-5,6-dione (pdon) 1,10-phenanthroline-5,6-diol (pdol)

Figure 1. Structures of the oxidized and reduced forms of the phenanthrolinedione employed in this study.

The present study was undertaken to determine the reasons for the variation in the magnitudes of currents for the electrochemical reduction of the pdon molecule. The results demonstrated that hydration of the quinoid carbonyl groups is induced by protonation or metalation of the pyridine nitrogen atoms of the pdon ligand. The resulting hydrated molecule is electroinactive (at potentials where unhydrated pdonH^+ is reduced) and it is in sluggish equilibrium with the electroactive, ortho quinone form of pdon. Rotating disk voltammetry was utilized to evaluate the rate and equilibrium constants governing the proton-induced hydration equilibrium. The hydration that is induced by coordination of pdon to Os(II) and Ni(II) metal centers was also inspected.

Experimental Section

Materials. 1,10-Phenanthroline-5,6-dione (pdon) was prepared and purified by a published procedure.[9] Solutions of the protonated, reduced ligand 1,10-phenanthroline-5,6-diol (pdolH^+) were prepared by electrochemical reduction of pdon at 0.1 V vs SCE at a platinum gauze electrode in the absence of air in 0.1 M CF_3COOH. $[\text{Os(bpy)}_2(\text{pdon})](PF_6)_2 \cdot H_2O$ was prepared by adaptation of a published procedure.[7] Anal. Calcd for $C_{32}H_{24}F_{12}N_6O_3OsP_2$: C, 37.46; H, 2.27; N, 8.12. Found: C, 37.57; H, 2.35, N, 8.22. Stock solutions of $\text{Ru(NH}_3)_6^{2+}$ were prepared by electrochemical reduction of $\text{Ru(NH}_3)_6^{3+}$ at −0.4 V vs SCE at a Pt gauze electrode in the absence of air. Acidic supporting

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electrolytes were prepared using CF_3SO_3H (Aldrich). Buffer solutions at pH values above 3 were prepared by addition of NaOH to solutions containing 0.04 mol/L of CH_3COOH. All solutions were prepared from laboratory distilled water that had been further purified by passage through a purification train (Barnsted-Nanopure).

Apparatus and Procedures. Conventional electrochemical instrumentation and two-compartment cells were employed. Edge plane pyrolytic graphite disks (Union Carbide) mounted on stainless steel shafts with heat shrinkable tubing were used as working electrodes. The exposed surface (0.32 cm^2) was polished to a mirror finish on a polishing wheel using 0.05 μm alumina followed by sonication in pure water for 15 min. For experiments with adsorbed pdon (Figure 6) the electrode was polished with 600 grit silicon carbide paper to produce a rougher surface on which the adsoption of pdon is enhanced. The roughly polished electrode was immersed for 4 to 6 min in a 1 mM aqueous solution of pdon to obtain a saturated surface. The electrode was then washed and transferred to a pure supporting electrolyte solution to record cyclic voltammograms. The quantities of pdon adsorbed were somewhat dependent on the extent of polishing and corresponded to many monolayers of pdon based on the geometric area of the electrode. Electrode potentials were measured and are quoted with respect to a saturated calomel reference electrode (SCE). UV–vis spectra were recorded with a HP8452 diode array spectrophotometer (Hewlett Packard). Proton decoupled ^{13}C NMR spectra were obtained with a Bruker AM500 spectrometer. Digital simulations were performed using Digisim (Bioanalytical Systems, Inc.).

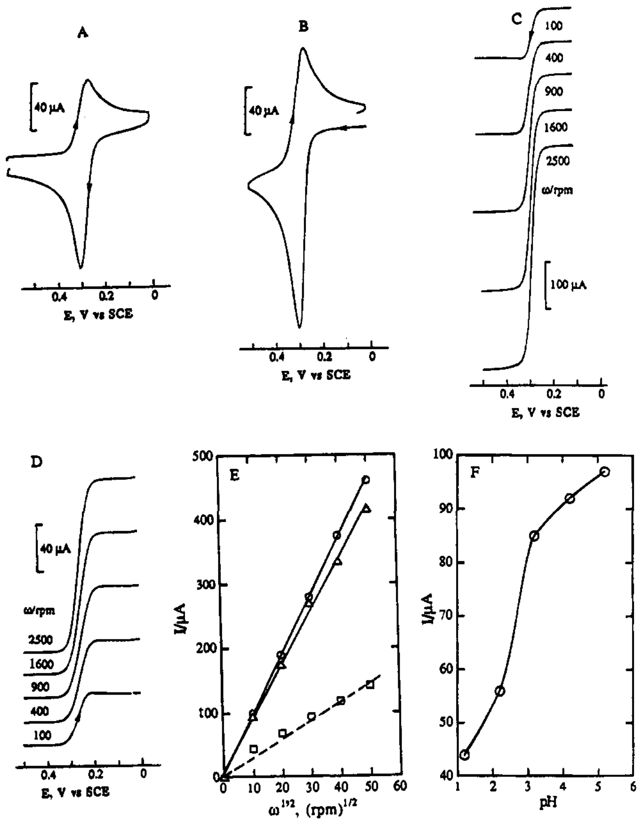

Figure 2. Cyclic voltammetry of 1 mM solutions of (A) $pdonH^+$ and (B) $pdolH^+$ at a polished edge plane graphite electrode in 0.1 M CF_3SO_3H. (C) Current potential curves for the oxidation of 1 mM $pdolH^+$ at the graphite disk electrode rotated at the indicated rates. Supporting electrolyte: 0.1 M CF_3SO_3H. (D) Repeat of (C) but for the reduction of 1 mM $pdonH^+$. (E) Levich plots of the anodic plateau currents from (C) (○), the cathodic plateau currents from (D) (□), and cathodic plateau currents measured at pH 4.6 (△). The dashed straight line was drawn through the points at $\omega^{1/2}$ = 40 and 50 $(rpm)^{1/2}$. (F) Plateau currents for the reduction of 1 mM pdon/$pdonH^+$ as a function of pH at an electrode rotation rate of 100 rpm.

Results

Voltammetry of pdon and pdol. The voltammetric behavior of the oxidized and reduced forms of the ligand, pdon and pdol (Figure 1), was examined first in supporting electrolytes at pH 1 where both forms exist as singly protonated cations.[1,6] The anomalous voltammetric behavior obtained under these conditions is evident in the cyclic voltammograms shown in Figure 2, parts A and B. The cathodic peak current for the reduction of $pdonH^+$ is notably smaller than the corresponding anodic peak current for the oxidation of $pdolH^+$ (Figure 2A) and both currents are smaller than those expected for a diffusion-limited, two-electron electrode reaction. The cyclic voltammogram for the oxidation of the same concentration of $pdolH^+$, shown in Figure 2B, has an anodic peak current that is larger than that in Figure 2A and is close to the value expected for a diffusion-controlled, two-electron oxidation. However, the cathodic peak current obtained during the second half of the cycle is much smaller. To minimize contributions to the currents from the adsorbed reactants (both pdon and pdol are adsorbed on graphite) we utilized steady-state rotating disk voltammetry with highly polished electrodes to obtain quantitative data. A set of rotating disk current–potential curves for the oxidation of $pdolH^+$ is shown in Figure 2C and the corresponding Levich plot[10] of the anodic plateau currents vs the electrode (rotation rate)$^{1/2}$ is shown as the open circles in Figure 2E. The anodic plateau currents lie on a straight line that passes through the origin and has a slope from which a reasonable value of the diffusion coefficient of 6.3×10^{-6} cm^2 s^{-1} can be calculated (assuming a two-electron oxidation). Sharply contrasting behavior was exhibited during similar experiments in which $pdonH^+$ was reduced at the rotating disk electrode. The set of cathodic current–potential curves is shown in Figure 2D and the plateau currents are plotted as the open squares in Figure 2E. The cathodic currents are much smaller than the anodic currents obtained with the same concentration of $pdolH^+$. When the pH of the supporting electrolyte is increased to values where pdon is not protonated (the reported pK_A of $pdonH^+$ is 2.4[1]) much larger reduction currents are obtained. A Levich plot for the reduction of pdon in a supporting electrolyte buffered at pH 4.6 is shown by the triangles in Figure 2E. The residual differences between the currents for the reduction of pdon at 4.6 and the oxidation of pdol at pH 1 probably reflect differences in their diffusion coefficients. Both the oxidation of $pdolH^+$ and the reduction of pdon are diffusion-convection-controlled, two-electron reactions. The electrochemistry of unprotonated pdol (the pK_A of $pdolH^+$ in 50% DMSO–50% H_2O is 5.3[6a]) cannot be studied in aqueous solution because of its very low solubility. The pH dependence of the plateau current for the reduction of $pdonH^+$/pdon at a fixed rotation rate is shown in Figure 2F. The current decreases by more than a factor of 2 when the pH is decreased from 5 to 1.

Reduction of $pdonH^+$ by Controlled Potential Electrolysis or by Reaction with $Ru(NH_3)_6^{2+}$. In contrast to the results just described, Eckert and Bruice reported that the electroreduction of $pdonH^+$ is a two-electron process on the basis of cyclic voltammetry conducted in a thin-layer electrochemical cell which required that a very slow potential scan rate (2 mV s^{-1}) be employed.[1] To determine if the difference in the duration of the voltammetric experiments was responsible for the difference in the behavior reported by Eckert and Bruice and that which we observed, exhaustive electrolyses of a solution of $pdonH^+$ at 0.1 V in a conventional electrochemical cell were carried out at a large platinum gauze electrode. The spectral changes observed during the course of the electrolysis are shown

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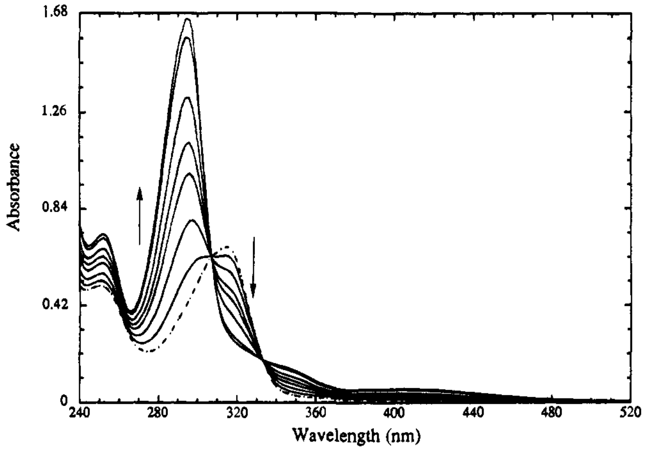


Figure 3. UV–vis spectra of aliquots of a 0.5 mM solution of pdonH$^+$ in 0.1 M CF_3SO_3H during its electrolytic reduction at 0.1 V. The dashed-dotted curve is the spectrum before the electrolysis. After the electrolysis was started, 0.3-mL aliquots of the solution, protected from air, were withdrawn about every 10 min and transferred to a 1-mm cuvette to record the spectra shown.

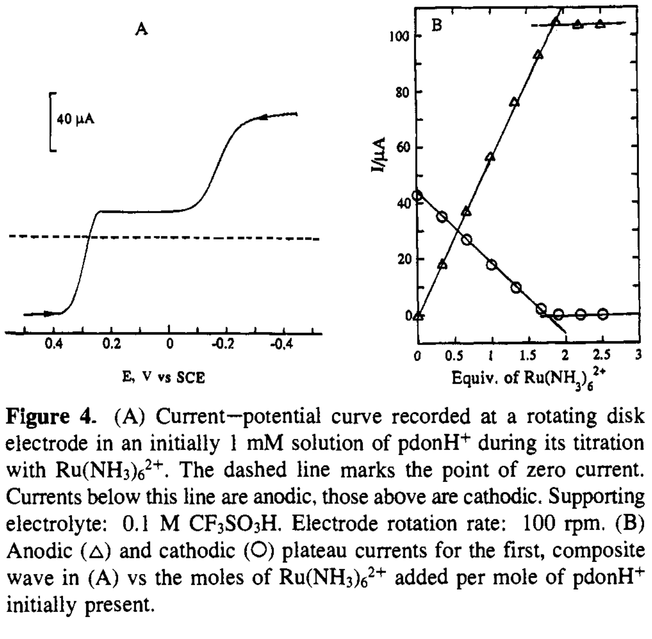


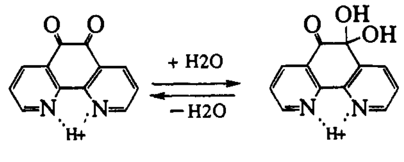
Figure 4. (A) Current–potential curve recorded at a rotating disk electrode in an initially 1 mM solution of pdonH$^+$ during its titration with $Ru(NH_3)_6^{2+}$. The dashed line marks the point of zero current. Currents below this line are anodic, those above are cathodic. Supporting electrolyte: 0.1 M CF_3SO_3H. Electrode rotation rate: 100 rpm. (B) Anodic (△) and cathodic (O) plateau currents for the first, composite wave in (A) vs the moles of $Ru(NH_3)_6^{2+}$ added per mole of pdonH$^+$ initially present.

in Figure 3. The clear isosbestic points indicate that pdonH$^+$ is reduced to a single species and the final spectrum obtained matches that of pdolH$^+$.[1] The cathodic charge consumed during the time required for completion of such electrolyses (ca. 70 min) corresponded to two electrons per molecule of pdonH$^+$, a result in agreement with the report of Eckert and Bruice.[1]

The reduction of pdonH$^+$ was also carried out by titration with a standard solution of $Ru(NH_3)_6^{2+}$. The formal potential of the $Ru(NH_3)_6^{3+/2+}$ couple, $E^f = -0.18$ V, is ample for the chemical reduction of pdonH$^+$ by $Ru(NH_3)_6^{2+}$ at pH 1. The titration was monitored with a rotating disk electrode. A typical current–potential curve recorded at an intermediate stage of the titration is shown in Figure 4A. It consists of an anodic plateau and two cathodic plateaux corresponding to the oxidation of pdolH$^+$, the reduction of unreduced pdonH$^+$ and the reduction of $Ru(NH_3)_6^{3+}$ generated in the titration reaction, respectively. Plots of the anodic plateau current and the first cathodic plateau current as a function of the moles of $Ru(NH_3)_6^{2+}$ added per mole of pdonH$^+$ initially present are shown in Figure 4B. Approximately 2 mol of $Ru(NH_3)_6^{2+}$ are consumed by each mole of pdonH$^+$ at the end point of the titration marked by the abrupt change in the slopes of the titration lines. (The difference in the slopes of the lines is as expected on the basis of the behavior that was shown in Figure 2E.)

Thus, the reduction of pdonH$^+$ consumes fewer than two electrons per molecule in cyclic or rotating disk voltammetric experiments that last only a few seconds but the reduction becomes a quantitative two-electron chemical or electrochemical process in experiments that extend over longer periods of time.

NMR Measurements. The behavior described thus far is consistent with the presence of a slowly established, pH-dependent equilibrium in which pdonH$^+$ molecules are converted to an electroinactive form. A likely possibility for this equilibrium is a hydration reaction:



Such hydration of the carbonyl functionalities of aldehydes and ketones is well-known to convert them from electroreducible into electroinactive functional groups.[11] To obtain evidence of the hydration reaction, the ^{13}C NMR spectra of pdon and pdonH$^+$ were recorded. In order to increase the solubility of the unprotonated molecule its solutions were prepared in a mixture of 50% D_2O–50% CD_3CN. The ^{13}C spectrum obtained contained the six resonances expected for a molecule of pdon with a single peak in the region between 175 and 195 ppm, where the resonance of carbonyl groups is expected to appear.[12] A spectrum was also recorded in 0.1 M CF_3SO_3D in D_2O where pdon is monoprotonated.[1] A more complex spectrum containing many peaks was obtained. However, between 175 and 195 ppm two peaks were present instead of the single resonance obtained with the unprotonated molecule. In addition, a new pair of resonances appeared near 90 ppm where responses from carbinols are expected.[12] The appearance of two resonances attributable to carbinol groups suggests that both carbonyl groups may be hydrated in a fraction of the molecules. The ^{13}C NMR spectra at pH 1 were consistent with the presence of a mixture containing unhydrated, singly hydrated, and doubly hydrated molecules that did not interchange significantly on the NMR time scale.

Hydration Induced by Coordination of Metal Cations. The complexation of metal cations to the pyridine nitrogen atoms of pdon also diminishes the plateau currents for the electroreduction of the coordinated ligand. In Figure 5A is shown the current–potential curve recorded at a rotating graphite disk electrode with a solution of $Os(bpy)_2(pdon)^{2+}$ (bpy = 2,2′-bipyridine). The anodic wave near 0.8 V corresponds to the oxidation of Os(II) to Os(III), an uncomplicated, one-electron process. Hydration of the coordinated pdon ligand (to produce pdon–H_2O) would produce a mixture of $Os(bpy)_2(pdon)^{2+}$ and $Os(bpy)_2(pdon-H_2O)^{2+}$ complexes in aqueous solutions of the parent complex. However, the difference between the equilibrium affinities for Os(II) of the hydrated and unhydrated forms of the ligand is apparently not sufficient to yield separated waves for the oxidations of the two types of complex. The cathodic wave near 0.1 V corresponds to the reduction of $Os^{II}(bpy)_2(pdon)^{2+}$ to $Os^{II}(bpy)_2(pdol)^{2+}$. This is a two-electron (two-proton) process but the cathodic plateau current is only slightly larger than the anodic plateau current that provides an internal calibration of the current corresponding

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[12] Borrel, T. N. *Interpreting Spectra of Organic Molecules*; University Science Books: 1988; pp 97–115.

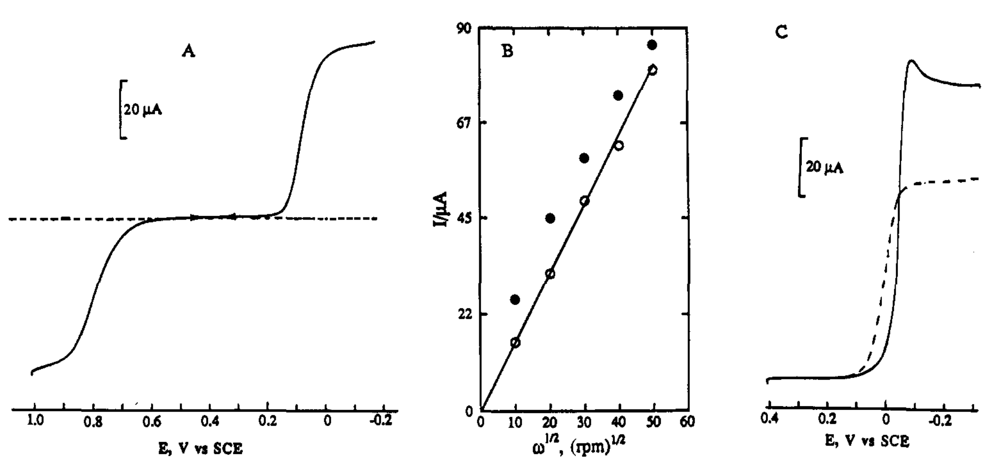


Figure 5. (A) Current–potential curve recorded at a rotating disk electrode in a 0.5 mM solution of $Os(bpy)_2(pdon)^{2+}$. Supporting electrolyte: 0.04 M acetate buffer at pH 5.2. Electrode rotation rate: 400 rpm. (B) Levich plots of the anodic (●) and cathodic (○) plateau currents from (A). (C) Current–potential curve for a 1 mM solution of pdon before (solid line) and after (dashed line) addition of 10 mM Ni^{2+}. Supporting electrolyte as in (A). Rotation rate: 100 rpm.

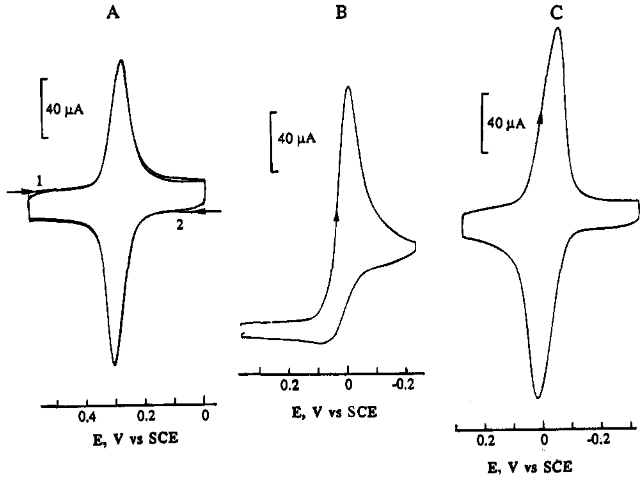


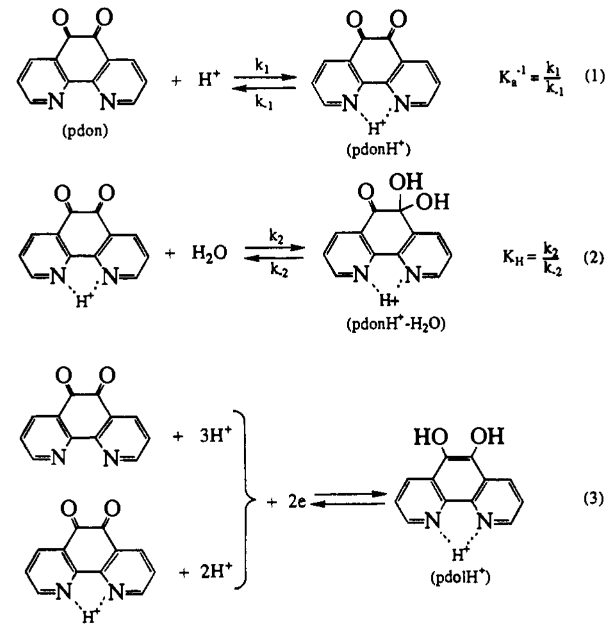
Figure 6. (A) Cyclic voltammetry of 2.6×10^{-9} mole cm^{-2} of pdon adsorbed on a roughly polished pyrolytic graphite electrode. Supporting electrolyte: 0.1 M CF_3SO_3H. The initial electrode potential was (1) 0.6 or (2) 0 V. Scan rate: 50 mV s^{-1}. (B) Cyclic voltammetry of a 1 mM solution of pdon at pH 5.2 recorded with an alumina-polished pyrolytic graphite electrode to minimize the adsorption of pdon. Supporting electrolyte: 0.04 M acetate buffer at pH 5.2. Scan rate 50 mV s^{-1}. (C) Repeat of (A) with 3.9×10^{-9} mole cm^{-2} of pdon adsorbed on the roughly polished electrode. Supporting electrolyte as in (B).

to a one-electron, diffusion-convection-controlled electrode reaction of the molecule. The Levich plot of the anodic plateau currents (open points in Figure 5B) confirms that the rate of oxidation of the Os(II) center of the complex is limited only by its rate of arrival at the electrode surface. By contrast, the currents for the reduction of the coordinated ligand (solid points in Figure 5B) exhibit the hallmarks of an electrode reaction that is limited by a slow chemical step which precedes the electrode reaction, e.g., dehydration of the carbonyl groups of the coordinated ligand. Both $Os(bpy)_2(pdon)^{2+}$ and $Os(bpy)_2(pdon)^{3+}$ are inert toward substitution of the coordinated ligands and, as expected for such complexes, neither the anodic nor the cathodic plateau current is affected by changes in pH.

Substitutionally labile metal complexes of the pdon ligand also show diminished ligand reduction currents. For example, in Figure 5C are shown current–potential curves for the reduction of pdon before and after an excess of Ni^{2+} was added to the solution. The supporting electrolyte was buffered at pH 5.2 to facilitate the coordination of Ni^{2+} by the pdon ligand. An initially peaked current plateau was typically observed with solutions of the free ligand at pH values of 5 or greater. This behavior is believed to reflect the low solubility of the unprotonated reduced ligand, pdol.[3] The cathodic plateau currents at pH 5 tended to decrease slowly with continuous electrolysis as an insoluble film collected on the electrode surface. Repolishing the electrode restored the original plateau current. The primary point to be noted in Figure 5C is the significant decrease in the steady-state plateau current that is produced by the addition of Ni^{2+} (dashed curve in Figure 5C). This decrease may be attributed to the partial hydration of the carbonyl groups of the coordinated ligand. In addition, the positive shift in the potential where the ligand is reduced reflects the stronger coordination of Ni^{2+} to the reduced than to the oxidized form of the ligand. Unlike the free ligand, the complex of Ni^{2+} with pdol is soluble at pH 5.

Electrochemistry of pdon Adsorbed on Graphite. The pdon molecule adsorbs spontaneously and strongly on graphite surfaces where it can be used to bind metal cations to the surface of electrodes.[7,8] As one of our objectives was to exploit such surface-confined transition metal complexes as electrocatalysts, the electrochemical behavior of the pdon ligand in the adsorbed state was of interest. In Figure 6A are shown cyclic voltammograms for pdon adsorbed on the surface of a graphite electrode that was polished with 600 grit SiC paper instead of alumina to obtain a rougher surface on which adsorption is enhanced. After the pdon was adsorbed, the electrode was transferred to the pure supporting electrolyte (0.1 M CF_3SO_3H) to record the two voltammograms. For the first voltammogram (curve 1) the electrode potential was maintained at 0.6 V before initiating the scan to more negative potentials so that the adsorbed molecule was present initially in its oxidized and (presumably) protonated state, pdonH$^+$. In the second voltammogram (curve 2) the initial potential was 0 V so that the adsorbed molecule was in its reduced state, pdolH$^+$, and the potential was scanned to more positive potentials. Although the anodic peak currents are slightly larger in both cases, the areas under the peaks are essentially equal. Thus, in contrast with the behavior of pdonH$^+$ in solution, the molecule appears not to undergo significant hydration when adsorbed on the graphite surface (or, if the adsorbed molecule is hydrated, the dehydration equilibrium is established much more rapidly than is the case for pdonH$^+$ in solution). The possibility that adsorbed pdon is a much weaker base that is not protonated at pH 1 can also not be excluded on the basis of the presently available data.

Scheme 1



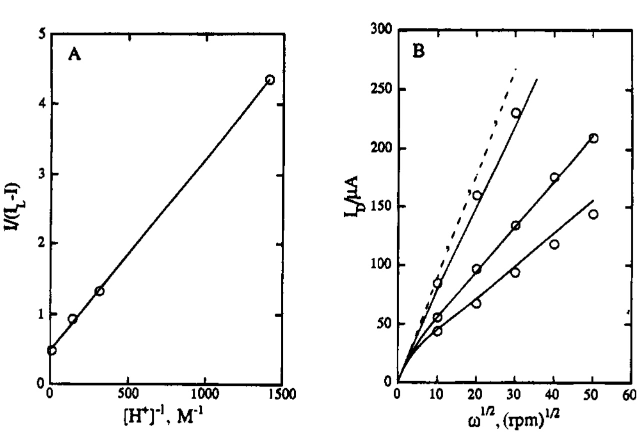


Figure 7. (A) A plot prepared according to eq 4 (see text). (B) Comparison of calculated (solid curves) and experimental (plotted points) plateau currents for the reduction of a 1 mM solution of pdon at pH (top to bottom) 3.2, 2.2, 1.0. The lines were calculated on the basis of Scheme 1 using $k_{-2} = 0.5$ s^{-1} to obtain the best agreement with experiment. Other parameters were $K_a = 5.6 \times 10^{-3}$ M^{-1}, $K_H = 2.0$, $D = 6.3 \times 10^{-6}$ cm^2 s^{-1}. Reaction 1 was assumed to remain at equilibrium. The dashed straight line shows the plateau current corresponding to the diffusion-convection-limited reduction of the pdon.

Adsorption on roughly polished graphite allows the electrochemistry of the reduced ligand to be observed at pH values where its low solubility prevents the observation of voltammetric responses from the dissolved molecule. In Figure 6B is shown a cyclic voltammogram for a solution of pdon at pH 5.2. There is almost no anodic peak for the oxidation of the reduced molecule because it is removed from solution by precipitation. However, when the voltammetry is carried out with the pdon adsorbed on the roughly polished graphite electrode at the same pH (Figure 6C) a fully reversible response results with equal anodic and cathodic peak areas. The adsorbed pdol retains its electroactivity. The electrochemical irreversibility of the pdon/pdol couple (at pH 5.4) was also noted by Eckert and Bruice,[1] who attributed it to intermolecular self-complexation of pdol rather than to its insolubility.

Discussion

The addition of H_2O to the carbonyl groups of aldehydes and ketones has long been known to produce the corresponding diols which are not reducible at electrode surfaces.[11] The effect of protonation of the nitrogen sites of a variety of pyridinecarboxaldehydes on their hydration has also been investigated.[13,14] The behavior of pdon is similar in that the hydration reaction at the carbonyl group is induced by protonation of the remote pyridine nitrogen atoms of the 9,10-phenanthroline portion of the molecule. The observed electrochemical behavior and the ^{13}C NMR spectra can be accounted for in terms of Scheme 1. The electroreducible species in Scheme 1 are pdonH$^+$ and pdon. The hydrated form of the molecule, pdonH$^+$–H_2O, is not electroreducible but is in equilibrium with non-hydrated, electroactive pdonH$^+$. The total reduction currents measured at rotating disk electrodes result from the reduction of the pdonH$^+$ and pdon initially present plus the additional pdonH$^+$ formed by the reverse of reaction 2 at the electrode surface. The rate at which reaction 2 responds to changes in the concentration of pdonH$^+$ is sufficiently slow that none of the initially present pdonH$^+$–H_2O is converted to pdonH$^+$ at electrode rotation rates of 2500 rpm or greater. This assertion follows from the currents at $\omega^{1/2} = 40$ and 50 (rpm)$^{1/2}$ in Figure 2E. A straight line drawn through these two points passes through the origin (dashed line in Figure 2E) showing that the currents measured at the higher electrode rotation rates provide information on the initial composition of the solution as if the equilibrium in reaction 2 were "frozen" in place. Rotating disk plateau current measured under these circumstances can be used to obtain estimates of the equilibrium constants for reactions 1 and 2 in Scheme 1. A simple derivation leads to eq 4

$$\frac{I}{I_L - I} = K_H^{-1} + \left(\frac{K_A}{K_H}\right)[H^+]^{-1} \qquad (4)$$

where I is the measured plateau current at rotation rates where the equilibrium of reaction 2 is frozen, I_L is the corresponding Levich current that would be measured if the equilibrium were instantaneously established, and K_A^{-1} and K_H are the equilibrium constants for reactions 1 and 2, respectively. Thus, a plot of $I/(I_L - I)$ vs $[H^+]^{-1}$ should be linear with a slope and intercept that allow K_H and K_A to be estimated. Such a plot is shown in Figure 7A from which K_H and K_A were calculated as 2.0 and 5.6×10^{-3} M^{-1}, respectively. This value of K_A is somewhat greater than the value evaluated by Eckert and Bruice (3.9×10^{-3} M^{-1}) without consideration of the possible hydration reaction.

With values of K_H and K_A in hand, the plateau currents measured at rotation rates where the hydration equilibrium is not frozen can be used to estimate the rate constants for reaction 2. A commercially available simulation program (Digisim) was employed to fit the experimental plateau currents to those calculated for varying values of k_{-2} at several pH values assuming that the proton transfer reactions involved in reaction 1 remained at equilibrium. The results of this procedure are shown in Figure 7B where the lines are calculated and the plotted points are the experimental plateau currents. The data are reasonably well accommodated with a single value of $k_{-2} = 0.5$ s^{-1} at all three pH values. The hydration and dehydration rates of aldehydes and ketones are acid and base catalyzed.[13-16] The fact that a single rate and equilibrium constant account for

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(16) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973.

the plateau currents measured at pH values of 1, 2.2, and 3.2 in Figure 7B indicates an apparent lack of such catalysis of the hydration and dehydration of pdonH$^+$. The reasons may include the weaker basicity of the quinoid oxygen atoms and the positive charge carried by the molecule undergoing hydration.

At pH values above 4, where very little of the pdon is protonated, the plateau currents for its reduction are essentially equal to the diffusion-convection-limited values with no evidence for hydration of the neutral pdon. Since the hydration/dehydration rates are not expected to increase as the pH approaches neutrality, it seems safe to conclude that unprotonated pdon molecules are not significantly hydrated, as was assumed in Scheme 1 and in the calculations involved in Figure 7.

The fact that protonation of the pyridine nitrogen atoms of pdon induces the hydration of the resulting cation is in accord with trends established with other carbonyl compounds where decreases in the electron-donating character of substituents groups in the molecules enhance the extent of their hydration.[13-17] Indeed, Eckert and Bruice suggested that the higher basicity of the nitrogen atoms in the isomeric 4,7-phenanthroline-5,6-dione was a likely indicator for substantial hydration of this molecule. In addition, they pointed to the very small reduction currents obtained for this isomer in acidic supporting electrolytes as support for the presence of substantial hydration. The results obtained in the present study of the more weakly basic 1,10-phenanthroline-5,6-dione isomer are entirely consistent with this conjecture of Eckert and Bruice.[1] The same authors also examined the kinetics of the homogeneous oxidation of a variety of organic substrates by pdon (and its isomers). The reaction rates involved were much smaller than the rate of dehydration of pdonH$^+$$-H_2$O as measured in this study so that the kinetic results reported in ref 1 would not have been seriously affected by the neglect of the hydration/dehydration equilibrium.

The coordination of Os(bpy)$_2^{2+}$ to the pdon ligand also induces the hydration of its carbonyl groups (Figure 5A). The equilibrium constant for the hydration reaction estimated from the plateau current measured at 2500 rpm is 0.9 which is somewhat smaller than the value ($K_H = 2$) obtained when protonation of the nitrogen atoms induces the hydration. The smaller value of K_H could be the result of back-bonding by the Os(II) center to the pdon ligand which would be expected to affect the hydration in the opposite direction from simple protonation. However, a broader set of data is needed to establish the factors that control the hydration equilibria of metal complexes of the pdon ligand.

Evans and Griffith examined the electrochemistry of pdon[6a] and its complexes with several metal cations[6b] in a mixed solvent (50% DMSO$-$50% H$_2$O). Experiments were largely restricted to measurements of half-wave potentials although ratios of anodic to cathodic cyclic voltammetric peak currents that exceeded unity were reported, a feature that was attributed to the adsorption of pdol on the electrode. The addition of Ni^{2+} to solutions of pdon was also observed to cause the polarographic reduction current of the ligand to diminish.[6b] This behavior was assumed to reflect a smaller diffusion coefficient for the complex than for the free ligand. On the basis of the results of the present study, the observations of Evans and Griffith seem more likely to have resulted from hydration of the pdon ligands coordinated to Ni^{2+}, although the extent of hydration may have been smaller in the mixed solvent that they employed.

Conclusions

The primary result of this study was the establishment of Scheme 1 as a reasonable basis to account for the electrochemical behavior of pdon in aqueous acid. Analogous schemes in which metal cations coordinated to the 9,10-phenanthroline group replace the proton as the inducer of the hydration reaction also seem likely to be able to explain the electrochemistry of such complexes. Hydration equilibria like that shown in reaction 2 of Scheme 1 could become important in studies of the kinetics of the oxidation of organic reductants by pdon/pdonH$^+$ in cases where the rates of these oxidations were comparable to the rate of the reverse of reaction 2. The previous kinetic studies of Bruice and Eckert[1] involved slower oxidation reactions which should not have been affected by the processes depicted in Scheme 1.

The large effects of hydration on the redox behavior of the pdon/pdol couple in the adsorbed state will be important in studies of adsorbed metal$-$pdon complexes as electrocatalysts.

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(17) March, J. *Advanced Organic Chemistry Reaction, Mechanisms and Structure*; Wiley: New York, 1992; pp 882–884.