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Electrochemical Assessment of the Stability of $[Os(NH_3)_5(OH_2)]^{2+}$ in Aqueous Solutions

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The $[Os(NH_3)_5(OH_2)]^{2+}$ complex in aqueous acid has been widely regarded as short-lived on the basis of results reported in an early pioneering electrochemical study.[1] More recently, a much longer-lived Os(II) species generated by reduction of $[Os(NH_3)_5(OH_2)]^{3+}$ but of uncertain composition has been reported.[6] In the present study the lifetime of $[Os(NH_3)_5(OH_2)]^{2+}$ in aqueous acid was determined by steady-state voltammetry at a carbon microelectrode and by comparing experimental with simulated cyclic voltammograms obtained for solutions of $[Os(NH_3)_5(OH_2)]^{3+}$. Rate constants for the oxidation of $[Os(NH_3)_5(OH_2)]^{2+}$ by H^+, CH_3COOH (HA), and H_2O were evaluated as $k_H = 17\ M^{-1}\ s^{-1}$, $k_{HA} = 1.2\ M^{-1}\ s^{-1}$, and $k_{H_2O} = 4.1 \times 10^{-4}\ s^{-1}$. These values are shown to be compatible with the data in ref 1 and come close to accounting for the long-lived species described in ref 6 which may be $[Os(NH_3)_5(OH_2)]^{2+}$ itself. A revised value of 4.85 was measured for the pK_A of $[Os(NH_3)_5(OH_2)]^{3+}$. Adsorption of an Os complex on the surface of mercury, but not glassy carbon, electrodes is shown to enhance greatly the rate with which protons undergo direct electroreduction.

The electrochemical behavior of the $[Os(NH_3)_5(OH_2)]^{3+/2+}$ couple in aqueous solutions was first examined by Gulens and Page in a pioneering early study.[1] Their results included the indications that $[Os(NH_3)_5(OH_2)]^{2+}$ is rapidly oxidized by protons to produce $[Os(NH_3)_5(OH_2)]^{3+}$ and H_2. Second-order rate constants for this reaction in the range of ca. $(2-5) \times 10^5\ M^{-1}\ s^{-1}$ were obtained from polarographic and cyclic voltammetric data obtained with strongly buffered solutions of $[Os(NH_3)_5(OH_2)]^{3+}$. Subsequent workers have relied upon this report in analyzing the behavior of solutions of $[Os(NH_3)_5(OH_2)]^{2+}$.[2−6] In one recent report,[6] evidence was presented in support of the proposal that an Os(II) complex produced by the reduction of $[Os(NH_3)_5(OTf)]^{2+}$ ($OTf^- = CF_3SO_3^-$) with Zn(Hg) in aqueous solutions survived for times much longer than would be compatible with the rate constant found by Gulens and Page.[1] It was concluded that a complex of Os(II) that was not $[Os(NH_3)_5(OH_2)]^{2+}$ must have been formed to account for the observed longevity of the reduced complex.[6] However, the actual lifetime of $[Os(NH_3)_5(OH_2)]^{2+}$ itself in aqueous acid is far greater than would be expected from the rate constants in ref 1. In fact, additional voltammetric data reported in the same study with unbuffered solutions of $[Os(NH_3)_5(OH)_2]^{3+}$ (but not analyzed to obtain a rate constant) are not compatible with the high values of the rate constant ($(2-5) \times 10^5\ M^{-1}\ s^{-1}$) obtained in acetate buffers. Much smaller rate constants for the oxidation of $[Os(NH_3)_5OH_2]^{2+}$ by protons result if these data are analyzed by means of digital simulation procedures that were unavailable at the time that Gulens and Page conducted their experiments.[1] Since the $[Os(NH_3)_5(OH_2)]^{2+}$ complex can be a very useful synthon in the preparation of other complexes of $Os(NH_3)_5^{3+}$ and $Os(NH_3)_5^{2+}$,[5,6] we decided to re-examine the electrochemistry of $[Os(NH_3)_5(OH_2)]^{3+}$ and $[Os(NH_3)_5(OH_2)]^{2+}$ in aqueous acid. Our objectives were to employ electrochemical methods to measure the lifetime of the reduced complex by taking advantage of steady-state voltammetry at microelectrodes and by utilizing a commercially available simulation program to analyze cyclic voltammograms.[7] The results reveal that $[Os(NH_3)_5(OH_2)]^{2+}$ reacts with protons at a much lower rate than suggested by the results of Gulens and Page.[1] In addition, we obtained a revised value for the pK_A of $[Os(NH_3)_5(OH_2)]^{3+}$ (4.85) that is somewhat lower than the value estimated in ref 1 (5.3) and regularly quoted in the subsequent literature.

Experimental Section

Materials. $[Os(NH_3)_5(OTf)](OTf)_2$ ($OTf^- = CF_3SO_3^-$) was prepared from OsO_4 (Aldrich) according to the published procedures[8] except that the microcrystalline final product was collected by centrifugation instead of filtration. $[Os(NH_3)_5(OH_2)](OTf)_3$ was prepared by the procedure of Lay et al.[9] CH_3SO_3Na (Aldrich) was recrystallized from H_2O. Other chemicals were reagent grade and were used as received. The pH of unbuffered supporting electrolyte solutions was adjusted by addition of aliquots of 0.1 M NaOH or 0.1 M CH_3SO_3H solutions. Laboratory deionized water was further treated by passage through a purification train (MilliQ Plus).

Apparatus and Procedures. Conventional electrochemical cells and commercially available instrumentation were employed. The 0.24 cm^2 glassy carbon disk electrode (Pine Instrument Co.) was used for both cyclic voltammetric and rotating disk measurements. It was polished with moist 0.05 μm alumina on a polishing wheel before each set of measurements. A microelectrode was constructed by sealing (under vacuum) a carbon fiber (diameter = 0.012 cm) in a fine tapered glass capillary by adapting the procedure of Bard et al.[10] A hanging mercury drop electrode (EG&G Princeton Applied Research Model 303) was employed for some measurements. Potentials were measured and are reported with respect to a saturated calomel electrode (SCE). Experiments were conducted at the ambient laboratory temperature, 24 ± 1 °C.

Results

Cyclic Voltammetry of $[Os(NH_3)_5(OTf)]^{2+}$ and $[Os(NH_3)_5(OH_2)]^{3+}$. In accord with the results of Gulens and Page,[1] we

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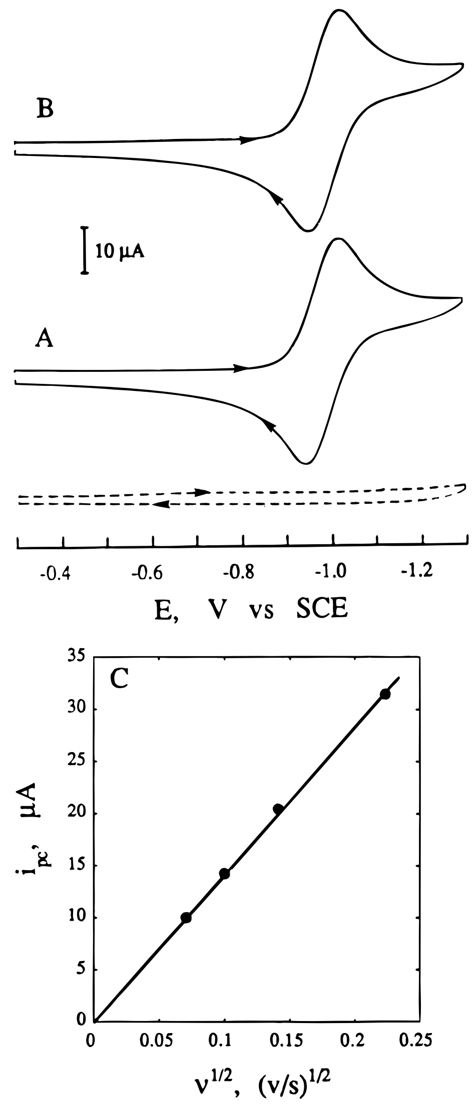

Figure 1. (A) Cyclic voltammogram for 0.81 mM $[Os(NH_3)_5(OH_2)]^{3+}$ in unbuffered 0.1 M CH_3SO_3Na (pH ~ 4). Scan rate: 50 mV s^{-1}. The dashed curve was recorded in the pure supporting electrolyte. (B) As in (A) except that the solution was prepared by dissolution of solid $[Os(NH_3)_5(OTf)](OTf)_2$ just before the voltammogram was recorded. (C) Cathodic peak currents vs the potential (scan rate)$^{1/2}$ for voltammograms like the one in (A).

found unbuffered CH_3SO_3Na to be a good supporting electrolyte in which to inspect the electrochemistry of various $Os(NH_3)_5L^{n+/(n-1)+}$ couples ($L = OTf^-, OH_2, OH^-$). Shown in Figure 1A is a cyclic voltammogram for a 0.8 mM solution of $[Os(NH_3)_5(OH_2)]^{3+}$ in 0.1 M CH_3SO_3Na recorded at the glassy carbon electrode. The average of the two peak potentials, −0.97 V, agrees with that reported by Gulens and Page, and the equality of the two peak currents indicates that the $[Os(NH_3)_5(OH_2)]^{2+}$ product of the reduction is stable for the 5−6 s required to record the voltammogram. In Figure 1B is shown the voltammogram obtained immediately after solid $[Os(NH_3)_5(OTf)](OTf)_2$ was dissolved in the supporting electrolyte solution. It is essentially identical to the voltammogram for $[Os(NH_3)_5(OH_2)]^{3+}$ in Figure 1A. The half-life for aquation of $[Os(NH_3)_5(OTf)]^{2+}$ is known to be ca. 13 min [3] so the similarity of the voltammetric responses in Figure 1A,B means either that the formal potentials of the aqua and OTf^- couples are about the same or that the aquation of $[Os(NH_3)_5(OTf)]^{2+}$ is catalyzed within the diffusion layer at the electrode surface by electron transfer between $[Os(NH_3)_5(OTf)]^{2+}$ and $[Os(NH_3)_5(OH_2)]^{2+}$ (formed by the very rapid aquation of $[Os(NH_3)_5OTf]^{+}$). A similar electron-transfer-catalyzed aquation of $[Os(NH_3)_5X]^{2+}$ ($X^- = Cl^-, I^-$) was proposed by Gulens and Page.[1] The essential identity of the voltammograms in Figure 1A,B means that cyclic voltammetry does not provide a means for distinguishing between the aqua and OTf^- complexes of $Os(NH_3)_5^{3+}$.

The cathodic peak currents of voltammograms like those in Figure 1A,B are proportional to the potential (scan rate)$^{1/2}$ (Figure 1C). From the slope of the line in Figure 1C a diffusion coefficient of 6.3×10^{-6} cm^2 s^{-1} was calculated for $[Os(NH_3)_5(OH_2)]^{3+}$. This value is smaller than that reported by Gulens and Page[1] (9×10^{-6} cm^2 s^{-1}), but it is in line with the reported value for $Ru(NH_3)_6^{3+}$ (6.2×10^{-6} cm^2 s^{-1}).[12]

Cyclic voltammograms recorded at a scan rate of 50 mV s^{-1} with solutions of $[Os(NH_3)_5(OH_2)]^{3+}$ in unbuffered supporting electrolytes between pH 2 and 4 exhibited no evidence of loss of the $[Os(NH_3)_5(OH_2)]^{2+}$ produced at the electrode surface (Figure 2A). At pH values above 4.5 it was necessary to employ buffered supporting electrolytes to prevent the appearance of double peaks caused by the substantial increase in the pH at the electrode surface produced by the reduction of $[Os(NH_3)_5OH]^{2+}$ (upper curve in Figure 2B). With appropriate buffers only a single peak was obtained (lower curve in Figure 2B), and it was possible to monitor the formal potential of the Os(III)/Os(II) couple over a wide range of pH values. As is shown in the Supporting Information, a plot of the formal potential (taken as the average of the cathodic and anodic peak potentials of voltammograms like those in Figure 2A) vs pH consists of horizontal and inclined portions that intersect at pH 4.85 which corresponds to the pK_A for reaction 1. This value is somewhat smaller than the pK_A obtained by Gulens and Page from spectrophotometric measurements, pK_A = 5.3.[1] The pK_A evaluated from electrochemical data was confirmed by a pH titration of a solution of $[Os(NH_3)_5(OH_2)]^{3+}$ with standard base. The midpoint of the titration curve (cf. Supporting Information) also yielded a pK_A value of 4.85. The variation of the formal potential for the Os(III)/Os(II) couple with pH indicated that half-reactions 2a,b apply to the couple.

$$[Os(NH_3)_5(OH_2)]^{3+} = [Os(NH_3)_5(OH)]^{2+} + H^+ \qquad pK_A = 4.85 \quad (1)$$

pH < 4.8:

$$[Os(NH_3)_5(OH_2)]^{3+} + e^- = [Os(NH_3)_5(OH_2)]^{2+} \quad (2a)$$

pH > 4.8:

$$[Os(NH_3)_5(OH)]^{2+} + e^- + H^+ = [Os(NH_3)_5(OH_2)]^{2+} \quad (2b)$$

The Os(II) complex produced in half-reaction 2a or 2b persists in aqueous acidic solutions for several minutes if the concentration of protons is low. For example, curve A in Figure 3 is the current−potential curve recorded at a rotating disk electrode in a 1.1 mM solution of $[Os(NH_3)_5(OH_2)]^{3+}$ in 0.1 M CH_3SO_3Na. The cathodic plateau current of 36 μA is the value expected for the diffusion−convection-limited reduction of $[Os(NH_3)_5(OH_2)]^{3+}$ to $[Os(NH_3)_5(OH_2)]^{2+}$. Curve B in Figure 4 was obtained by treating a more concentrated solution of $[Os(NH_3)_5(OH_2)]^{3+}$ with Zn(Hg) for a few minutes, transferring an aliquot of the reduced solution under argon to the same, deaerated supporting electrolyte used in A, and immediately

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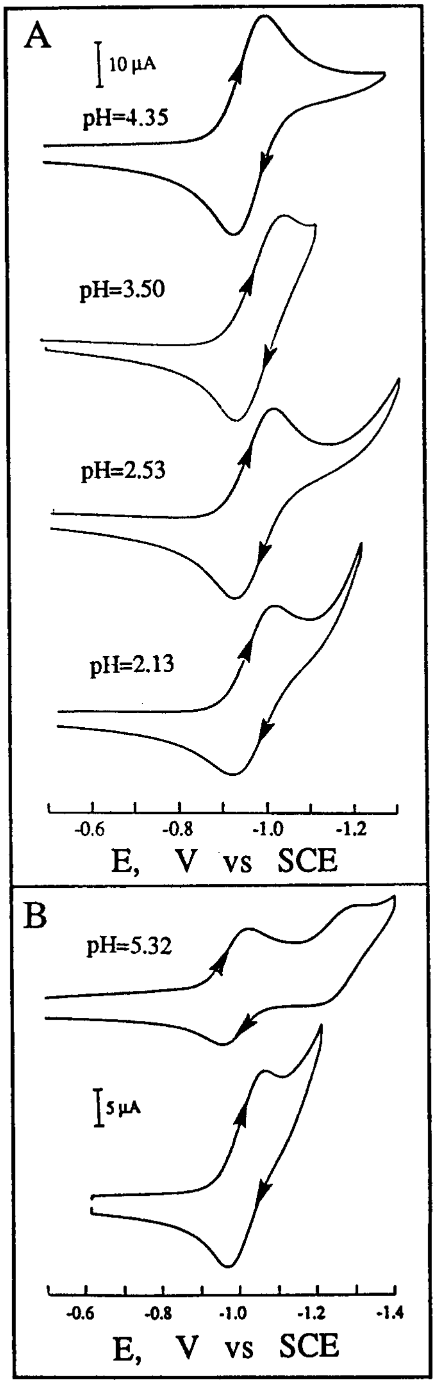

Figure 2. (A) Cyclic voltammograms for 0.72 mM $[Os(NH_3)_5(OH_2)]^{3+}$ in solutions of 0.1 M CH_3SO_3Na adjusted to the indicated pH values with CH_3SO_3H. (B) Top curve, as in (A); bottom curve, after the solution was buffered at the same pH with an acetate buffer (0.01 M).

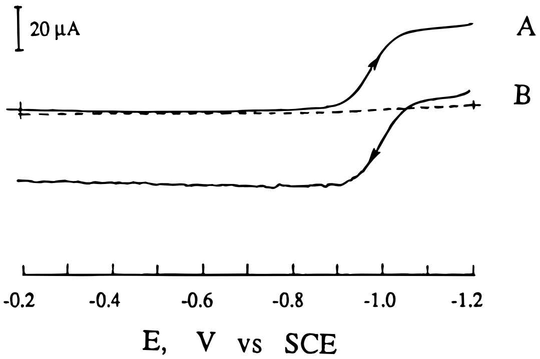

Figure 3. Steady-state current−potential curves recorded at the rotated glassy carbon electrode in 0.1 M CH_3SO_3Na (pH ∼ 4). Rotation rate: 100 rpm. (A) Reduction of 1.1 mM $[Os(NH_3)_5(OH_2)]^{3+}$. (B) Oxidation of 1.1 M $[Os(NH_3)_5(OH_2)]^{2+}$. (The reduction of the Zn^{2+} also present in the solution begins at ca. −1.25 V.) The dashed line shows the response obtained in the absence of either Os complex.

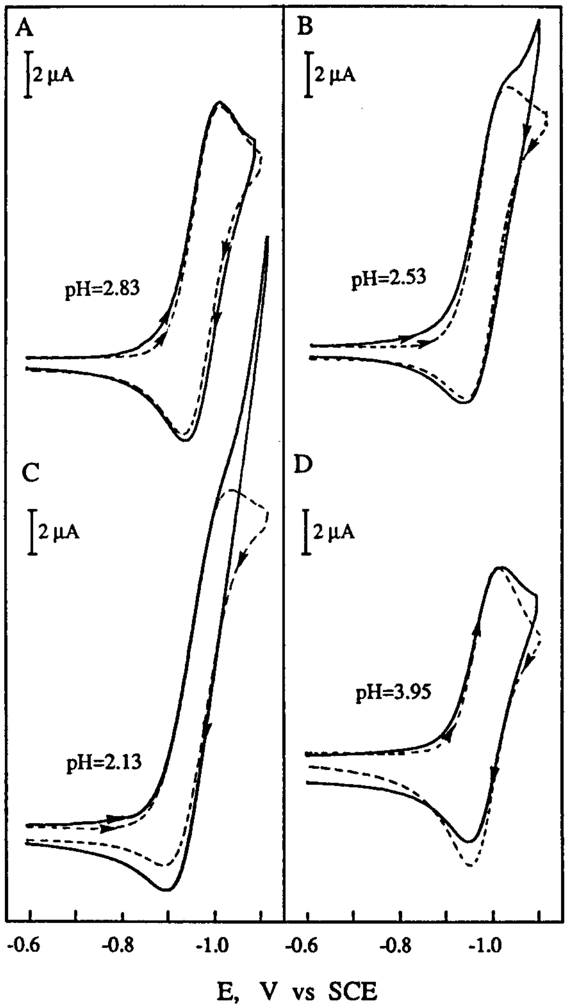

Figure 4. Comparison of experimental (solid curves) with simulated (dashed curves) cyclic voltammograms for the reduction of 0.74 mM $[Os(NH_3)_5(OH_2)]^{3+}$ in unbuffered acidic supporting electrolytes of the specified pH. The simulation was based on the mechanism and parameters given in Scheme 1. Scan rate: 5 mV s^{-1}. The values of k_H and k_{H_2O} used in the simulations were as follows: (A) $k_H = 20\ M^{-1}\ s^{-1}$, $k_{H_2O} = 4.1 \times 10^{-4}\ s^{-1}$; (B) $k_H = 17\ M^{-1}\ s^{-1}$, $k_{H_2O} = 4.1 \times 10^{-4}\ s^{-1}$; (C) $k_H = 12\ M^{-1}\ s^{-1}$, $k_{H_2O} = 4.1 \times 10^{-4}\ s^{-1}$; (D) $k_H = k_{H_2O} = 0$.

recording the current−potential curve at the rotating disk electrode. The current response is almost entirely anodic, showing that the $[Os(NH_3)_5(OH_2)]^{2+}$ produced in the reduction by Zn(Hg) persists for the 2−3 min required to carry out the transfer and record curve B. With time, the anodic plateau current of curve B diminished and the cathodic plateau increased, as expected for the slow conversion of $[Os(NH_3)_5(OH_2)]^{2+}$ into a mixture of $[Os(NH_3)_5(OH_2)]^{3+}$ and $[Os(NH_3)_5(OH_2)]^{2+}$ through oxidation of the reduced complex by protons and air that could not be completely excluded from entering the solution during the continuous rotation of the electrode. It is particularly significant that the half-wave potentials of curves A and B in Figure 4 are essentially identical, as is to be expected if the product of the electroreduction reaction in curve A is the reactant that undergoes electro-oxidation in curve B, namely, $[Os(NH_3)_5(OH_2)]^{2+}$.

Rate of Disappearance of $[Os(NH_3)_5(OH_2)]^{2+}$ from Unbuffered Acidic Solutions. Difficulties in preventing leakage of air into solutions of $[Os(NH_3)_5(OH_2)]^{2+}$ in which rotating electrodes were operating led us to monitor continuously the decrease in the concentration of the reduced complex by using a carbon fiber microelectrode that was maintained at a potential, −0.7 V, where the anodic oxidation of $[Os(NH_3)_5(OH_2)]^{2+}$ proceeded at a diffusion-controlled rate to produce a steady-state current at the microelectrode.[13] A typical current−time curve and a plot of the logarithm of the current vs time are given in the Supporting Information. The latter plot was linear with a slope corresponding to a rate constant for the disappearance of $[Os(NH_3)_5(OH_2)]^{2+}$ of 4.1×10^{-4} s^{-1}. As the concentration of $[Os(NH_3)_5(OH)_2]^{2+}$ decreased, the pH of the unbuffered supporting electrolyte increased.[6] The apparent lack of sensitivity of the rate of the decomposition reaction to this change in pH suggested that water rather than protons was being reduced by the $[Os(NH_3)_5(OH_2)]^{2+}$.

To obtain additional rate data at lower pH values where the reaction rates were faster than was suitable for the steady-state method just described, cyclic voltammetry was employed with solutions of $[Os(NH_3)_5(OH_2)]^{3+}$. The experimental voltammograms were compared with those calculated from a commercially available program (Digisim[7]) with the rate constant for the decomposition reaction adjusted to obtain the best agreement between the experimental and calculated voltammograms. The Digisim program requires that a reaction scheme be specified with appropriate kinetic parameters. The catalytic reaction mechanism that was used is shown in Scheme 1.

The formal potential of half-reaction 3 was set at the value measured at pH values below the pK_A of the Os(III) complex because we were interested in simulating cyclic voltammograms obtained at low pH values. The rate constant for the half-reaction was assigned a large value in keeping with the Nernstian behavior of the Os(III)/Os(II) couple. The equilibrium constant for reaction 4 was assigned a large value because the reaction is irreversible. The calculated voltammograms did not change if the values of k_s and K_4 were increased or decreased by 1 order of magnitude. The actual mechanisms of reactions 4 and 5 are unimportant to the simulation. The essential feature is the stoichiometry of the totally irreversible reactions in which the Os(II) complex is oxidized. The rate constant for reaction 4 was varied in the simulations to obtain the best agreement with experiment. Reaction 5 was also treated as irreversible, and its rate constant was assigned the value of 4.1×10^{-4} s^{-1} on the basis of the kinetic data obtained with the microelectrode. The diffusion coefficients of both complexes were taken as 6.3×10^{-6} cm^2 s^{-1}, and that for H$^+$ was taken as 1×10^{-4} cm^2 s^{-1}.

Scheme 1

$$[Os(NH_3)_5(OH)_2]^{3+} + e^- \overset{k_s}{\rightleftharpoons} [Os(NH_3)_5(OH)_2]^{2+}$$
$$E^\circ = -0.975 \text{ V}, k_s > 10^2 \text{ cm s}^{-1} \quad (3)$$

$$[Os(NH_3)_5(OH)_2]^{2+} + H^+ \xrightarrow{k_H} [Os(NH_3)_5(OH)_2]^{3+} + 0.5H_2$$
$$K_4 > 10^{10} \quad (4)$$

$$[Os(NH_3)_5(OH)_2]^{2+} + H_2O \xrightarrow{k_{H_2O}}$$
$$[Os(NH_3)_5(OH)_2]^{3+} + 0.5H_2 + OH^-$$
$$K > 10^{10}, k_{H_2O} = 4.1 \times 10^{-4} \text{ s}^{-1} \quad (5)$$

In Figure 4 are shown the experimental (solid curves) and the simulated (dashed curves) voltammograms. Reasonable agreement between the measured and calculated curves was obtained using the values of k_H given in the figure caption. At pH 2.53 and 2.13 the calculated peak currents are smaller than the experimental values because the reduction of protons directly at the electrode surface (a process too complex to be reliably included in Scheme 1) overlaps the Os-catalyzed reduction of protons. The values of k_H obtained from the simulations in Figure 4 are reasonably constant with an average value of 17 M^{-1} s^{-1}. The relatively small value of k_{H_2O} obtained from the experiments with the microelectrode ($k_{H_2O} = 4.1 \times 10^{-4}$ s^{-1}) means that reaction 5 in Scheme 1 is unimportant at pH values where reaction 4 proceeds rapidly enough to produce enhanced cathodic peak currents. At pH values above ca. 3.5, reactions 4 and 5 are both too slow to produce significant effects on the cathodic peak current even at scan rates as low as 5 mV s^{-1} (Figure 4D).

In ref 1 a second-order rate constant for reaction 4 of ca. 2×10^5 M^{-1} s^{-1} was calculated. However, this value was obtained from cyclic voltammetric measurements conducted in concentrated acetate buffer solutions where the species being reduced by $[Os(NH_3)_5(OH_2)\ ]^{2+}$ could have included CH_3COOH as well as H$^+$. To determine if this possibility might account for the much larger rate constant reported in ref 1 than the value we obtained in unbuffered solutions, we repeated the cyclic voltammetric experiments of Figure 4 with a supporting electrolyte solution consisting of 0.1 M CH_3SO_3Na + 0.48 M CH_3COOH. The pH of the solution was 2.53, the same value employed in Figure 4A where the source of the protons was 2.95 mM CH_3SO_3H instead of 0.48 M CH_3COOH. The resulting voltammogram (shown in the Supporting Information) exhibited such an intense catalytic current that no cathodic peak or plateau was evident at a scan rate of 5 mV s^{-1}. However, when the scan rate was increased to 50 mV s^{-1}, a cathodic shoulder became evident in the cyclic voltammogram. A voltammogram was calculated with the Digisim for the higher scan rate by adding reaction 6 to those in Scheme 1 to describe the operative reaction mechanism. The value of k_{HA} that

$$[Os(NH_3)_5(OH_2)]^{2+} + CH_3COOH \xrightarrow{k_{HA}}$$
$$[Os(NH_3)_5(OH_2)]^{3+} + 0.5H_2 + CH_3COO^-$$
$$K > 10^{10} \quad (6)$$

produced the best agreement between the calculated and experimental voltammograms (cf. Supporting Information) was 1.2 M^{-1} s^{-1}. With the solution containing 0.48 M CH_3COOH this value of k_{HA} means that reactions 4 and 5 of Scheme 1 contributed very little to the enhanced cathodic peak currents obtained in solutions containing CH_3COOH. The enhanced current is provided almost entirely by reaction 6.

The rate constant of 2×10^5 M^{-1} s^{-1} given by Gulens and Page[1] was calculated without including the possibility of reaction 6 in the mechanism. In the acetate buffer solution employed in ref 1 ($[CH_3COOH] = 1.2$ M, $[H^+] = 5 \times 10^{-5}$ M), the pseudo-first-order rate constant actually measured, $k_{obs} = 10$ s^{-1}, must have been a composite: $k_{obs} = k_{HA}[CH_3COOH] + k_H[H^+]$. With $k_H = 17$ M^{-1} s^{-1}, the second term is negligible and one calculates $k_{HA} = 8$ M^{-1} s^{-1}, which is larger than the value ($k_{HA} = 1.2$ M^{-1} s^{-1}) used to obtain the best agreement between calculated and experimental voltammograms. However, the substantial improvement in the agreement between the two values supports the suggestion that Gulens and Page measured the catalytic reduction of acetic acid and not protons.

Adsorption of Catalytically Active Species on the Surfaces of Electrodes. Gulens and Page examined the electrochemistry

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of $[Os(NH_3)_5(OH_2)]^{3+}$ at mercury electrodes,[1] while glassy carbon electrodes were employed in the present study. The magnitudes of the currents for the catalytic reduction of protons in unbuffered acidic solutions as reported by Gulens and Page correspond to values of k_H much larger than the value we measured at glassy carbon electrodes. To examine the origin of this discrepancy, we carried out experiments with a hanging mercury drop electrode under conditions similar to those used by Gulens and Page. For example, the solid curve in Figure 5A shows the voltammogram obtained with a hanging mercury drop electrode in a supporting electrolyte adjusted to pH 2.53 at a scan rate of 50 mV s^{-1}. There is substantial catalytic current, but if a glassy carbon electrode is used in the same solution (dashed curve in Figure 5A), there is essentially no catalyzed reduction of protons. This comparison makes it clear that the catalysis is much enhanced on the mercury electrode. The catalytic reduction of protons at mercury is so rapid that the anodic current for the oxidation of $[Os(NH_3)_5(OH_2)]^{2+}$ generated in the solution at the electrode surface is masked by the large cathodic current that continues to flow at the potential (−0.95 V) where the anodic peak would appear (solid curve in Figure 5A).

The higher catalytic current density at mercury than at glassy carbon electrodes appears to be the result of the spontaneous adsorption on Hg (but not on glassy carbon) of an Os complex that is highly active as an electrocatalyst for the direct, electrochemical reduction of protons. The spontaneous adsorption of such an electrocatalyst was demonstrated by results obtained with a much more dilute solution of $[Os(NH_3)_5(OH_2)]^{3+}$ as summarized in Figure 5B,C. The solid curve in Figure 5B is a cyclic voltammogram recorded immediately after the mercury electrode was placed in a 5×10^{-5} M solution of $[Os(NH_3)_5(OH_2)]^{3+}$ in a supporting electrolyte containing 10^{-3} M protons. The concentration of $[Os(NH_3)_5(OH_2)]^{3+}$ is so low that its reduction produces only the small wave near −0.95 V. The prominent wave near −1.1 V results from the catalyzed reduction of protons. The dashed curve in Figure 5B, recorded in the absence of $[Os(NH_3)_5(OH_2)]^{3+}$, shows that the uncatalyzed reduction of protons does not commence before −1.4 V. The curves in Figure 5C were recorded at the same mercury electrode at various later times. The current for the reduction of protons increased and the peak potential shifted to even more positive values, presumably because the quantity of electrocatalyst adsorbed on the electrode surface increased. To demonstrate that the catalyst was attached to the electrode surface, the solution used in Figure 5C was carefully drained away from the hanging mercury drop electrode and replaced with the Os-free supporting electrolyte. The cyclic voltammogram shown in Figure 5D was then recorded. The reduction of protons continued to be catalyzed to yield a prominent cathodic wave which persisted for several minutes. However, when the mercury drop was dislodged and replaced by a fresh electrode, a cyclic voltammogram that matched the dashed curve in Figure 5B was obtained.

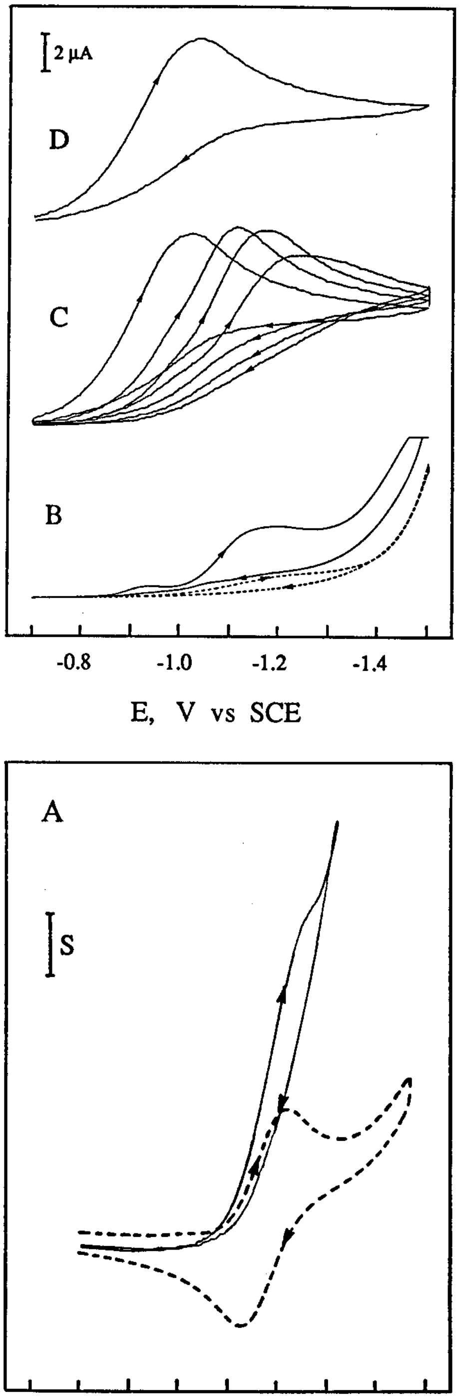

Figure 5. Cyclic voltammetry of $[Os(NH_3)_5(OH_2)]^{3+}$ recorded at a hanging mercury drop electrode. (A) Solid curve: 0.88 mM $[Os(NH_3)_5(OH_2)]^{3+}$ in 0.1 M CH_3SO_3Na adjusted to pH 2.53 with CH_3SO_3H. $S = 2$ μA. Dashed curve: Voltammogram obtained in the same solution with a glassy carbon electrode. $S = 12.5$ μA. Scan rate: 50 mV s^{-1}. (B) Solid curve: Mercury electrode; 0.05 mM $[Os(NH_3)_5(OH_2)]^{3+}$ in 0.1 M CH_3SO_3Na adjusted to pH 3 with CH_3SO_3H. Dashed curve: Voltammogram recorded in the pure supporting electrolyte. Scan rate 50 mV s^{-1}. (C) Repeat of (B) after the mercury electrode had been exposed to the solution for (from right to left) 10, 15, 25, and 85 min. (D) Voltammogram obtained with the electrode used in (C) after the solution was carefully replaced with the pure supporting electrolyte without dislodging the hanging mercury drop.

An attempt was made to obtain an electrochemical response from the species on the mercury electrode surface that is responsible for the catalytic reduction of protons. However, transfer of a mercury electrode like the one in Figure 5D to a neutral, 0.1 M solution of CH_3SO_3Na, where the catalytic current is much smaller, produced no detectable response from a surface-confined species. Thus, either the active form of the electrocatalyst is present in quantities too small to detect or else it is not electroactive within the accessible range of potentials. One possibility is that the catalyst is $[Os(NH_3)_5(OH_2)]^{2+}$ adsorbed in minute quantities and more catalytically active in the adsorbed state than in solution. Whatever the nature of the electrocatalyst, its presence on the mercury electrode surface is evident from the results in Figure 5 which help to explain the otherwise puzzling difference between the high rates of catalytic reduction of protons in unbuffered supporting electrolytes observed by Gulens and Page[1] and those observed at glassy carbon electrodes in the present study.

Discussion

The results of this re-examination of the electrochemical behavior of the $[Os(NH_3)_5(OH_2)]^{3+/2+}$ couple have shown that the reduced form of the complex is considerably longer-lived in aqueous media than had been suggested in the earlier report of Gulens and Page.[1] The combination of the data presented in this study indicates that $[Os(NH_3)_5(OH_2)]^{2+}$ reduces water, protons, and general acids along three parallel reaction pathways with the dominant pathway determined by the solution pH and the concentration of general acid (HA) present. The observed rate constant for the oxidation of the reduced complex, k_{obs}, can be expressed as in eq 7 and the values estimated for the

$$k_{obs} = k_{H_2O} + k_H[H^+] + k_{HA}[HA] \qquad (7)$$

three rate constants are $k_H = 17\ M^{-1}\ s^{-1}$, $k_{HA} = 1.2\ M^{-1}\ s^{-1}$ for HA = CH_3COOH, and $k_{H_2O} = 4.1 \times 10^{-4}\ s^{-1}$. The relative values of these rate constants are not unreasonable considering the relative strengths of the three acids. The rate constants are also compatible with the results of Gulens and Page. In particular, they account for the higher catalytic currents in concentrated acetate buffers than in unbuffered solution at the same pH and the lack of catalytic reduction currents in unbuffered solutions of $[Os(NH_3)_5(OH)]^{2+}$ at pH 7 at scan rates as low as 10 mV s^{-1}.[1] The small catalytic currents reported at pH 4 (unbuffered) by Gulens and Page probably resulted from the reduction of protons directly at the electrode surface catalyzed by an adsorbed complex as demonstrated in Figure 5. The same phenomenon, i.e., catalysis by an adsorbed Os complex, would also account for the observation[1] that controlled potential electrolysis of solutions of $[Os(NH_3)_5OH_2]^{3+}$ at mercury pool electrodes consumed more than one electron per Os(III) and led to the continuous reduction of protons.

The value of the pK_A for $[Os(NH_3)_5(OH_2)]^{3+}$ evaluated from both the pH dependence of the formal potential of the $[Os(NH_3)_5(OH_2)]^{3+/2+}$ couple and by direct titration of a solution of $[Os(NH_3)_5(OH_2)]^{3+}$ was pK_A = 4.85. This value is about 0.5 pK_A units lower than the value obtained by Gulens and Page from a less direct spectrophotometric method.[1] We believe the lower value to be the more reliable estimate. It corresponds to a weaker acidity of the Os than of the corresponding Ru complex (pK_A = 4.1 [14]) which may be attributed, in part, to the larger size of the Os complex.

The results obtained in this study did not provide evidence for a second form of the reduced Os(II) complex as proposed by Call et al.[6] Contrary to their report, we found that 100% of the Os(II) complex produced by reduction of $[Os(NH_3)_5OTf]^{2+}$ or $[Os(NH_3)_5OH_2]^{3+}$ with Zn(Hg) gives rise to an anodic response at the same potential where $[Os(NH_3)_5(OH_2)]^{3+}$ undergoes electroreduction (Figure 4A) and where the product of the electroreduction is electro-oxidized (Figure 1). The rate constant we estimated for the reduction of H_2O by $[Os(NH_3)_5(OH_2)]^{2+}$, $k_{H_2O} = 4.1 \times 10^{-4}\ s^{-1}$, is only ca. three times larger than the value evaluated by Call et al.[6] from the rate of disappearance of the species that reacted rapidly with acetone (at 24 instead of 22 °C) in solutions prepared by the reduction of $[Os(NH_3)_5OTf]^{2+}$ with Zn(Hg). Given the uncertainties inherent in the kinetic measurements and the fact that Call et al.[6] were unable to detect the anodic electrochemistry of $[Os(NH_3)_5(OH_2)]^{2+}$ that was observed by Gulens and Page[1] and in the present study, we believe that the reduced complex examined by Call et al. may, in fact, have been $[Os(NH_3)_5(OH_2)]^{2+}$.

The pH dependence of the formal potential of the $[Os(NH_3)_5(OH)]^{2+}/[Os(NH_3)_5(OH_2)]^{2+}$ couple shown in Figure 3A has consequences when Zn(Hg) is used to reduce the Os(III) complex. If the reduction of H_2O by the Os(II) complex causes the pH of the solution to increase above ca. 5.6, so that the formal potential of the Os(III)/Os(II) couple becomes more negative than ca. −1.0 V, Zn(Hg) becomes too weak a reductant to reduce $[Os(NH_3)_5OH]^{2+}$ and preparative procedures that depend upon the continuous reduction of this complex will fail. This feature may be one of the reasons that freshly activated Mg, a much stronger reductant, is sometimes specified as the reducing agent to be used in preparing solutions of Os(II).[15] If the pH of reactant solutions is controlled appropriately, we have observed Zn(Hg) to be an entirely satisfactory chemical reductant of $[Os(NH_3)_5(OH)]^{2+}$ as well as $[Os(NH_3)_5(OH_2)]^{3+}$.

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Supporting Information Available: Three figures containing (i) a plot of the formal potential of the $[Os(NH_3)_5(OH_2)]^{3+/2+}$ couple vs pH, (ii) the pH of a solution of $[Os(NH_3)_5(OH_2)]^{3+}$ during its titration with standard NaOH, (iii) the time dependence of the steady-state anodic current for the oxidation of $[Os(NH_3)_5(OH_2)]^{2+}$ measured with a carbon microelectrode and the corresponding plot of ln(current) vs time, and (iv) cyclic voltammograms for the reduction of $[Os(NH_3)_5(OH_2)]^{3+}$ in the presence of 0.48 M CH_3COOH at scan rates of 5 and 50 mV s^{-1} and a voltammogram calculated using Digisim at the higher scan rate (3 pages). Ordering information is given on any current masthead page.

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