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Electrochemical Study of Aquapentaammineruthenium(II) Using Activated Glassy-Carbon Electrodes

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Direct electrochemical evidence has been obtained for the Ru(IV)/Ru(III) couples $[Ru^{IV}(NH_3)_5(O)]^{2+}/[Ru^{III}(NH_3)_5(OH)]^{2+}$ and $[Ru^{IV}(NH_3)_5(O)]^{2+}/[Ru^{III}(NH_3)_5(OH_2)]^{3+}$ by using activated glassy-carbon electrodes.

Introduction

The characterization of the oxoruthenium(IV) complex[1] $[Ru(bpy)_2(py)O]^{2+}$ (bpy is 2,2'-bipyridine; py is pyridine) has led to investigations of the properties[2] of ruthenium oxo compounds, their involvement in proton-coupled electron transfer,[3] and their catalytic activity toward the oxidation of organic substrates[4] and, more recently, chloride and water.[5] Inasmuch as the relative stabilities of oxidation states II and III in ruthenium complexes are greatly influenced by the nature of the ligands,[6] we sought to form and characterize complexes in which the oxo group coexists with electron-donating ligands. Such complexes would allow comparisons to be made that could lead to insight concerning the effects of changes in the coordination environment on redox behavior and hopefully lead to the preparation of a family of redox catalysts with a wider range of potentials and selectivity. Moreover, the relatively negative reduction potentials associated with Ru(III)/Ru(II) couples where the ruthenium is bound to electron-donating ligands could result in compounds in oxidation state II that are capable of functioning as two-electron reductants.

Although the electrochemistry of the pentaammine complexes of ruthenium has been studied by many workers,[6b,7] such studies have led only to information concerning the III/II couple. However, when the complex $[Ru(NH_3)_5OH_2]^{3+}$ is examined over the pH range 1–9 with glassy carbon as the working electrode, we have been able to observe an additional wave that *we attribute to a Ru(IV)/Ru(III) couple involving the oxo complex* $[(NH_3)_5Ru^{IV}=O]^{2+}$. In order to avoid problems associated with nonequilibrium proton content, processes of the type $[Ru^{III}(NH_3)_5OH]^{2+} \rightleftharpoons [Ru(NH_3)_5O^{2+}]^{2+}$ may proceed by proton-coupled electron-transfer mechanisms and previous work has shown that this can lead to kinetic effects both in chemical reactions[3] and in electrode processes.[8] The key to our success in observing the Ru(IV)/Ru(III) couple in this work has been our taking advantage of the ability of carbon-based electrodes to be "activated" toward redox processes of this kind by anodization.[8a]

Experimental Section

Materials. $[Ru(NH_3)_5OH_2]_2(S_2O_6)_3\cdot2H_2O$ was used as a source of $[Ru(NH_3)_5OH_2]^{3+}$. The complex, which was first reported by Gleu,[9] was prepared by dissolving freshly prepared $[Ru(NH_3)_5O-H](S_2O_6)$[9] in the minimum volume of hot 2–3 M trifluoromethanesulfonic acid and allowing it to crystallize. In a second preparation, 1.5 M dithionic acid was used and the product crystallized from aqueous ethanol. The dithionic acid was prepared by passing an aqueous solution of $Na_2S_2O_6\cdot2H_2O$ through Dowex 50W-X8 ion-exchange resin in the H+ form. The purity of the compound was tested by converting a weighed amount of the salt into $[Ru(NH_3)_5Cl]^{2+}$ by heating in hydrochloric acid and then comparing the electronic spectrum with that of an authentic sample of $[Ru(NH_3)_5Cl]Cl_2$ that was prepared from $[Ru(NH_6)_6]Cl_3$.[10] The spectra in 1 M HCl were

found to be identical with a λ_{max} at 327 nm and molar absorptivity 1.76×10^3 mol⁻¹ dm³ cm⁻¹. Anal. Calcd for $Ru_2H_{38}N_{10}O_{22}S_6N$; N, 15.14; H, 4.14. Found: N, 14.86; H, 4.28.

Buffers and pH Measurements. The solutions that were used for cyclic voltammetry contained a buffer at a concentration of 0.02 M and $NaClO_4$ at 0.1 M as supporting electrolyte. Solutions were made in water distilled over alkaline potassium permanganate. The following buffers were used: for the pH range 2.7–5.3, potassium hydrogen phthalate with appropriate amounts of $HClO_4$ or KOH; for the range 6.2–7.5, $K_2HPO_4/HClO_4$; for pH 7.9–8.7, tris(hydroxymethyl)-aminomethane/$HClO_4$. For values below pH 2.7 appropriate concentrations of $HClO_4$ were used. At the conclusion of each electrochemical run, the pH of the test solution was determined with a Radiometer PhM62 pH meter equipped with separate glass and reference electrodes that had been calibrated by using two standard buffers spanning the pH value that was being determined.

Electrochemical Measurements. Cyclic and differential-pulse voltammetry were carried out on a PAR Model 174A potentiostat in conjunction with a locally produced triangular-wave generator. Cyclic voltammograms were run at scan rates of 20, 50, 100, and 200 mV/s. Differential-pulse measurements were determined at scan rates of 5 mV/s and a modulation amplitude of 5 mV. A three-electrode system was used with a saturated sodium chloride calomel electrode[11] as a reference electrode, Pt wire as an auxiliary electrode, and a Teflon-shrouded disk electrode (Pt, Au, graphite paste, or glassy carbon) as the working electrode. The test solutions were kept under argon during the measurement and contained the complex at a concentration of $(1–2) \times 10^{-3}$ M. Measurements were taken at room temperature (24 ± 2 °C).

Activation of Electrodes. As mentioned above, the couple attributed to $[Ru(NH_3)_5O]^{2+}/[Ru(NH_3)_5OH_2]^{3+}$ could be observed only when glassy-carbon electrodes that had been activated in a prescribed way were used. The treatment involved maintaining the electrodes at positive potentials near the anodic decomposition potential of the aqueous buffered medium (e.g. +1.6V at pH 1–3; +1.5 V at pH 3–5; +1.4 V at pH 5–8) for 6–9 min and then exposing the electrode briefly

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(3) (a) Binstead, R. A.; Moyer, B. A.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2897. (b) Gilbert, J. A.; Gersten, S. W.; Meyer, T. J. *Ibid.* **1982**, *104*, 6872.
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(8) (a) Cabaniss, G. E.; Diamantis, A. A.; Linton, R. W.; Murphy, W. R., Jr.; Meyer, T. J. *J. Am. Chem. Soc.*, in press. (b) Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3978. (c) Engstrom, R. C. *Anal. Chem.* **1982**, *54*, 2310.
(9) Gleu, K.; Rehm, K. *Z. Anorg. Allg. Chem.* **1936**, 237.
(10) Pell, S.; Armor, J. N. *Inorg. Chem.* **1973**, *12*, 873.
(11) All potentials are referenced vs. the saturated sodium chloride calomel electrode, which is +0.234 V vs. the normal hydrogen electrode.[13a]

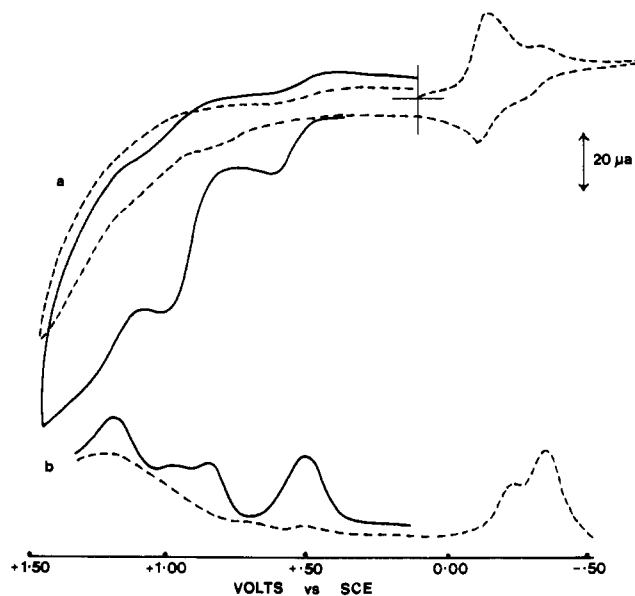†The University of Adelaide.
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Figure 1. (a) Cyclic voltammogram of [Ru(NH₃)₅OH₂]³⁺ at pH 5.30 using an activated glassy-carbon electrode (—) and a polished glassy-carbon electrode (- - -) at a scan rate of 100 mV/s. (b) Differential voltammogram of *a* obtained at scan rates of 5 mV/s and a modulation amplitude of 5 mV.

to a negative potential (−0.6 to −0.8 V) until the current returned to the normal background value. During the exposure to positive potentials, large initial anodic currents of up to 100 μA were observed. Electrodes treated in this way were "activated" and were capable of generating waves in cyclic voltammograms and peaks in differential-pulse experiments, which were not observed when Pt, Au, or untreated grahite-paste or glassy-carbon electrodes were used. The activation of the electrode persisted after rinsing or sonicating in distilled water; the electrodes could be used repeatedly in several runs, at various pH values, over periods of at least 3 days without losing their activity. Polishing the surface with diamond paste, or better with Al₂O₃ (1 μm) followed by diamond paste, and sonicating in distilled water restored the electrode to its inactive form. The background voltammograms obtained from such activated electrodes in degassed buffer had a difference between i_c and i_a of 8–12 μA in the potential range +1.1 to −0.8 V at scan rates of 100 mV/s, as compared to 4–6 μA observed with freshly polished and sonicated electrodes under comparable conditions. Harsher treatment of the electrodes than the one described produced background currents unacceptable for cyclic voltammetry. Analogous treatment of graphite-paste electrodes also produced active behavior.[12] Au and Pt electrodes, however, were unaffected.

Spectra. Absorption spectra in the visible and ultraviolet regions were obtained on a Bausch & Lomb Spectronic 2000 spectrophotometer. The large-scale electrolyses were attempted with both reticulated vitreous carbon electrodes (12 holes/linear in.; ERG, Inc.) and 15-mm diameter glassy-carbon disks (Atomergics) activated as described above. Titration with ceric ion was attempted with a solution of (NH₄)₂Ce(NO₃)₆ (primary standard grade; G. F. Smith) in 1 M HClO₄.

Results

Voltammograms Using Activated Electrodes. The electrochemistry of [Ru(NH₃)₅(OH₂)]³⁺ was investigated over the pH range 1–8.7 by cyclic and differential-pulse voltammetry. Figures 1 and 2 show the results of typical experiments. In the 0- to −0.6-V region, the III/II redox couple is clearly visible irrespective of the type of electrode used, i.e. Au, Pt, activated or nonactivated glassy-carbon, or graphite paste. However, in the 0–1.5-V region there are two additional anodic waves that are resolved only when an activated glassy-carbon electrode is used for the analysis. It should be noted that neither
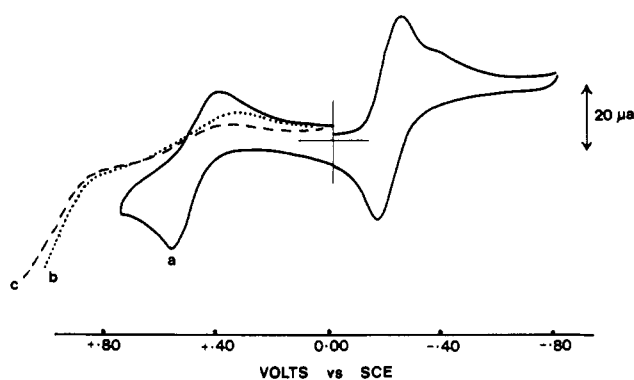
(12) Rice, M. E.; Galus, Z.; Adams, R. N. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *143*, 89.

Figure 2. Cyclic voltammogram of [Ru(NH₃)₅OH₂]³⁺ at pH 3.72 using an activated glassy-carbon electrode. Switching potentials (scan rate 50 mV/s): (a) +0.75 V; (b) +1.20 V; (c) +1.40 V.

Table I. Peak Separations ΔE_p and ($E_{1/2}$) Values for the IV/III and III/II Couples at Different Scan Rates[a]

	scan rate, V/s			
pH	0.020	0.050	1.00	2.00
	IV/III Couple			
2.25	0.190	0.190	0.275	...
	(0.725)	(0.725)	(0.712)	...
4.75	0.130	0.165	0.210	0.255
	(0.415)	(0.415)	(0.420)	(0.420)
6.57	0.165	0.190	0.225	0.265
	(0.380)	(0.380)	(0.380)	(0.390)
7.90	0.170	0.205	0.230	0.285
	(0.295)	(0.300)	(0.305)	(0.305)
	III/II Couple			
2.74	0.060	0.075		0.090
	(−0.160)	(−0.160)	...	(−0.160)
4.72	0.070	0.085	0.100	...
	(−0.205)	(−0.200)	(−0.200)	...
6.57	0.070	0.080	0.080	0.090
	(−0.305)	(−0.310)	(−0.315)	(−0.310)

[a] ΔE_p and $E_{1/2}$ values (in parentheses) in V vs. SSCE.

of these waves is in the background nor do they arise from the S₂O₆²⁻ anion used as the counterion of the complex Ru salt. These waves, when observed with a nonactivated carbon electrode, Au, or Pt, appear at best as slight shoulders, often merging with the oxidative background of the medium. The reductive waves associated with these two oxidations are less well-defined, giving rise to a broad wave in the region of +0.3 to +0.4 V. If the scan direction is reversed after the first anodic wave, the peak current of the broad reduction increases, indicating that they are associated.

It seems reasonable that the first oidative wave and its reducible counterpart can be assigned to the Ru(IV)/Ru(III) interconversion. The peak-to-peak potential separation of the oxidative and reductive waves ($\Delta E_p = E_{p,a} - E_{p,c}$) increases with scan rate, as can be seen from the data at selected pH values given in Table I, which is characteristic of a moderately slow ("quasi-reversible") charge-transfer process.[13b]   By contrast, the ΔE_p value for the III/II couple is relatively constant (ca. 60–65 mV) in the range of scan rates investigated, demonstrating that this redox process is several order of magnitude faster than the IV/III process. The increase in the ΔE_p value for the IV/III couple at faster scan rates is consistent with the operation of kinetic factors that slow the rate of electron transfer at the electrode surface and is associated with the electrode activation requirements of proton-coupled electron-transfer steps. When peak currents were

(13) (a) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980; inside back cover. (b) *Ibid.* p 230. (c) *Ibid.* pp 190–196. (d) *Ibid.* p 195. (e) *Ibid.* p 218.

plotted vs. (scan rate)$^{1/2}$, a good linear relationship was observed with a high correlation coefficient (>0.990), indicating that the process is diffusion controlled and adsorption of the ruthenium complex on the electrodes is not involved.[13e] As noted in a related paper,[8a] the effects observed by activating the electrodes are not isolated to the aqua pentaammine complex and appear to be a general feature of many molecules. The most dramatic effects are observed for redox couples where proton composition problems can exist.

Differential-pulse voltammetry with glassy-carbon electrodes provides plots of Δi_p vs. E such that the redox couples give rise to peaks. This technique has been useful in revealing the presence of redox couples occurring in the vicinity of the solvent oxidative decomposition limit,[5a,14] as can be seen clearly in Figure 1b. In addition, monitoring the appearance of these peaks during the activation process has been useful in devising the conditions and procedures described in the Experimental Section for the activation of the electrodes. The increased charge-transfer rate exhibited at activated electrodes is manifested by larger Δi_p(max), decreased peak width at half-height, and a shift of the peak potential to more negative values (e.g., a decrease in the activation energy for the charge transfer).[13c] From the above as criteria, conditions for treating the electrodes could be developed that produced an improved response, without at the same time giving rise to excessively large background currents.

Additional information concerning the electrode charge-transfer processes is offered by the peak width at half-height in the differential-pulse voltammograms. Data were obtained at 20 different pH values for which the peak width at half-height ranged from 0.115 to 0.200 V (mean 0.160) and from 0.093 to 0.120 V (mean 0.110) for the IV/III and III/II couples, respectively. For reversible charge-transfer processes, the limiting peak width at half-height ($w_{1/2}$) is given by eq 1

$$w_{1/2} = \frac{3.52RT}{nF} = \frac{90.4 \text{ mV}}{n} \quad (T = 25 \text{ °C}) \quad (1)$$

(where n is number of electrons) as the modulation amplitude tends toward zero.[13d] All of the values of $W^{1/2}$ observed for both couples are larger than 0.0904 V, consistent with one-electron-transfer processes that occur with moderate rates of heterogeneous charge transfer.

Effect of pH on the Reduction Potentials. The effect of pH on the reduction potential of the IV/III and III/II couples is shown in Figure 3. The III/II redox potential is independent of pH up to pH 4, with an average value of –0.158 V. Above pH 4, the $E_{1/2}$ value varies linearly with a slope of –0.057 V/pH (standard error 0.002 V), indicative of a one-proton one-electron process. The two lines intersect at pH 4.02.

The plot of the IV/III redox potential vs. pH also shows a discontinuity at pH 4.0. If the maxima of the differential-pulse voltammograms are used to determine the redox potential, a slope of –0.070 V/pH (standard error 0.002 V) is obtained in the pH region 4.75–8.67, while a slope of –0.059 V/pH (standard error 0.002 V) is obtained from cyclic voltammetry data. Below pH 4, a slope of –0.108 V/pH (standard error 0.005 V) is obtained from differential–pulse voltammetry data and a slope of –0.110 V/pH results from cyclic voltammetry data (note that only three $E_{1/2}$ values were obtained by this technique in this pH region). The theoretical slope for a one-proton one-electron redox process is 0.059 V/pH and for a two-proton one-electron process is 0.118 V/pH.[15] Comparison of the cyclic voltammetry data with

(14) (a) Takeuchi, K. J.; Samuels, G. J.; Gersten, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1407. (b) Takeuchi, K. J.; Samuels, G. J.; Meyer, T. J., manuscript in preparation.
(15) Sawyer, D. T.; Roberts, J. L. "Experimental Electrochemistry for Chemists"; Wiley: New York, 1974; pp 191–2.
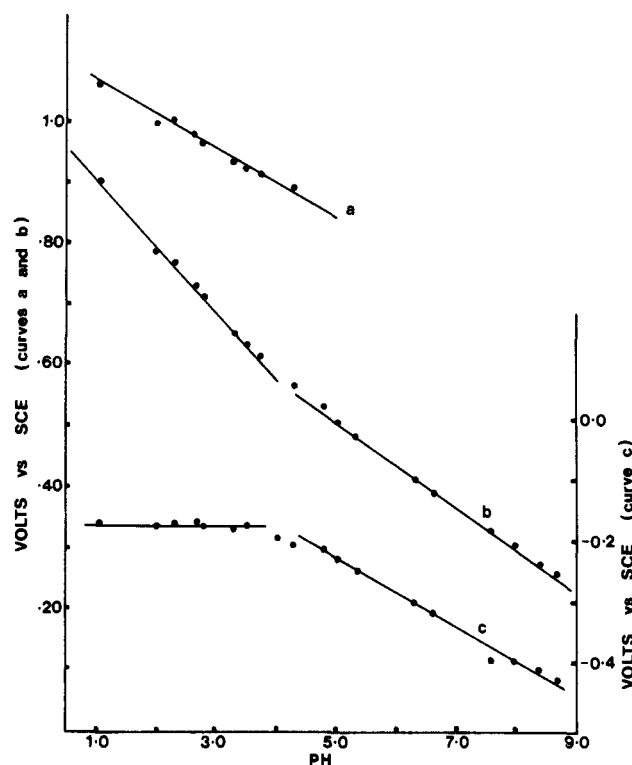
Figure 3. Effect of pH on reduction potential (straight lines calculated by linear regression): (a) E_{max} of differential-pulse voltammograms for the redox couple more positive than the IV/III couple (potential scale on left hand side); (b) E_{max} of differential-pulse voltammograms of the IV/III couple (potential scale on left hand side); (c) $E_{1/2}$ for the III/II couple (potential scale on right hand side).

these predictions allows the conclusion that the IV–III redox process is one-proton one-electron above pH 4 and is two-proton one-electron below pH 4. This is compelling evidence for the one-electron nature of the wave assigned to the IV/III redox process. The discrepancy between the cyclic and differential-pulse voltammetry measurements is likely due to the way that slow heterogeneous charge transfer is manifested in the two techniques. Assuming that the heterogeneous electron-transfer reaction is equally slow in both directions, the cyclic voltammetry response will simply show an increased value of ΔE_p, and the method normally used to calculate $E_{1/2}$ = $(E_{p,a} - E_{p,c})/2$ will yield essentially the true thermodynamic value of $E_{1/2}$, since the kinetic effects will cancel themselves out. This is not the case with differential-pulse voltammetry. Differential-pulse voltammetry responds to slow charge-transfer kinetics in the same way as linear-sweep voltammetry or polarography, e.g. the measured $E_{1/2}$ shifts away from the thermodynamic $E_{1/2}$ as the rate decreases.[13c] Therefore, any charge-transfer kinetics, whether due to innate mechanistic features or electrode activation sensitivities, will add rather than cancel.

Attempts were made to prepare the $[(NH_3)_5RuO^{2+}]$ species electrochemically and chemically. Oxidation with a large surface area glassy-carbon electrode or a reticulated vitreous carbon electrode that had been activated as described above produced n values consistently greater than 1 and residual currents above background. Titration with ceric ion using organic redox indicators like phenylanthranilic acid produced low stoichiometries. This is likely due to preferential oxidation of the indicator by the Ru(IV) species. Further efforts are being made to prepare the oxo species, but initial results are not encouraging apparently because of the instability of the Ru(IV) complex.

In addition to the waves described above, two additional oxidative waves appear at more positive potentials. The first

of these has a distinct E_p (anodic) maximum in the region +0.8 to +1.10 V whereas the second appears as a shoulder on the anodic decomposition of the buffer. In differential-pulse voltammograms the former gives rise to a peak of about the same height and width at half-height as the IV/III wave. The peak is particularly sharp and intense in the pH 1–3 region. The peak potential shows a pH dependence of −0.056 V/pH (standard error 0.004 V) in the region pH 1.00–3.70. At higher pH values, there is no regular dependence on pH and an additional shoulder alters the symmetry of the peak. The peak width at half-height suggests a one-electron transfer and quasi-reversible behavior similar to that of the IV/III wave. The last anodic peak occurs at about +1.20 V; it is well-defined in the pH range 4.75–6.24. Outside this range, however, it is reduced to a shoulder on a base line that ascends steeply toward the potential of the oxidative decomposition of the medium.

When phthalate (or acetate) buffers are used for the pH range 2.74–5.30 an additional wave is seen both in cyclic voltammetry and in differential-pulse experiments at potentials of −0.35 to −0.36 V. The reduction potential, which is independent of pH, is attributed to the formation of the carboxylato complex $Ru(NH_3)_5(phthalate)$. The $E_{1/2}$ of other (carboxylato)pentaammineruthenium(III) complexes correlates with the pK_a of the carboxylic acid,[16] and on that basis the observed $E_{1/2}$ is consistent with the reported values. Reaction of carboxylato ligands with $[Ru(NH_3)_5OH_2]^{2+}$ proceeds rapidly, and use is made of this fact to prepare the Ru(III) complexes[17] that are formed only slowly by the anation of $[Ru(NH_3)_5OH_2]^{3+}$.[18] The electrochemical behavior of the system is entirely consistent with the reduction of Ru(III) to Ru(II), anation of Ru(II) as $[Ru(NH_3)_5OH_2]^{2+}$, and oxidation of the resulting phthalato complex to Ru(III) at the electrode. As might be expected, the height of the wave at −0.350 V is increased by conditions favoring accumulation of the reduction product such as slow scan rates and repeated cycling or by maintaining the electrode at potentials more negative than that of the Ru(III)/Ru(II) couple. The formation of the carboxylato complex is also favored by high buffer concentrations and by high pH values at the same buffer concentration. No appreciable accumulation of $[Ru(NH_3)_5(phthalate)]^+$ was observed in the test solution over a period of 30 min. Cyclic voltammograms of such solutions show only traces of the complex when scanning from an initial potential of 0.0 toward more negative potentials at scan rates of 100 mV/s. The formation of the complex during slow scans is dramatically illustrated in the differential-pulse experiment in Figure 1 where a slow scan rate (5 mV/s) is employed starting from a negative potential. A similar but less pronounced interaction between the buffer anion and aquopentaammineruthenium(III) was observed with phosphate buffers.

Discussion

Clear evidence has been obtained for the presence of both III/II and IV/III redox couples in the $[Ru(NH_3)_5(OH_2)]^{3+}$ system. Although III/II redox couples are well-known in ruthenium chemistry,[7,19] heretofore, the occurrence of IV/III couples has been relatively rare and has only recently been reported for polypyridine complexes of ruthenium.[1,5b] We have noted a similar behavior in a preliminary study of Ru(Hedta)(OH₂) using activated electrodes.

The pH dependence of the electrochemical processes shown in Figure 3 are revealing as to the proton content of the Ru-
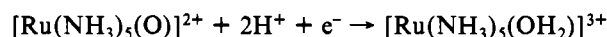
(III) and Ru(II) species. The break in the $E_{1/2}$ vs. pH plot is consistent with previously reported pK_a values of 4.20[20] 3.70, 3.90[21] and 4.10 for $[Ru(NH_3)_5(OH_2)]^{3+}$. In acid solution, the redox reaction

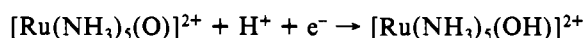$$[Ru(NH_3)_5(OH_2)]^{3+} + e^- \rightarrow [Ru(NH_3)_5(OH_2)]^{2+}$$
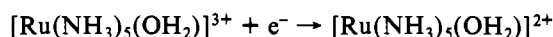
is independent of pH, but above pH 4, the $E_{1/2}$ is dependent on $[H^+]$ and the redox reaction becomes

$$[Ru(NH_3)_5(OH)]^{2+} + H^+ + e^- \rightarrow [Ru(NH_3)_5(OH_2)]^{2+}$$
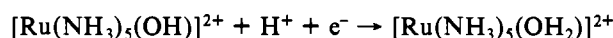
From the pH dependence of the Ru(IV)/Ru(III) redox potential, two protons are lost upon oxidation to Ru(IV) in acid solution and one proton is lost in the pH range 4.00–8.67. The relevant reactions must be
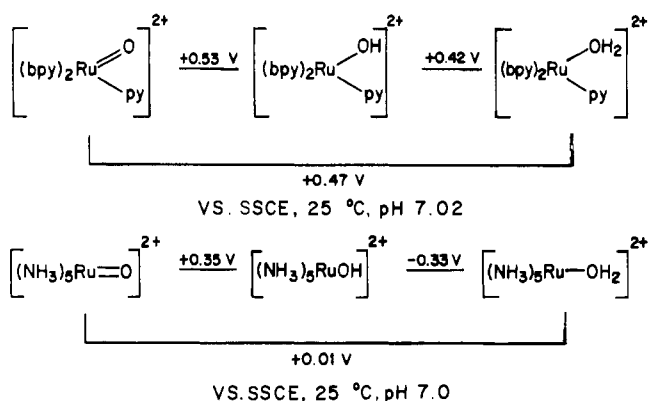
$$[Ru(NH_3)_5(O)]^{2+} + 2H^+ + e^- \rightarrow [Ru(NH_3)_5(OH_2)]^{3+}$$

below pH 4 and

$$[Ru(NH_3)_5(O)]^{2+} + H^+ + e^- \rightarrow [Ru(NH_3)_5(OH)]^{2+}$$

between pH 4.00 and 8.67.

The ruthenium(IV) complex has been formulated as containing an oxo group by analogy with $[Ru(bpy)_2(py)(O)]^{2+}$.[1,5b] However, an alternate formulation consistent with the pH dependence data would be $[Ru(NH_3)_4(NH_2)(OH)]^{2+}$. The possibility of (hydroxyamido)ruthenium(IV) seems unlikely because of the difference in the affinity for protons of the two centers. The first pKa for $[Ru(NH_3)_6]^{2+}$ [22] is 13.1, and as mentioned above, the pK_a for $[Ru(NH_3)_5(OH_2)]^{3+}$ is 4.02. It is therefore reasonable to assume that the same relative affinity for protons also obtains for NH_2 and OH coordinated to Ru(IV). However, it should be noted that care must be taken in using such arguments because of the apparent importance of $p\pi \rightarrow Ru(IV)$ π bonding in stabilizing Ru(IV) and other higher oxidation states.[14]

Comparisons with Bipyridine Complexes. The redox potentials for the $[Ru(NH_3)_5(OH_2)]^{3+}$ and $[Ru(bpy)_2(py)(OH_2)]^{2+}$ systems are compared in the following Latimer diagrams:[23]

$$[(bpy)_2Ru{=}O\ py]^{2+} \xrightarrow{+0.53\ V} [(bpy)_2Ru{-}OH\ py]^{2+} \xrightarrow{+0.42\ V} [(bpy)_2Ru{-}OH_2\ py]^{2+}$$

$$+0.47\ V$$

VS. SSCE, 25 °C, pH 7.02

$$[(NH_3)_5Ru{=}O]^{2+} \xrightarrow{+0.35\ V} [(NH_3)_5RuOH]^{2+} \xrightarrow{-0.33\ V} [(NH_3)_5Ru{-}OH_2]^{2+}$$
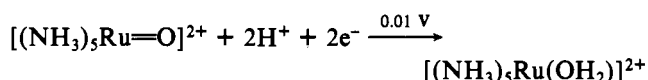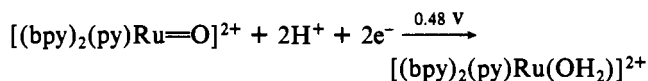
$$+0.01\ V$$

VS. SSCE, 25 °C, pH 7.0

The most striking difference is in the reduction potentials for the III/II couples which show that the ammine complex is much easier to oxidize from Ru(II) to Ru(III) than the polypyridine complex. This is a consequence of the stabilization of Ru(II) by electron-accepting ligands, which was alluded to in the Introduction.[6] The IV/III couples, on the other hand, have reduction potentials that are much closer,

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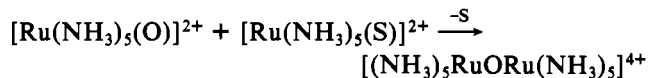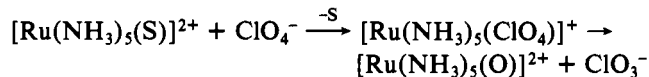(19) Poon, C. K.; Che, C. M.; Kan, Y. P. *J. Chem. Soc., Dalton Trans.* **1980**, 128.

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although in the polypyridine coordination environment Ru(IV) is still a marginally better oxidant than in the ammine environment. The similarity in IV/III potentials suggests that the comparable σ donor abilities of the ammine and polypyridyl ligands predominate in controlling the IV/III couples and the $d\pi \rightarrow \pi^*$ interaction, which is important in stabilizing Ru(II), does not play a significant role in the higher oxidation states. This is expected, given the larger $d\pi \rightarrow \pi^*$ separation and smaller radial extension of the $d\pi$ orbitals in the higher oxidation states.

The changes in redox potentials induced by replacing bipyridine ligands with ammine ligands have profound consequences on the Ru(IV)/Ru(II) redox potential. At pH 7, the potentials for the two complexes acting as two-electron oxidants are

$$[(bpy)_2(py)Ru{=}O]^{2+} + 2H^+ + 2e^- \xrightarrow{0.48\ V}$$
$$[(bpy)_2(py)Ru(OH_2)]^{2+}$$

$$[(NH_3)_5Ru{=}O]^{2+} + 2H^+ + 2e^- \xrightarrow{0.01\ V}$$
$$[(NH_3)_5Ru(OH_2)]^{2+}$$

For the bipyridine system, there is little difference thermodynamically (0.05 V) between Ru(IV) acting as a one- or two-electron oxidant and only a small energy penalty must be paid for the complex to utilize a two-electron vs. a one-electron pathway. For the ammine system, there is a much larger difference between redox potentials for $[(NH_3)_5RuO]^{2+}$ acting as a one- or two-electron oxidant (0.36 V), which could influence the mechanistic details of its redox chemistry. However, evidence is available, suggesting the importance of two-electron steps in the ammine system as well. An example is the appearance of the oxo-bridged Ru(III) dimer as the product of ClO_4^- oxidation in acetone, where the suggested mechanism was[24] (S is acetone)

$$[Ru(NH_3)_5(S)]^{2+} + ClO_4^- \xrightarrow{-S} [Ru(NH_3)_5(ClO_4)]^+ \rightarrow$$
$$[Ru(NH_3)_5(O)]^{2+} + ClO_3^-$$

$$[Ru(NH_3)_5(O)]^{2+} + [Ru(NH_3)_5(S)]^{2+} \xrightarrow{-S}$$
$$[(NH_3)_5RuORu(NH_3)_5]^{4+}$$

The presence of the irreversible oxidative waves at potentials positive of the IV/III wave is a clear indication that further oxidation of the complex beyond $[(NH_3)_5RuO]^{2+}$ does occur. Note the results of the switching potential experiment in Figure 2. The possibility that this oxidation involves the ammine ligands was tested by a preliminary investigation of the [Ru(NH$_3$)$_6$]$^{3+}$ complex. Figure 4 shows that, by using activated electrodes, [Ru(NH$_3$)$_6^{3+}$ can be oxidized at pH 7.52 but not at pH 1.00 or 3.70. This behavior is similar to that observed in the oxidation of [Ru(terpy)(bpy)(NH$_3$)]$^{2+}$ (terpy = 2,2′,2″-terpyridine), which undergoes a series of facile one-electron oxidation steps from the ammine to the nitrosyl.[25] This suggests that oxidation of [Ru(NH$_3$)$_6$]$^{3+}$ proceeds in a
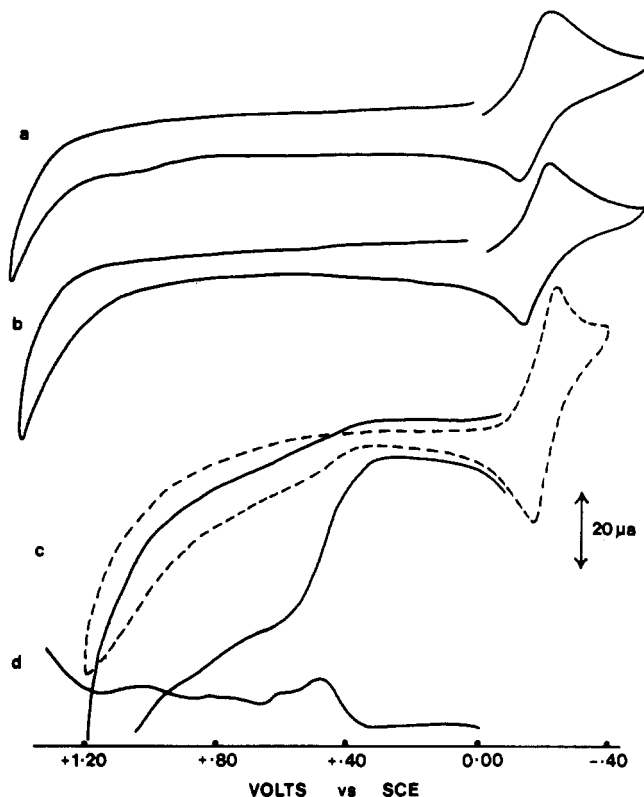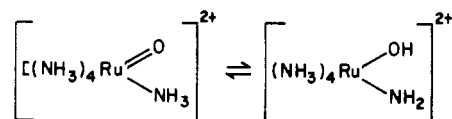

Figure 4. Cyclic voltammograms (a, at pH 1.00; b, at pH 3.72; c, at pH 7.52) of [Ru(NH$_3$)$_6$]$^{3+}$ using an activated glassy-carbon electrode (—) and polished glassy carbon electrode (---) (scan rate 100 mV/s). Differential-pulse voltammogram (d, at pH 7.52) using an activated glassy-carbon electrode (scan rate 5 mV/s; modulation amplitude 5 mV).

similar fashion and is corroborated by the work of Armor, who showed that the hexaammine is oxidized to [Ru(NH$_3$)$_5$-(NO)]$^{3+}$ in basic solution.[25c] For [Ru(NH$_3$)$_5$(OH$_2$)]$^{3+}$, the requirement of an activated electrode for resolution of the higher oxidative waves and the pH dependence of oxidations past the IV/III wave suggest that electron transfer coupled with proton loss from a coordinated ammine group may be involved in the subsequent oxidations. Conceivably, an internal proton transfer of the type

$$\left[(NH_3)_4Ru{\Big\langle}{\overset{O}{\underset{NH_3}{}}}\right]^{2+} \rightleftharpoons \left[(NH_3)_4Ru{\Big\langle}{\overset{OH}{\underset{NH_2}{}}}\right]^{2+}$$

could play a role in such processes. It should be noted that Ru(IV) imido and Ru(III) amido intermediates have been suggested to play an important role in the oxidation of coordinated ammonia.[25a]

Registry No. [Ru(NH$_3$)$_5$OH$_2$]$_2$(S$_2$O$_6$)$_3$, 91294-87-0; [Ru(NH$_3$)$_5$OH$_2$]$^{3+}$, 25590-52-7; [Ru(NH$_3$)$_5$O]$^{2+}$, 91294-88-1; [Ru(NH$_3$)$_5$OH]$^{2+}$, 38331-41-8; [Ru(NH$_3$)$_5$(OH$_2$)]$^{2+}$, 21393-88-4; [Ru(NH$_3$)$_6$]$^{3+}$, 18943-33-4; C, 7440-44-0.

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