simulated CV *i–E* profiles is excellent for an EC mechanism over a wide range of concentration ratios and scan rates. The second is that there is no evidence for O_2 catalysis with an electrode that has been exposed to a FeTMPyP solution and then thoroughly rinsed with distilled water in contrast to the case of CoTMPyP and CoTPyP, where strong surface adsorption occurs. We do recognize, however, that FeTMPyP adsorption can occur, depending on the anion present in solution. Thus, adsorption of FeTMPyP is evident when perchlorate, borate, iodide, or bromide are present in solution.

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Registry No. Fe^{III}TMPyP, 60489-13-6; Fe^{II}TMPyP, 71794-64-4; H_2O_2, 7722-84-1; O_2, 7782-44-7; H_2O, 7732-18-5; TPyP, 16834-13-2.

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Reactions of Tris- and Bis(2,2′-bipyridine)rhodium(II) Complexes in Aqueous Solution

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Pulse-radiolytic methods have been used to characterize $Rh(bpy)_3^{2+}$ and $Rh^{II}(bpy)_2(aq)$. The rhodium(II) complexes are produced by one-electron reduction of $Rh(bpy)_3^{3+}$ and $Rh(bpy)_2(OH)_2^+$, respectively, by either e_{aq}^- or $R\cdot = (CH_3)_2\dot{C}OH$ (the radical produced predominantly by the reaction of 2-propanol with the hydroxyl radical). For reduction by R·, rate constants of 2.3×10^9 M^{-1} s^{-1} for $Rh(bpy)_3^{3+}$ and 2.4×10^8 M^{-1} s^{-1} for $Rh(bpy)_2(OH)_2^+$ at 25 °C were found. Small amounts of "double reduction" give $Rh(bpy)_3^+$, which undergoes bipyridine dissociation with $k = 5 \times 10^4$ s^{-1} at 25 °C. The bis complex $Rh^{II}(bpy)_2(aq)$ exhibits two dissociable protons implicating pK_a ($Rh(bpy)_2(H_2O)_2^{2+}$–$Rh(bpy)_2(H_2O)(OH)^+$) = 8.6 and pK_a ($Rh(bpy)_2(H_2O)(OH)^+$–$Rh(bpy)_2(OH)_2^0$ = 11.1. In the absence of added bpy or $Rh(bpy)_3^{3+}$, $Rh^{II}(bpy)_2$ undergoes rapid dimerization ($k = (2.3 \times 10^{11}) \exp(-4.3 \text{ kcal mol}^{-1}/RT)$ at pH 8.9), and the dimer ultimately converts to $Rh(bpy)_2^+$ and $Rh(bpy)_2(OH)_2^+$ ($k = 0.9 \times 10^{-2}$ s^{-1} at 25 °C, 0.8×10^{-1} s^{-1} at 60 °C). Reaction of bipyridine with $Rh(bpy)_2(H_2O)_2^{2+}$ to give $Rh(bpy)_3^{2+}$ proceeds with $k = 0.3 \times 10^9$ M^{-1} s^{-1}, while for the reverse reaction $k = 0.6$ s^{-1} at 25 °C and 4.3 s^{-1} at 50 °C. Disproportionation of $Rh(bpy)_3^{2+}$ to $Rh(bpy)_2^+$ and $Rh(bpy)_3^{3+}$ proceeds via reduction of $Rh^{II}(bpy)_2$ by $Rh(bpy)_3^{2+}$ ($k = 3.0 \times 10^8$ M^{-1} s^{-1} at pH 8.9 and 25 °C).

Introduction

Monomeric d^7 complexes of second and third transition series metal centers are unstable with respect to dimerization to metal–metal-bonded species, to disproportionation to the $d^6 + d^8$ counterparts, or to both. Thus little information concerning the elementary coordination chemistry of these species is available. For the $4d^7$ center rhodium(II), exceptions include the ammines[1] $Rh(NH_3)_6^{2+}$ and $Rh(NH_3)_4^{2+}(aq)$ generated in pulse radiolysis of $Rh(NH_3)_6^{3+}$ and $Rh(dmgH)_2$ produced[2] by flash photolysis of $[Rh(dmgH)_2PPh_3]_2$ (dmgH is the monoanion of 2,3-butanedione dioxime or dimethylglyoxime), among others.[3] Our work with $Rh(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and $Rh^{II}(bpy)_2$ originated because these complexes are implicated as intermediates in a water photoreduction system,[4–6] and we have continued[7,8] these studies in order to attain a greater understanding of the nature and reactivity of these species. Here we report results that lead to the conclusion that these complexes are six-coordinate but extremely substitution labile. Bis(bipyridine)rhodium(II) has an extremely high affinity for a third bipyridine molecule and for itself (dimer formation), but under all circumstances the rhodium(II) complexes eventually disproportionate to rhodium(I) and rhodium(III). Our observations on $Rh(bpy)_3^{2+}$ are in agreement with but are an extension of those recently reported by Mulazanni and co-workers.[9]

Experimental Section

The 2,2′-bipyridine complexes $[Rh(bpy)_3](ClO_4)_3$ and $[Rh(bpy)_2(H_2O)_2](ClO_4)_3$ were prepared as described in ref 6. In some experiments sulfate salts (as solutions) were used. These were prepared via anion exchange of the perchlorate salts.[6] Fischer Certified 2-propanol was used as obtained. Generally the solutions were 1.0% by volume 2-propanol (0.13 M). Reagent grade sodium phosphate and borate salts were used as buffers with the total buffer concentration being in the $(2–5) \times 10^{-3}$ M range. Milli-Q water was used in all the solutions, and argon was the blanket gas.

Pulse radiolysis was carried out with 2-MeV electrons produced by a Van de Graaff accelerator. The pulse lengths were varied but were usually in the range of 0.2–3 μs, and the electron currents ranged up to 0.4 A. The electron beam passed through the 0.5-cm dimension and the analyzing light through the 2-cm dimension of a 2 × 1 × 0.5 cm Supersil cell. The light passed through the cell one or three times for path lengths of 2 or 6 cm. The light was produced by a Xe arc when time periods shorter than 10^{-4} s were studied and by a quartz-iodine lamp (above 400 nm) or a D_2 arc (below 400 nm) for longer periods. The D_2 arc could be pulsed to increase its output a factor of 8 for periods up to 5 ms. The cell was thermostated between 5 and 75 °C with most work done at 25 °C.

Results

Production of Rhodium(II) Complexes. The radiolysis of aqueous solutions produces hydroxyl radicals, hydrated electrons, and hydrogen atoms in the ratios 2.8:2.7:0.6. Some

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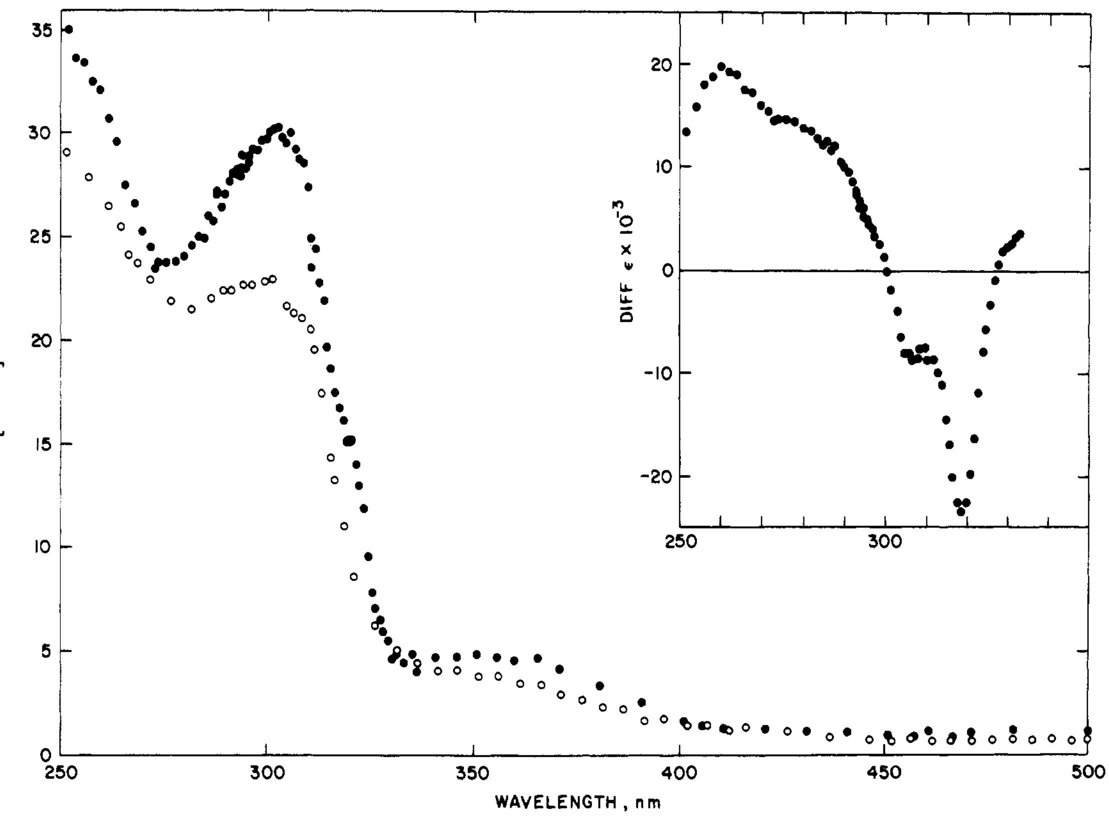

Figure 1. Spectra of Rh(II) complexes prepared by reduction of (1–2) × 10^{-5} M Rh(III) complexes in 0.013 M 2-propanol at pH 8.8: (●) $Rh(bpy)_3^{2+}$; (○) $Rh^{II}(bpy)_2(aq)$. The units of the extinction coefficients are M^{-1} cm^{-1}. The spectra were obtained by adding that of the parent Rh(III) complex to the observed difference spectrum (shown for $Rh(bpy)_3^{2+}$ in the insert).

hydrogen and hydrogen peroxide are also produced. The e_{aq}^- reduces Rh(III) complexes directly, and in the presence of 2-propanol, the OH radicals and H atoms produce 2-propanol radicals, which are also capable of reducing certain Rh(III) complexes. (In reality, ~15% of the 2-propanol radical produced from reaction with OH is the β-abstraction product $(\dot{C}H_2)CH_3CHOH$. We have not attempted to determine its fate in these systems.) If the complex is $Rh(bpy)_3^{3+}$, then

$$e_{aq}^- + Rh(bpy)_3^{3+} \rightarrow Rh(bpy)_3^{2+} \quad (1)$$

$$OH \text{ (or H)} + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O \text{ (or } H_2) \quad (2)$$

$$(CH_3)_2\dot{C}OH + Rh(bpy)_3^{3+} \rightarrow Rh(bpy)_3^{2+} + (CH_3)_2CO + H^+ \quad (3)$$

The rate constants for reactions 1 and 3 are reported[9] to be 8.1 × 10^{10} and 1.8 × 10^9 M^{-1} s^{-1}. We measured k_3 by following the growth of absorbance at 360 nm following the pulse. Reaction 1 was complete in less than 10^{-6} s, and a slower rise due to reaction 3 was observed. The rate constant k_3 was found to be (1.2 × 10^{12}) exp(−3.7 kcal mol^{-1}/RT) M^{-1} s^{-1} or 2.3 × 10^9 M^{-1} s^{-1} at 25 °C.

Reactions analogous to (1) and (3) are observed for $Rh(bpy)_2(OH)_2^+$ ions:

$$e_{aq}^- + Rh(bpy)_2(OH)_2^+ \rightarrow Rh^{II}(bpy)_2(aq) \quad (4)$$

$$(CH_3)_2\dot{C}OH + Rh(bpy)_2(OH)_2^+ \rightarrow Rh^{II}(bpy)_2(aq) + (CH_3)_2CO + H^+ \quad (5)$$

where $Rh^{II}(bpy)_2(aq)$ represents any or all of $Rh(bpy)_2(H_2O)_2^{2+}$, $Rh(bpy)_2(H_2O)OH^+$, and $Rh(bpy)_2(OH)_2$ forms. The rate constant k_4 was measured to be 4.5 × 10^{10} M^{-1} s^{-1}. The growth of absorbance at 360 nm was followed after the completion of reaction 4, and k_5 was found to be 2.4 × 10^8 M^{-1} s^{-1} at pH 8.8 and 25 °C. (At pH 12, where the 2-propanol radical is deprotonated, the rate constant was near 10^{10} M^{-1} s^{-1}.) The observed rate constant increased with increasing dose per pulse due to the reaction

$$(CH_3)_2\dot{C}OH + Rh^{II}(bpy)_2 \rightarrow Rh(bpy)_2^+ + (CH_3)_2CO + H^+ \quad (6)$$

The value estimated for k_6 from this effect is about 2 × 10^9 M^{-1} s^{-1}.

The various Rh(II) complexes and the eventual $Rh(bpy)_2^+$ product all react efficiently with oxygen. The argon bubbling method used appeared to leave small amounts of O_2 in the sample, about 10^{-7} M or less. Such small concentrations have little effect on reactions occurring within 10^{-3} s but seriously distort results at longer times, particularly during Rh(I) growth, which occurs on time scales of seconds. This O_2 effect was eliminated by preirradiating the sample with a small dose, which produced about 5 × 10^{-7} M Rh(II). Upon more extensive pulsing of the sample other effects due to the Rh(I) and free bipyridine products were observed. If an effect of multiple pulsing was found, then only the first pulse following the preirradiation was used or the results of several pulses were extrapolated to zero dose.

Spectra of Rhodium(II) Complexes. The spectra observed for the Rh(II) complexes are shown in Figure 1. The $Rh(bpy)_3^{2+}$ spectrum was obtained by following the growth due to reaction 3 after completion of reaction 1. The ratio of total radical reduction to e_{aq}^- reduction was 2.1 ± 0.1 at all wavelengths (2.26 is expected if both α- and β-abstraction products R· react; 2.10 is expected if only the α-R· isomer reacts). The $Rh^{II}(bpy)_2(aq)$ spectrum was determined from growth during the reduction of Rh(III) by e_{aq}^- (reaction 4) because the rate of reaction 5 was too slow at the Rh(III) concentration practical in the UV (about 10^{-5} M).

The observed spectra are, of course, difference spectra between the Rh(II) product and the Rh(III) reactant, as shown for $Rh(bpy)_2^{3+}$ in the inset of Figure 1. At wavelengths longer

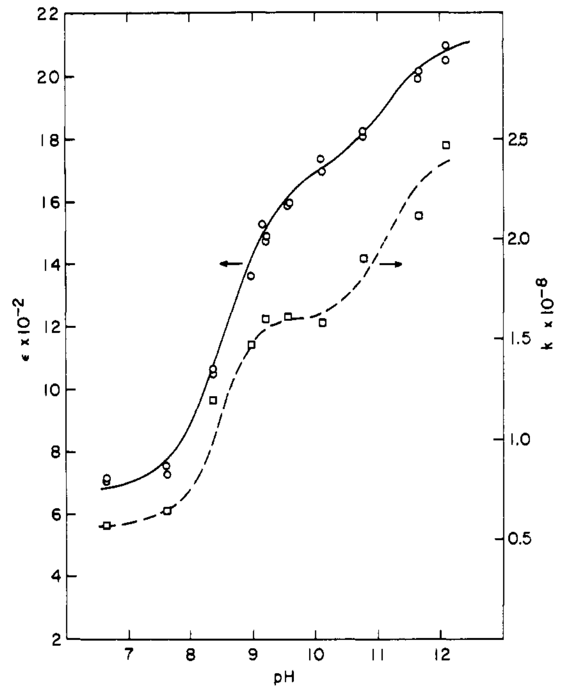

Figure 2. Dependence of the $Rh^{II}(bpy)_2(aq)$ extinction coefficient at 390 nm on pH (circles) and the dependence of the dimerization rate constant, k_9 ($M^{-1}\ s^{-1}$), on pH (squares).

than 350 nm for $Rh(bpy)_3^{3+}$ solutions and 390 nm for $Rh(bpy)_2(OH)_2^+$ solutions the Rh(III) absorption is negligible. Below these wavelengths the observed spectra have sharp changes from large positive values to large negative values. The difference spectrum observed on pulsing $Rh(bpy)_3^{3+}$ solutions agrees with that in the literature.[9] (We attribute the greater absorption seen at 490 nm in ref 9 to Rh(I) formed in the pulse, vide infra.) In order to obtain the Rh(II) spectra, it was necessary to measure the Rh(III) complexes at the same resolution (4-nm full width at half maximum) and to pay particular attention to the wavelength calibration.

The 360-nm band of $Rh(bpy)_3^{2+}$ was found to be essentially independent of temperature. At 360 nm the ratio of extinction coefficients at 75 °C to that at 8 °C was 1.03. The ratio was 0.93 at 380 nm (on the side of the band), which might indicate a narrowing of the peak at higher temperature.

Bis(2,2′-bipyridine)rhodium(III) Solutions. The bis(2,2′-bipyridine)rhodium(III) complex and the tris(2,2′-bipyridine)rhodium(III) complex were studied by themselves and in mixtures. The bis complex has, in addition to the bipyridine ligands, two waters of hydration and should exhibit two acid dissociations (eq 7 and 8). The change in extinction coefficient

$$Rh(bpy)_2(H_2O)_2^{2+} \rightleftharpoons Rh(bpy)_2(H_2O)OH^+ + H^+ \quad (7)$$

$$Rh(bpy)_2(H_2O)OH^+ \rightleftharpoons Rh(bpy)_2(OH)_2 + H^+ \quad (8)$$

with pH is shown in Figure 2, from which it is found that $pK_7 = 8.6$ and $pK_8 = 11.1$. Each pK is about 4 units higher than the corresponding pK values of the Rh(III) complex, 4.8 and 6.8.[6]

The $Rh^{II}(bpy)_2(aq)$ complexes disappear by dimerization (eq 9). The rate of disappearance is second order ($2k_9$-

$$2Rh^{II}(bpy)_2 \rightarrow [Rh^{II}(bpy)_2]_2(aq) \quad (9)$$

$[Rh^{II}(bpy)_2]^2$), and the rate constant k_9 varies with pH as shown in Figure 2. Reaction 9 is, of course, five separate reactions, and the individual rate constants could be extracted from the data of Figure 2, but the results would not be too meaningful. It is clear that the smaller the charge on the transition state the greater the rate constant. At pH 8.9, k_9 is $(2.3 \times 10^{11}) \exp(-4.3\ kcal\ mol^{-1}/RT)\ M^{-1}\ s^{-1}$ or $1.7 \times 10^8\ M^{-1}\ s^{-1}$ at 25 °C.

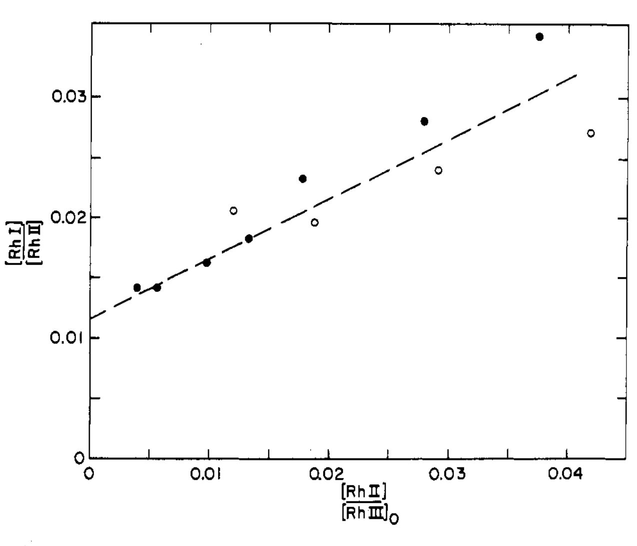

Figure 3. Dependence of the yield of Rh(I), produced by radical reduction of $Rh(bpy)_3^{2+}$, on $Rh(bpy)_3^{2+}$ and $Rh(bpy)_3^{3+}$ concentrations: (●) 10^{-3} M $Rh(bpy)_3^{3+}$; (○) 3×10^{-4} M $Rh(bpy)_3^{3+}$.

Tris(2,2′-bipyridine)rhodium(III) Solutions. The principal species produced upon reduction of $Rh(bpy)_3^{3+}$ solutions is $Rh(bpy)_3^{2+}$. A minor secondary reduction to form $Rh(bpy)_2^+$ was observed, however, and had some interesting aspects. In 10^{-3} M $Rh(bpy)_3^{3+}$, 0.1 M 2-propanol solution, reaction 3 is 95% complete in 2 μs. The absorption spectrum obtained upon pulsing this solution is unchanging from 2 μs to 10 ms at all wavelengths except near 500 nm. In this region a growth of absorbance is seen with a rate constant of $5.0 \times 10^4\ s^{-1}$. The extent of the growth increased with radiation dose delivered to the sample and was larger at the same dose in a more dilute (3×10^{-4} M) solution. The absorption spectrum of the increase in absorbance was that of $Rh(bpy)_2^+$. The Rh(I) is attributed to the reduction of Rh(II) by radicals, for instance

$$Rh(bpy)_3^{2+} + e_{aq}^- \rightarrow Rh(bpy)_3^+ \quad (10)$$

in competition with reaction 1. The observed growth step is due to

$$Rh(bpy)_3^+ \rightarrow Rh(bpy)_2^+ + bpy \quad (11)$$

with $k_{11} = 5.0 \times 10^4\ s^{-1}$. Hydrated electrons are most certainly involved in this double reduction, but 2-propanol radicals may react similarly. Only a few percent of the Rh(II) is further reduced, so this mechanism can be adequately represented by the low-conversion approximation

$$\frac{[Rh(I)]_f}{[Rh(II)]} = \frac{1}{2}\frac{k_{10}}{k_1}\frac{[Rh(II)]}{[Rh(III)]} \quad (12)$$

where $[Rh(I)]_f$, the final Rh(I) concentration after completion of reaction 11, is calculated with the assumption that the extinction coefficient of $Rh(bpy)_3^+$ is negligible compared to that of $Rh(bpy)_2^+$. The data are plotted according to eq 12 in Figure 3, and the observed slope is 0.5, about as expected. The intercept, indicating that about 1% of the Rh(I) is further reduced even at low Rh(II), is not predicted by eq 12. Actually, the intercept is expected from a consideration of "spur" reactions. The radicals are produced several pairs at a time in small spurs by the radiation. Radical–radical reactions occur in these spurs while they are diffusing into the bulk of the solution, and reaction between two e_{aq}^- is one of the sources of H_2 in water radiolysis. Double reduction in the spur by reactions 1 and 10 should occur to about the same extent as the H_2 yield is reduced. On this basis, 0.8% of Rh(II) should be further reduced in 3×10^{-4} M Rh(III) solution and 1.3%

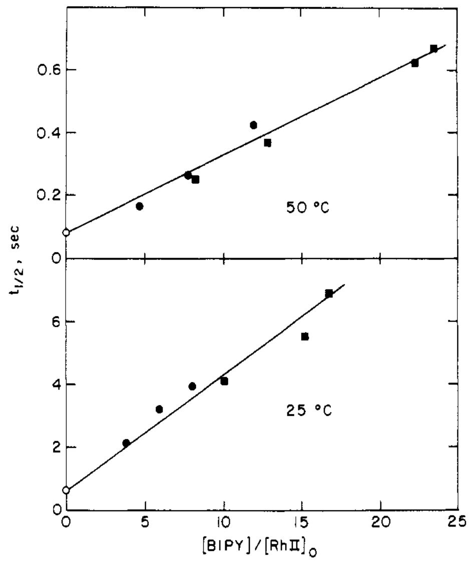

Figure 4. Dependence of the half-life for $Rh(bpy)_2^+$ formation from $Rh(bpy)_3^{2+}$ on bipyridine and $Rh(bpy)_3^{2+}$ concentrations at pH 8.8: (●) 1.0×10^{-5} M bipyridine; (■) 3.0×10^{-5} M bipyridine.

in 10^{-3} M solution, consistent with the observed intercept.

The remaining $Rh(bpy)_3^{2+}$ eventually produces $Rh(bpy)_2^+$ by a first-order reaction, which may be interpreted according to the mechanism given by eq 13, 7, and 14.[5,6] This mechanism, with $Rh(bpy)_2(H_2O)_2^{2+}$ assumed at its steady-state concentration and (7) at equilibrium, leads to

$$Rh(bpy)_3^{2+} \rightleftharpoons Rh(bpy)_2(H_2O)_2^{2+} + bpy \qquad (13)$$

$$Rh(bpy)_2(H_2O)_2^{2+} \rightleftharpoons Rh(bpy)_2(H_2O)OH^+ + H^+ \qquad (7)$$

$$Rh(bpy)_2(H_2O)OH^+ + Rh(bpy)_3^{2+} \rightarrow Rh(bpy)_2^+ + Rh(bpy)_3^{3+} \qquad (14)$$

$$\frac{k_{-13}[H^+][bpy]}{k_{14}K_7}\left(\frac{1}{X_0} - \frac{1}{X}\right) + \ln\left(\frac{X}{X_0}\right) = -2k_{13}t \qquad (15)$$

where X is the $Rh(bpy)_3^{2+}$ concentration. It may be seen that when [bpy] is negligible the reaction will be first order, as observed, and at high [bpy] the reaction will appear second order. At 10^{-5} M bpy the reaction is indistinguishable experimentally from second order and was so treated. If the first half-life of the reaction is denoted by $t_{1/2}$

$$t_{1/2} = \frac{\ln 2}{2k_{13}} + \frac{k_{-13}[H^+]}{2k_{13}k_{14}K_7}\,\frac{[bpy]}{[Rh(bpy)_3^{2+}]_0} \qquad (16)$$

The rate constant k_{13} was found to be 0.6 s^{-1} at 25 °C and 4.3 s^{-1} at 50 °C. Sufficient bipyridine is formed in a pulse to affect the observed rate constant, and so these values were obtained by using a series of small pulses on one sample and extrapolating to zero dose.

With added bipyridine, $t_{1/2}$ was calculated from second-order kinetic fits, and plots against $[bpy]/[Rh(bpy)_3^{2+}]_0$ are shown in Figure 4. The slope at pH 8.8 and 25 °C is 0.37 s, while at pH 8.28, a factor of 3.3 in acid concentration, the slope is a factor of 4.8 larger. The predicted hydrogen ion proportionality is partly a consequence of assuming that only $Rh(bpy)_2(H_2O)OH^+$, among the three $Rh^{II}(bpy)_2$ species, participates in reaction 14. If $Rh(bpy)_2(OH)_2$ reacts faster than $Rh(bpy)_2(H_2O)OH^+$, then a greater hydrogen ion dependence would result.

In order to further unravel the mechanism, it is necessary to determine either k_{-13} or k_{14} separately. Both reactions were studied. It is convenient to rewrite the reactions in terms of the total $Rh^{II}(bpy)_2(aq)$ species present (eq $-13'$ and $14'$).

$$Rh^{II}(bpy)_2(aq) + bpy \rightarrow Rh(bpy)_3^{2+} \qquad (-13')$$

$$Rh^{II}(bpy)_2(aq) + Rh(bpy)_3^{2+} \rightarrow Rh(bpy)_2^+ + Rh(bpy)_3^{3+} \qquad (14')$$

Reaction 14′ was studied in mixtures of $Rh(bpy)_3^{3+}$ and $Rh(bpy)_2(OH)_2^+$ at concentrations such that both $Rh(bpy)_3^{2+}$ and $Rh^{II}(bpy)_2(aq)$ were produced but with $Rh(bpy)_3^{2+}$ in excess. This situation minimized the effect of dimerization, reaction 9, on the results. The growth of $Rh(bpy)_2^+$ was monitored at 510 nm and treated as a second-order reaction with unequal reactant concentrations. The total Rh(II) concentration is known from radical yields and dose, and the ratio $r = [Rh^{II}(bpy)_2(aq)]_0/[Rh(bpy)_3^{2+}]_0$ may be calculated in an internally consistent manner as follows: After reaction 14′ is complete, the absorbance increases further but slowly as the excess $Rh(bpy)_3^{2+}$ reacts according to reaction 13. If f is the ratio of absorbance at the end of reaction 14 to the total absorbance several seconds later when reaction 13 is complete, then

$$r = \frac{f - 2\epsilon_{II}/\epsilon_I}{2 - f - 2\epsilon_{II}/\epsilon_I}$$

where ϵ_{II}/ϵ_I is the ratio of extinction coefficients of the Rh(II) species to that for $Rh(bpy)_2^+$ and is 0.1. The mixtures used had $[Rh(bpy)_2(OH)_2^+]$ and $[Rh(bpy)_3^{3+}]$ in the ratios of 1:1 and 3:1, which produced r values of 0.25 and 0.56. The low r values result from k_3 being considerably larger than k_5. Both mixtures gave $k_{14'} = 3.0 \times 10^8$ M^{-1} s^{-1} at 25 °C and pH 8.9.

Reaction $-13'$ was studied by observing the effect of added bipyridine on the disappearance of $Rh^{II}(bpy)_2(aq)$ (to form a dimer at low [bipyridine] and $Rh(bpy)_3^{2+}$ at high [bipyridine]). With 1.0×10^{-5} M or 2.6×10^{-5} M free bipyridine added to the $Rh(bpy)_2(OH)_2^+$ at pH 8.8 the increase in absorbance at 420 nm was nearly first order and extrapolation to zero dose gave an apparent $k_{-13'} = 1.6 \times 10^8$ M^{-1} s^{-1} at both bipyridine concentrations. There is an ambiguity in the interpretation of this rate constant. The apparent value would be the true value if the absorbance change is due solely to production of $Rh(bpy)_3^{2+}$. If it were all due to residual amounts of dimer formation via reaction 9 in competition with reaction $-13'$, then the growth would depend on the square of the $Rh^{II}(bpy)_2$ concentration, or $k_{apparent} = 2k_{-13'}$. Both products seem to contribute to the absorbance, so the average of the two interpretations is used, $k_{-13'} = 1.2 \times 10^8$ M^{-1} s^{-1}. At this pH, $Rh(bpy)_2(H_2O)_2^{2+}$ is 39% of $Rh^{II}(bpy)_2(aq)$, so $k_{-13} = 3 \times 10^8$ M^{-1} s^{-1}. The stability constant of $Rh(bpy)_3^{2+}$ is k_{-13}/k_{13} or 5×10^8 M^{-1}.

The rate constants k_{13}, $k_{-13'}$, and $k_{14'}$ are overdetermined. The internal consistency can be checked by computing the slope observed at 25 °C in Figure 4, 0.37 s. The calculated values would be $k_{-13}/2k_{13}k_{14'}$, which is 0.33 s.

Activation energies were measured for most of the reactions involved in the $Rh(bpy)_3^{2+}$ disappearance. The value of k_{13} is $(6.0 \times 10^{10}) \exp(-15.0 \text{ kcal mol}^{-1}/RT)$ M^{-1} s^{-1} and $k_{14'}$ is $(6.0 \times 10^{11}) \exp(-4.5 \text{ kcal mol}^{-1}/RT)$ M^{-1} s^{-1}, which combine with the data of Figure 4 to give $k_{-13'}$ as $(1.7 \times 10^8) \exp(+1.2 \text{ kcal mol}^{-1}/RT)$ M^{-1} s^{-1} at pH 8.8. The negative activation energy for reaction $-13'$ comes from the reciprocal dependence on K_7, for which a $\Delta H°$ of a few kilocalories per mole is reasonable.

The $Rh^{II}(bpy)_2(aq)$ Dimer. The spectrum of the dimer at pH 12 is shown in Figure 5. The data show an apparent peak at 490 nm, but this is most likely due to $Rh(bpy)_2^+$ formed by reaction 6, since $Rh(bpy)_2^+$ has an intense ($\epsilon = 1.0 \times 10^4$ M^{-1} cm^{-1}) absorption peak at 510 nm. The apparent extinction coefficient of the dimer is about 15% larger at pH 6.6 and 20% larger at pH 12 than it is at pH 9, indicating possible pKs of 7 and 11. The $(CH_3)_2\dot{C}OH$ radical has a pK of 12, however,

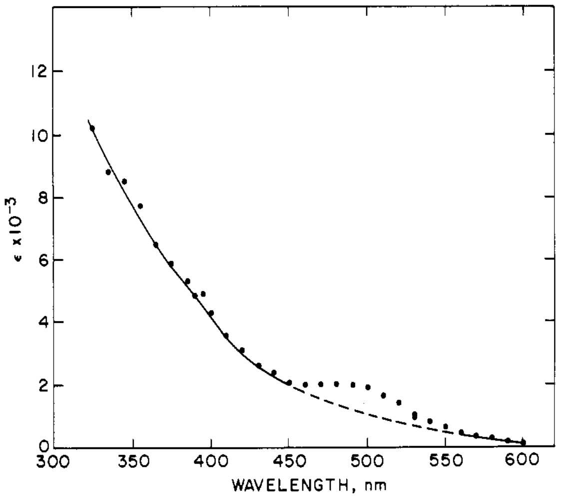

Figure 5. Spectrum of the $Rh^{II}(bpy)_2$ dimer (ε per rhodium) at pH 12 obtained by adding the spectrum of parent $Rh(bpy)_2(OH)_2^+$ to the observed difference spectrum.

and $Rh^{III}(bpy)_2$ has a pK at 6.8, so in view of the minor participation of reaction 6 in competition with that of reaction 5, which involves both these species, the apparent pKs are very dubious.

The dimer is relatively long-lived but eventually disproportionates:

$$[Rh^{II}(bpy)_2]_2(aq) \rightarrow Rh(bpy)_2(OH)_2^+ + Rh(bpy)_2^+ \quad (17)$$

The production of $Rh(bpy)_2^+$ can be observed at 510 nm, and the stoichiometry of the Rh(III) product is inferred from the fact that multiple pulsing of the sample does not produce any effects that would appear if free bipyridine were produced. The rate of reaction 17 could be followed only very poorly at 25 °C in pulse radiolysis experiments, as the time scale involved is in the hundreds of seconds region, but led to a value of about 0.01 s^{-1} for k_{17}. At 60 °C, however, a more definite value of 0.08 s^{-1} was observed. The best value of k_{17} at 25 °C, 0.009 s^{-1}, was determined to reasonable precision (±15%) by irradiating a sample in a 1-cm cuvette and following the reaction in a Cary 210 spectrophotometer. The temperature dependence of k_{17} is $(1.3 \times 10^7) \exp(-12.5 \text{ kcal}/RT)$.

The dimer does not dissociate into two $Rh^{II}(bpy)_2(aq)$ ions, the reverse of reaction 9, before decay according to reaction 17. This was determined by again performing irradiation of $Rh(bpy)_2(OH)_2^+$ solution at pH 8.9 in a 1-cm cuvette and injecting sufficient bipyridine to produce 5×10^{-5} and 8×10^{-5} M solutions before following the reactions in the Cary 210 spectrophotometer. Production of $Rh(bpy)_2^+$ occurred with a rate constant of 0.007 s^{-1} in both solutions, a slightly smaller value than k_{17}. The dissociation reaction would lead to formation of $Rh(bpy)_3^{2+}$ via reaction 13 and eventual formation of $Rh(bpy)_2^+$ through reaction 14. The observed rate would then be equal to or (because of an induction period while building up $Rh(bpy)_3^{2+}$) less than the rate of dissociation. The similarity of rates in the absence and presence of bipyridine and the lack of bipyridine concentration effects indicates that k_{-9} is less than 0.005 s^{-1}, and so the equilibrium constant for reaction 9 is greater than 3×10^{10} M^{-1}.

Discussion

Coordination Chemistry of Rhodium(II). Our observations indicate that $Rh(bpy)_3^{2+}$ and $Rh^{II}(bpy)_2(aq)$ are six-coordinate: the fact that $Rh(bpy)_3^{3+}$ is reduced to a transient whose spectrum does not change in the micro- to millisecond time range and the fact that $Rh^{II}(bpy)_2(aq)$ reacts with bpy to give this transient require the existence of $Rh(bpy)_3^{2+}$. Earlier, as an explanation of the irreversible $Rh(bpy)_3^{3+}$ electrochemistry,[5] we speculated that $Rh(bpy)_3^{2+}$ might exist predominantly in the monodentate $Rh(bpy)_2(bpy)^{2+}$ form, but we have found no spectral evidence for conversion of the primary reduction product (presumably containing three bidentate bpy ligands since $Rh(bpy)_3^{3+}$ does) to such a secondary product. Furthermore, the irreversibility of the electrochemistry in aqueous solutions has been traced to other reactions.[8] The $Rh(bpy)_3^{2+}$ description is also supported by the invariance of the product's spectrum with pH in the range 3–10.[9] The formulation of the $Rh(bpy)_2(OH)_2^+$ reduction product as six-coordinate seems required by the fact that it manifests two titratable protons in the pH range 8–11. Thus $Rh^{II}(bpy)_2(aq)$ is formulated as $Rh(bpy)_2(H_2O)_2^{2+}$ at pH <8.6, $Rh(bpy)_2(H_2O)(OH)^+$ at pH 8.6–11.1, and as $Rh(bpy)_2(OH)_2^0$ at pH >11.1. (These species have been invoked previously[9] to account for the chain aquation of $Rh(bpy)_3^{3+}$ in very alkaline solution, but they apparently were not studied directly.) The aquo- and hydroxo-containing bis(bipyridine)rhodium(II) species, in principle, exist as cis and trans isomers. In the parent $Rh(bpy)_2(H_2O)_2^{2+}$, the bpy groups are assumed to be cis to each other and there is no reason to expect the geometry to change (and no evidence that it does) when $Rh(bpy)_2(H_2O)_2^{3+}$ is reduced to $Rh(bpy)_2(H_2O)_2^{2+}$. On the other hand, *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$ and *trans*-$Ru(bpy)_2(H_2O)_2^{3+}$ have recently been prepared[10] so that the possibility that the analogous rhodium(II) (and rhodium(III)) complexes possess this geometry cannot be dismissed.

From our kinetics and spectral studies we have obtained data bearing on the thermodynamics of Rh(II)–ligand binding. The affinity of $Rh(bpy)_2(H_2O)_2^{2+}$ for bpy, $K = 5 \times 10^8$ M^{-1} at 25 °C, greatly exceeds that reported for most other metal centers studied. For divalent first transition series complexes, binding constants typically range from 10^2 to 10^6 M^{-1} (that for Fe(II), 2×10^9 M^{-1}, is atypically large as a result of a spin change).[11] No values have been reported for second or third transition series divalent metal centers, but in view of the increased magnitude of the ligand field splitting for such metal ions, the stability constant extracted for $Rh(bpy)_3^{2+}$ may not be unusually large; the stability constant implicated for $Rh(bpy)_3^{3+}$ is 10^{13} M^{-1}.[6,12]

The acidity of $Rh^{II}(bpy)_2(H_2O)_2^{2+}$ (pK_a = 8.6, 11.1) is about four orders of magnitude less than that found for $Rh(bpy)_2(H_2O)_2^{3+}$ (pK_a = 4.8, 6.8[6] (μ = 0.5 M, 25 °C) and 4.4, 6.4[4]) and for *cis*-$Co(phen)_2(H_2O)_2^{3+}$ (pK = 4.45, 6.8)[11] but is considerably greater than that of $Ru(bpy)_2pyH_2O^{2+}$ (pK = 10.8).[13]

Substitution Rates. The rate constant for dissociation of bpy from $Rh(bpy)_3^{2+}$ determined here at 25 °C, k_{13} = 0.6 s^{-1} at pH >7, is in good agreement with that reported (0.45 ± 0.05 s^{-1} at pH 3–10) in ref 9 and is somewhat slower than that (3 s^{-1}) reported for $Co(bpy)_3^{2+}$ under comparable conditions.[14,15] For both metal centers these rate constants are believed to represent composite constants, $k_c = k_o k_d/(k_{-o} + k_d)$ for opening (k_o) to the monodentate form and dissociation (k_d) of bpy from the latter. For $Co(bpy)_3^{2+}$ k_o = 36 s^{-1} at 25 °C,[15]

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(10) Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.

(11) (a) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1975; Vol. 2, p 235. (b) *Spec. Publ.–Chem. Soc. No. 17.*

(12) Note that the value $K = 10^{-3}$ M^{-1} given in ref 6 for the reaction

$$Rh(bpy)_3^{3+} + 2OH^- \rightleftharpoons Rh(bpy)_2(OH)_2^+ + bpy$$

should be $K = 10^3$ M^{-1}. The latter taken with $Rh(bpy)_2(H_2O)_2^{3+}$ pK_a values of 4.8 and 6.8[6] gives 10^{13} M^{-1} for

$$Rh(bpy)_2(H_2O)_2^{3+} + bpy \rightleftharpoons Rh(bpy)_3^{3+}$$

(13) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436.

(14) Simic, M. G.; Hoffman, M. Z.; Cheney, R. P.; Mulazzani, Q. G. *J. Phys. Chem.* **1979**, *83*, 439.

(15) Davies, R.; Green, M.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1972**, 1171.

and for $Rh(bpy)_3^{2+}$ $k_o > 10$ s^{-1}.[9] The activation parameters ($\Delta H^\ddagger$ = 12–27 kcal mol^{-1}, $\Delta S^\ddagger$ = −10 to +15 eu for $Co(bpy)_3^{2+}$, $Ni(bpy)_3^{2+}$, and $Fe(bpy)_3^{2+}$) for k_o have been discussed for the first transition series complexes. Here we have determined $\Delta H^\ddagger$ = 14.5 kcal mol^{-1} and ΔS = −11 eu for the composite k_c ($=k_{13}$). The rate constant $k_{-13} = 3.0 \times 10^8$ M^{-1} s^{-1} for bpy substitution on $Rh(bpy)_2(H_2O)_2^{2+}$ substantially exceeds that for $Co(bpy)_2(H_2O)_2^{2+}$ and analogous complexes of the first transition series.[14,15]

Reduction Potentials. The reduction potential for the $Rh(bpy)_3^{3+}$–$Rh(bpy)_3^{2+}$ couple was recently estimated as −0.86 V vs. SHE in water.[8] From the equilibrium constant (K_{18} = 2.1) obtained for eq 18 at pH 8.1,[6] the formal potential for

$$Rh(bpy)_3^{2+} + Rh(bpy)_2(OH)_2^{+} \underset{-2H^+}{\overset{2H^+}{\rightleftharpoons}} Rh(bpy)_3^{3+} + Rh(bpy)_2(H_2O)_2^{2+} \quad (18)$$

the $Rh(bpy)(OH)_2^{+}$–$Rh(bpy)_2(H_2O)_2^{2+}$ couple at pH 8.1 is −0.84 V. When the pK_a values of $Rh(bpy)_2(H_2O)_2^{3+}$ (4.8 and 6.8[6]) and $Rh(bpy)_2(H_2O)_2^{2+}$ (8.6 and 11.1) are taken into account, the $E°$ for the $Rh(bpy)_2(H_2O)_2^{3+}$–$Rh(bpy)_2(H_2O)_2^{2+}$ couple is −0.57 V vs. SHE while that for the $Rh(bpy)_2(OH)_2^{+}$–$Rh(bpy)_2(OH)_2^{0}$ couple is −1.05 V vs. SHE. These results are consistent with the quenching rate constants reported in ref 6: the rate constant for oxidation of $^*Ru(bpy)_3^{2+}$, the luminescent metal-to-ligand charge-transfer excited state of $Ru(bpy)_3^{2+}$ ($^*E_{3,2}$ = −0.84 V),[16] by $Rh(bpy)_2(H_2O)_2^{3+}$ is comparable to that for oxidation by $Rh(bpy)_3^{3+}$, but the rate constant is at least 100 times smaller when $Rh(bpy)_2(OH)_2^{+}$ is used. The data bearing on the affinity of $Rh(bpy)_2(H_2O)_2^{2+}$ and $Rh(bpy)_2(H_2O)_2^{3+}$ for bpy provide an additional check: from the difference in the $Rh(bpy)_3^{3+}$–$Rh(bpy)_3^{2+}$ and $Rh(bpy)_2(H_2O)_2^{3+}$–$Rh(bpy)_2(H_2O)_2^{2+}$ reduction potentials, the affinity of $Rh(bpy)_2(H_2O)_2^{3+}$ for bpy is 0.8×10^5 greater than that of $Rh(bpy)_2(H_2O)_2^{2+}$ (K_{-13}). The magnitude of K for

$$Rh(bpy)_2(H_2O)_2^{3+} + bpy \rightleftharpoons Rh(bpy)_3^{3+} \quad (19)$$

is thus estimated as $(0.8 \times 10^5)(5.0 \times 10^8\ M^{-1}) = 4 \times 10^{13}$ M^{-1} in rather good agreement with the value $\sim 10^{13}$ M^{-1} estimated from direct measurements on the rhodium(III) complex.[6,12]

If additional information and assumptions are taken under consideration, some conclusions concerning the rhodium(II)–rhodium(I) couples can also be reached. The formal potential for

$$Rh(bpy)_2(OH)_2^{+} + 2e^- = Rh(bpy)_2^{+} + 2OH^- \quad (20)$$

is −0.43 V in 0.05 M NaOH.[6,17] The potential calculated for 1.0 M OH^- is −0.51 V. From the latter and the $Rh(bpy)_2(OH)_2^{+}$–$Rh(bpy)_2(OH)_2^{0}$ potential obtained above, the value estimated for the rhodium(II)–rhodium(I) couple is −0.03 V. Inclusion of

$$Rh(bpy)_2(OH)_2^{0} + e^- = Rh(bpy)_2^{+} + 2OH^- \quad (21)$$

and $Rh(bpy)_2(H_2O)_2^{2+}$ pK_a's, etc. yields $E°$ = +0.46 V for eq 22.

$$Rh(bpy)_2(H_2O)_2^{2+} + e^- = Rh(bpy)_2^{+} + 2H_2O \quad (22)$$

(Note that, because of complex rhodium(I) equilibria, eq 21 and 22 describe the net change only at $<10^{-5}$ M Rh(I) and that eq 22 is valid only above pH ~7 since $Rh(bpy)_2^{+}$ "protonates" to give $Rh(bpy)_2H(H_2O)^{2+}$, whose pK_a is 7.3.[18]) The information obtained above is summarized in the Latimer diagrams

$$\begin{tikzcd}
Rh(bpy)_2(H_2O)_2^{3+} \arrow[r, "-0.57\ V"] & Rh(bpy)_2(H_2O)_2^{2+} \arrow[r, "+0.46\ V"] & Rh(bpy)_2^{+} \arrow[ll, bend left, "-0.06\ V"]
\end{tikzcd}$$

$$\begin{tikzcd}
Rh(bpy)_2(OH)_2^{+} \arrow[r, "-1.05\ V"] & Rh(bpy)_2(OH)_2^{0} \arrow[r, "+0.03\ V"] & Rh(bpy)_2^{+} \arrow[ll, bend left, "-0.51\ V"]
\end{tikzcd}$$

Disproportionation Mechanisms. Two remarkable disproportionation mechanisms have emerged from these and earlier[5,6,9] studies. For $Rh(bpy)_3^{2+}$ the sequence implicated is given by eq 13, 7, and 14, while, for $Rh^{II}(bpy)_2$, $Rh(bpy)_2(OH)_2^{+}$ and $Rh(bpy)_2^{+}$ form through first-order disruption of the dimer (eq 17). Upper limits for the rate constants of the direct "symmetric" second-order paths (eq 23, 11, and 24,

$$Rh(bpy)_3^{2+} \rightleftharpoons Rh(bpy)_2(H_2O)_2^{2+} + bpy \quad (13)$$

$$Rh(bpy)_2(H_2O)_2^{2+} \rightleftharpoons Rh(bpy)_2(H_2O)(OH)^{+} + H^+ \quad (7)$$

$$Rh(bpy)_3^{2+} + Rh(bpy)_2(H_2O)(OH)^{+} \rightarrow Rh(bpy)_3^{3+} + Rh(bpy)_2^{+} + H_2O + OH^- \quad (14)$$

$$2Rh(bpy)_3^{2+} \rightleftharpoons Rh(bpy)_3^{3+} + Rh(bpy)_3^{+} \quad (23)$$

$$Rh(bpy)_3^{+} \rightarrow Rh(bpy)_2^{+} + bpy \quad (11)$$

$$2Rh(bpy)_2(H_2O)_2^{2+} \rightarrow Rh(bpy)_2(OH)_2^{+} + Ru(bpy)_2^{+} + 2H^+ \quad (24)$$

which are *not* observed) can be estimated from the data of Figure 4 and the value of k_{17} to be $k_{23} < 3 \times 10^4$ M^{-1} s^{-1} and $k_{24} < 2 \times 10^7$ M^{-1} s^{-1}. The relative favorability of eq 14 vs. eq 23, K_{14}/K_{23}, is determined by the relative affinities of $Rh^{II}(bpy)_2$ and $Rh^{I}(bpy)_2$ for a third molecule of bpy; i.e., eq 25 is eq 14 minus eq 23, and the equilibrium constant for eq

$$Rh(bpy)_2(H_2O)(OH)^{+} + Rh(bpy)_3^{+} \rightarrow Rh(bpy)_2^{+} + Rh(bpy)_3^{2+} + H_2O + OH^- \quad (25)$$

25 is given by K_{-13}/K_{-11}. Earlier we obtained $K_{-13} = 5 \times 10^8$ M^{-1}; K_{-11} is estimated to be $<2 \times 10^2$ M^{-1} from data in ref 18. Thus $K_{25} > 2.5 \times 10^6$ M, and with the assumption that the relative rates of eq 14 and 23 are dictated only by the relative free energy changes, k_{14} should be at least 10^3 $(=(2.5 \times 10^6)^{1/2})$ greater than k_{23}. In actuality k_{14} is $>10^4$ greater than k_{23}. (Ideally one would prefer to evaluate K_{25} from the difference in the $Rh(bpy)_3^{2+}$–$Rh(bpy)_3^{+}$ and the $Rh(bpy)_2^{2+}(aq)$–$Rh(bpy)_2^{+}$ potentials, but the value for the former is not known.[6] More speculatively, the $E°$ for $Rh(bpy)_3^{2+}$–$Rh(bpy)_3^{+}$ can be estimated as <−0.85 V from the observation that a one-electron reduction of $Rh(bpy)_3^{3+}$ is observed in acetonitrile under some circumstances.[19] With the latter value, $K_{25} > 10^{10}$, which is certainly consistent with the conclusions reached on the basis of the conservative analysis above.)

In considering the relative rates of eq 14 and eq 24, we are on firmer ground. The relative driving force is that for eq 18 introduced above (K_{18} = 2.1 at pH 8.1), and k_{14}/k_{24} is expected to be ~1 if the reactivities of $Rh(bpy)_3^{2+}$, $Rh(bpy)_2(H_2O)_2^{2+}$, etc. with respect to outer-sphere electron transfer are identical. In reality k_{24} is at least 10 times smaller than k_{14}, probably

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(16) (a) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717. (b) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *1978*, 1. (c) Sutin, N. *J. Photochem.* **1979**, *10*, 19. (d) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.

(17) The value originally[6] reported for the couple as written was −0.45 V vs. SHE, but under the conditions of the measurement, $[Rh(bpy)_2(OH_2^{+}]$ = (0.6–0.8) × 10^{-3} M and $[Rh(bpy)_2^{+}]$ = (0.2–0.4) × 10^{-3} M and about half the $Rh(bpy)_2^{+}$ is in the dimeric form $[Rh(bpy)_2]_2^{2+}$.[6,18] The correction for this effect is small but has been included.

(18) Chou, M.; Creutz, C.; Mahajan, D.; Sutin, N.; Zipp, A. P. *Inorg. Chem.* **1982**, *21*, 3989.

(19) Kew, G.; DeArmond, K.; Hanck, K. *J. Phys. Chem.* **1974**, *78*, 727.

because dimerization is so rapid rather than because eq 24 is especially slow.

Dimerization vs. Disproportionation of Rh(II). The kinetics implicate $K_9 > 3 \times 10^{10}$ M^{-1} for

$$2\mathrm{Rh(bpy)_2(H_2O)_2}^{2+} \rightleftharpoons [\mathrm{Rh^{II}(bpy)_2}]_2\mathrm{(aq)} \qquad (9)$$

The dimerization constant for the analogous reaction (26)

$$2\mathrm{Rh(dmgH)_2(PPh_3)} \rightleftharpoons [\mathrm{Rh(dmgH)_2PPh_3}]_2 \qquad (26)$$

is 1.5×10^{10} M^{-1} at 25 °C in ethanol. In contrast to the above, the $\mathrm{Rh^{II}(bpy)_2}$ dimer undergoes further reaction, disproportionation to $\mathrm{Rh(bpy)_2(OH)_2}^+$ and $\mathrm{Rh(bpy)_2}^+$ (eq 17). This is a consequence of the stability of the disproportionation products rhodium(I) + rhodium(III). From the $\mathrm{Rh^{III}}$–$\mathrm{Rh^{II}}$ and $\mathrm{Rh^{II}}$–$\mathrm{Rh^{I}}$ potentials derived earlier, the driving force for disproportionation (eq 24) is 1.3 eV and $K_{24} = 1.1 \times 10^{22}$. Thus the equilibrium constant for heterolytic cleavage of the dimer according to eq 17 could be as great as 10^{11} M.[20]

Spectra. The electronic structure of the $\mathrm{Rh(bpy)_3}^{3+}$ reduction product has been discussed[7] in terms of two limiting descriptions—$\mathrm{Rh^{II}(bpy)_3}^{2+}$ and $\mathrm{Rh^{III}(bpy)_2(bpy^-)}^{2+}$. The latter was proposed because the $\mathrm{Rh(bpy)_3}^{3+}$–$\mathrm{Rh(bpy)_3}^{2+}$ reduction potential is so similar to that of $\mathrm{M^{III}(bpy)_3}^{3+}$–$\mathrm{M^{III}(bpy)_2(bpy^-)}^{2+}$ couples[5,8,21b] and because the outer-sphere electron-exchange rate implicated for the couple is so great.[5,7,8] Despite these bound-bpy$^-$ characteristics the spectrum of $\mathrm{Rh(bpy)_3}^{2+}$ (Figure 1) is atypical of a bpy$^-$ complex; it lacks the intense near-UV–visible–near-infrared π–π^* and π^*–π^* absorption peaks.[21] To account for the presence of both metal-centered and ligand-centered reduction product characteristics, we have also considered the possibility of electron isomerism (eq 27)

$$\mathrm{Rh^{II}(bpy)_3}^{2+} \rightleftharpoons \mathrm{Rh^{III}(bpy)_2(bpy^-)}^{2+} \qquad (27)$$

with $K_{27} \approx 10^{-1}$ at room temperature.[7] As a test of this possibility the temperature dependence of the $\mathrm{Rh(bpy)_3}^{2+}$ spectrum was investigated in the expectation that a significant shift toward the ligand-centered isomer would give rise to large enhancements of the low-energy absorption. No such effect was found. Thus we consider the spectra of the Rh(II) complexes in terms of the features expected for low-spin d^7 complexes.

For monomeric low-spin d^7 $\mathrm{Rh(bpy)_3}^{2+}$, $\mathrm{Rh(bpy)_2(H_2O)_2}^{2+}$, etc. ligand field transitions are expected at ≤500 nm[22] but should be difficult to observe because of their weak intensity ($\epsilon < 100$ M^{-1} cm^{-1}). At higher energy, ligand-centered bpy π–π^* transitions are expected in the UV region. In addition, metal-to-ligand (MLCT) and ligand-to-metal (LMCT) charge-transfer, as well as charge-transfer-to-solvent (CTTS), transitions are possible. The spectra obtained for $\mathrm{Rh(bpy)_3}^{2+}$ and $\mathrm{Rh^{II}(bpy)_2(aq)}$ at pH 8.8 in Figure 1 show intense UV features whose detailed structure is difficult to ascertain precisely because of the sharp intense features of the parent rhodium(III) complexes. For $\mathrm{Rh(bpy)_3}^{2+}$ the ligand-localized bpy band I (possibly split) should fall between 285 and 307 nm.[23] The observed spectrum is consistent with band I in this region, and the ϵ values observed are similar to those of other $\mathrm{M(bpy)_3}^{2+}$ complexes. The bis(bipyridine) complex presents similar features in the band I region, and as expected, the molar absorptivity is about one-third lower. The shoulders at ~360 nm may be due to Rh(II) πd → bpy π^* charge transfer[24] since the transition energies and intensities are much too great for the Rh(II) σ^*d → bpy π^* transition.[25] Alternatively these could be due to CTTS or even to LMCT (bpy π → Rh(II) σ^*d) absorption. Intraligand and charge-transfer absorptions are also expected for the dimer $[\mathrm{Rh(bpy)_2}]_2\mathrm{(aq)}$ (presumably $[\mathrm{Rh(bpy)_2(H_2O)}]_2{}^{4+}$), and in addition, bonding-to-antibonding transitions within the Rh–Rh bond are predicted.[3] This transition could be the source of the increased intensity in the 420-nm shoulder of the dimer (as compared to that for the monomers) since excitation within the Rh(II)–Rh(II) bond is generally seen at 500 nm or less.[2,26–31] In principle, the electronic spectra of the Rh(II) monomers and dimer contain information bearing on the nature of ligand–metal and metal–metal interactions but few definitive conclusions can be reached at this time.

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Registry No. $\mathrm{Rh(bpy)_3}^{3+}$, 47780-17-6; $\mathrm{Rh(bpy)_2(OH)_2}^+$, 84107-62-0; $(\dot{\mathrm{C}}\mathrm{H_2})\mathrm{CH_3CHOH}$, 7277-18-1; OH, 3352-57-6; $\mathrm{Rh(bpy)_3}^{2+}$, 75924-14-0; $\mathrm{Rh(bpy)_2(H_2O)_2}^{2+}$, 84107-63-1; $\mathrm{Rh(bpy)_2}^+$, 47386-82-3; $\mathrm{(CH_3)_2CHOH}$, 67-63-0; bpy, 366-18-7.

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(20) In pronounced contrast, disproportionation of the Rh(II) dimer $[\mathrm{RhL_4I}]_2{}^{2+}$ to $\mathrm{RhL_4}^+$ and $\mathrm{RhL_4I_2}^{2+}$ (L = *p*-$\mathrm{CH_3C_6H_4NC}$) is poised in some solvents: Olmstead, M. M.; Balch, A. L. *J. Organomet. Chem.* **1978**, 148, C15.

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(22) This assumes that 10*Dq* for Rh(II) is comparable to that for Ru(II). For Ru(II), see: Lever, A. B. P. "Inorganic Electronic Spectroscopy"; American Elsevier: New York, 1968; p 305.

(23) McWhinnie, W. R.; Miller, J. D. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 162.

(24) The second πd → bpy π^* transition (which involves population of higher energy bpy π^* levels) should lie ~10×10^3 cm^{-1} higher in energy (Hanazaki, I.; Nagakura, S. *Inorg. Chem.* **1969**, *8*, 648) and could account for part of the intense absorption in the vicinity of 270 nm.

(25) The σ^*d (e_g in octahedral symmetry) to bpy π^* transition would be expected at very low energy since the energy gap between these levels is small. It would likely occur in the optical region of the spectrum only if the excited state were extremely distorted compared to the ground state. In any case the transition is forbidden in octahedral symmetry and appears not to have been observed in the lower symmetry $\mathrm{M(bpy)_3}^{n+}$ series.

(26) For $[\mathrm{Rh(dmgH)_2PPh_3}]_2$ an intense band ($\epsilon = 5 \times 10^4$ M^{-1} cm^{-1}) at ~450 nm is reported.[2,27] The carboxylate-bridged dimers manifest comparably intense absorption only below 300 nm[28,29] as do $[\mathrm{Rh(H_2O)_5}]_2{}^{4+}$[28,30] and Rh(II) dimers containing isocyanide ligands.[31]

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