the sequence for *cis*- and *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$ is reversed. The observed preferences for ethylenediamine loss therefore do not seem in any way related to the small difference in σ-donor ability of the two ligands.

The kinetic evidence for more facile ethylenediamine aquation cited in the Introduction is indicative that the enhanced ethylenediamine aquation may involve steric effects. Consistent with this is the observation that the enhancement of ethylenediamine loss is greater in the bis complexes than in the mono(ethylenediamine) complex. For these two types of complex, respectively, $\phi_{NH_3}/\phi_{total} = k_{NH_3}/(k_{NH_3} + 2k_{en})$ and $\phi_{NH_3}/\phi_{total} = 2k'_{NH_3}/(2k'_{NH_3} + k'_{en})$. Here the k_i represent the rate constants for photoaquation of the ligand i from the excited state of *cis*- or *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$ and k'_i are the analogous constants for $[Cr(en)(NH_3)_4]^{3+}$. Thus $k_{en} = 2.83k_{NH_3}$ and $k'_{en} = 1.64k'_{NH_3}$, respectively. These rate constant ratios reveal an almost threefold increase in k_{en} in the bis complexes in contrast to a 65% increase in the mono(ethylenediamine) complex. This is the type of result to be expected if the ethylenediamine chelate ring "bite" is such as to distort the chromium(III) octahedral environment and if the strain of two such rings is multiplicative in nature.

These results imply important consequences for the purely spectroscopic/theoretical models of photochemistry of complex ions. It must be emphasized that the observed results cannot be consistently related to any differences in the spectroscopic parameters for ethylenediamine and ammonia nor to any uncertainties in the σ- and π-donor strengths or the ligand field parameters. The absence of significant wavelength dependence also eliminates complications due to participation of different excited states yielding different percentages of ammonia. The results reflect pure differences in the relative leaving-group tendencies of ethylenediamine and ammonia from the respective participating excited states and are nonspectroscopic in origin. The results are therefore a clear experimental demonstration of the usual caution[5] that a number of other factors, in this case probably steric effects, which may not show up to any great extent in the ligand field spectra or their derived parameters, can have an important role in determining the detail of quantum yields for a given complex or series of complexes.

While the authors remain convinced that the spectroscopically based theories are an extremely useful and helpful guide for the experimental photochemist and also have played and are still playing a crucial role in stimulating important experimental work, this study demonstrates the need to take the cautionary warnings seriously and avoid being misled by theoretical predictions.

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Registry No. $[Cr(en)_3]^{3+}$, 15276-13-8; *cis*-$[Cr(en)_2(NH_3)_2]^{3+}$, 66008-05-7; *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$, 65982-64-1; $[Cr(en)(NH_3)_4]^{3+}$, 65982-66-3; $[Cr(NH_3)_6]^{3+}$, 14695-96-6.

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Photoinduced Oxygenation of *trans*-Aquohydridotetraamminerhodium(III). Evidence for a Transition-Metal Chain Carrier[1a]

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Ultraviolet excitations of aerated, acidic aqueous solutions of $Rh(NH_3)_4(OH_2)H^{2+}$ result in the efficient formation of $Rh(NH_3)_4(OH_2)O_2H^{2+}$. The rate of formation of hydroperoxide was found to be zero order in O_2 but first order in both substrate concentration and incident light intensity. The photoinitiated thermal reaction appears to be a chain reaction with $Rh(NH_3)_4{}^{2+}(aq)$ acting as a chain carrier which "activates" O_2 by coordination. The hydroperoxo complex decomposes very slowly, even in the presence of excess $Rh(NH_3)_4(OH_2)H^{2+}$, to form a colored, paramagnetic species identified as a superoxo complex.

Introduction

Complexes between hydrogen and transition-metal complexes have been of long and continuing interest. Early interest in these systems originated from the search for effective homogeneous hydrogenation catalysts.[2] Some of the more current interest derives from suggestions that hydrido complexes would be useful in cycles involving the photochemical cleavage of water.[3-5]

Hydridocobalamin[6-8] and hydridopentacyanocobaltates[9] are known but are very reactive species. These and some related hydrido complexes of cobalt(III) tend to be very labile substrates, unstable toward H^+ [6,10,11] and O_2.[6,12] As a consequence, it is very difficult to characterize them or to quantitatively investigate their solution behavior.[10]

The hydrido complexes of rhodium have been reported to be much less reactive than their cobalt analogues and they have

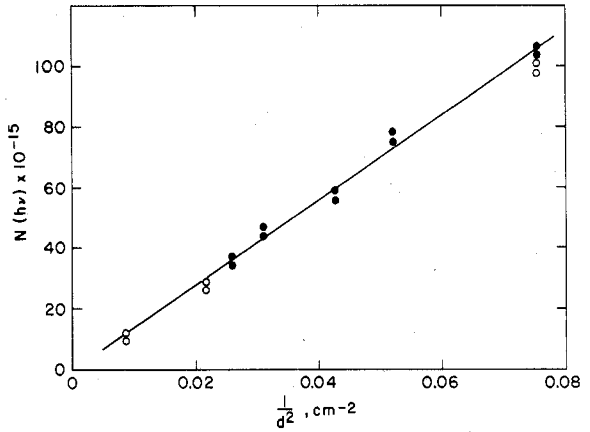

Figure 1. Calibration of the distance dependence of incident light intensity in the photolysis system. Ferrioxalate actinometer: open circles, 6×10^{-3} M $Fe(C_2O_4)_3{}^{3-}$; closed circles, 0.15 M $Fe(C_2O_4)_3{}^{3-}$. $N(h\nu)$ is the number of quanta per flash. The distance from flash source to photolysis cell is designated d.

been quite well characterized.[6,13-18] For example, *trans*-$Rh(NH_3)_4(OH_2)H^{2+}$ may be conveniently handled in an aerated, acidic aqueous solution.

We initiated this study as a part of our program of study with photohomolytic processes in transition-metal complexes.[19-23] This previous work has indicated that the minimum excitation energy required to cause homolysis of metal–ligand bonds is related to the homolytic bond energy and does not seem to be a significant function of the excited states initially populated by the absorption of light.[19] Thus rhodium–ligand homolyses[20,21] tend to occur at higher energy than cobalt–ligand homolyses.[19] In contrast to the ultraviolet excitations required for homolysis of metal–halide bonds in pentaammine complexes, cobalt–alkyl[22] and rhodium–alkyl[23] homolyses occur for relatively low-energy excitation. We would anticipate metal–hydride bonds to be intermediate in behavior between metal–halide and metal–alkyl bonds. Most of the systematic photochemical studies of hydrido complexes have been confined to polyhydrido species. For these systems the predominate process appears to be a concerted extrusion of H_2.[24-27] There seems to have been only one previous report of photolyses of a monohydrido complex.[28] We have found that homolytic processes in $Rh(NH_3)_5H^{2+}$ and $Rh(NH_3)_4(OH_2)H^{2+}$ initiate remarkable thermal reactions which dominate all chemical observations on these systems.

Experimental Section

Hydridopentaamminerhodium(III) sulfate was prepared according to a literature method.[13] Because of the small equilibrium constant for the ammonia aquation of the above complex, a slightly modified method was used to prepare the hydridoaquotetraamminerhodium(III) sulfate. $[Rh(NH_3)_5H]SO_4$ (1 g) was dissolved in deaerated H_2O (15 mL) and a few drops of concentrated sulfuric acid were added. Then acetone was added to the resulting solution until precipitation of a white solid was completed. The solid was separated by filtration and was washed with acetone.

To prepare [*trans*-$Rh(NH_3)_4(OH_2)H]SO_4$, 0.6 g of $[Rh(NH_3)_5H]SO_4$ was dissolved in 5 mL of N_2-deaerated water, and the solution was mixed with 1 mL of deaerated 6 N H_2SO_4. The white crystalline solid was collected by filtration and washed with deaerated acetone. Standard literature procedures were used to prepare $[Rh(NH_3)_4(OH_2)C_2H_5](ClO_4)_2$.[13,23,29]

Experimental (H and N) analyses were consistently in excellent agreement with expectation (average deviations of less than 2% from expectation).

Continuous photolyses were performed using apparatus and technique as described previously.[19-23] Deaeration was accomplished by means of Cr^{2+}-scrubbed, entrained N_2.

Studies of the photoinduced reaction were performed using a Xenon Corp. spectroscopic flash module as the excitation source. Aliquots of sample solution were placed in a 1-cm path length quartz cuvette which was sealed by means of a serum cap. An optical bench was arranged with the cell holder mounted so that the lamp to sample cell distance could be reproducibly varied. Actinometry was performed using ferrioxalate.[30] Figure 1 indicates the variation (and reproducibility) of flash intensity with distance for this system.

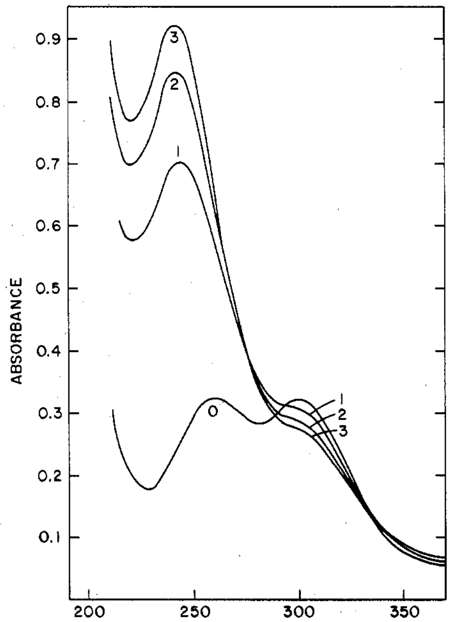

Figure 2. Changes in absorption spectrum observed following the 250-J flash of a $Rh(NH_3)_4(OH_2)H^{2+}$ solution in a 1-cm cuvette: initial spectrum (before irradiation), 0; 3 min after irradiation, 1; 6 min after irradiation 2; 9 min after irradiation, 3. Bottom curve is cell blank. Approximate isosbestic points were observed at 275 and 340 nm.

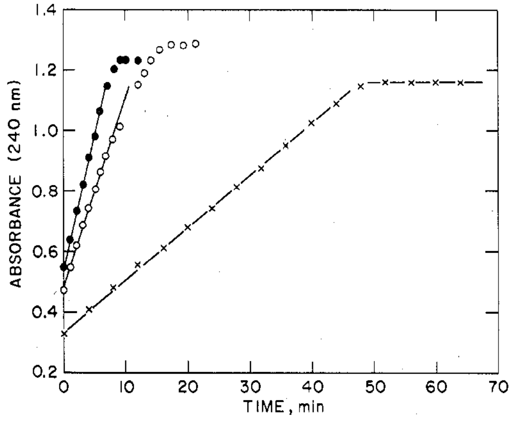

Figure 3. Photoinduced dark reaction monitored at 240 nm for various substrate concentrations: $[Rh(NH_3)_4(OH_2)H^{2+}] = 9.8 \times 10^{-4}$ M, ×; 2.2×10^{-3} M, ○; 3.4×10^{-3} M, ● (single flash, all solutions 0.1 M in $HClO_4$, cell to lamp distance 4.4 cm).

For the kinetic studies the cell was transferred to a Cary 14 spectrophotometer as quickly as possible following the flash pulse. Timing was commenced with the firing of the flash lamp. The flash pulse was of a few microseconds in duration (~15 J/flash).

Results

Continuous 254-nm photolysis of $Rh(NH_3)_5H^{2+}$ in deaerated solution resulted in the small spectroscopic changes associated with replacement of coordinated NH_3 by H_2O: a decrease in absorbance between 354 and 225 nm. Smaller absorbance changes resulted when *trans*-$Rh(NH_3)_4(OH_2)H^{2+}$ was irradiated at 254 nm in deaerated solutions. Most of the observed changes in such "deaerated" solutions can be attributed to small residual amounts of oxygen in solution.

When either complex was irradiated in aerated solution, very large changes in ultraviolet absorptivity occurred. As shown

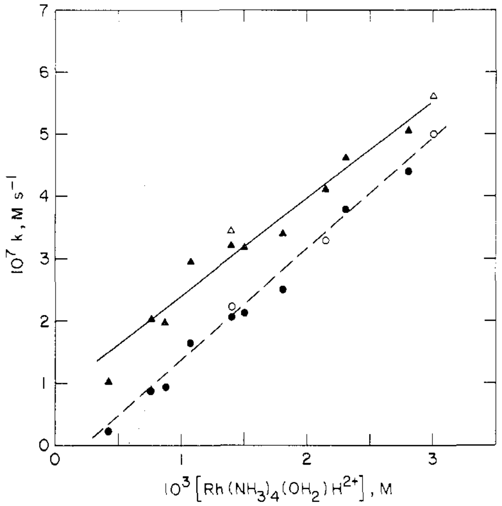

Figure 4. Pseudo-zero-order rate constant for $Rh(NH_3)_4(OH_2)O_2H^{2+}$ formation as a function of $[Rh(NH_3)_4(OH_2)H^{2+}]$: circles, $k_{obsd} = (dA(240\ nm)/dt) \div (4025\ M^{-1}\ cm^{-1})$; triangles, correction applied for variations of substrate absorbance using Beer's law and ϵ(301 nm) 317 $M^{-1}\ cm^{-1}$ for $Rh(NH_3)_4(OH_2)H^{2+}$; open figures (circles or triangles), oxygen-saturated solution; closed figures, air-saturated solution.

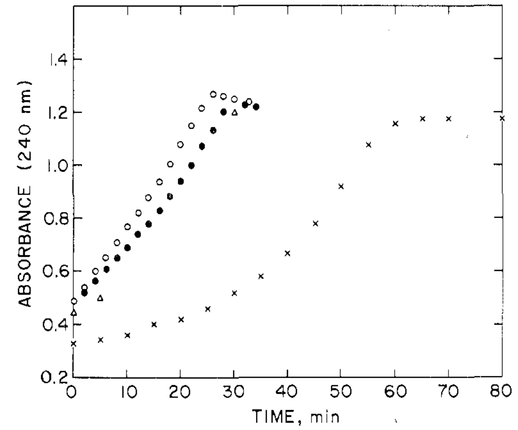

Figure 5. Photoinduced dark reaction for very small intensities of absorbed radiation: for $[Rh(NH_3)_4(OH_2)H^{2+}] = 2.2 \times 10^{-3}$ M, cell to lamp distance 6.0 cm (open circles) or 6.9 cm (closed circles); for $[Rh(NH_3)_5(OH_2)H^{2+}] = 1.5 \times 10^{-3}$ M, cell to lamp distance 10.45 cm (×); for $[Rh(NH_3)_5(OH_2)H^{2+}] = 2.2 \times 10^{-3}$ M, $[H_2O_2] = 5 \times 10^{-4}$ M, cell to lamp distance 10.45 cm (▵) (all solutions 0.1 M in $HClO_4$).

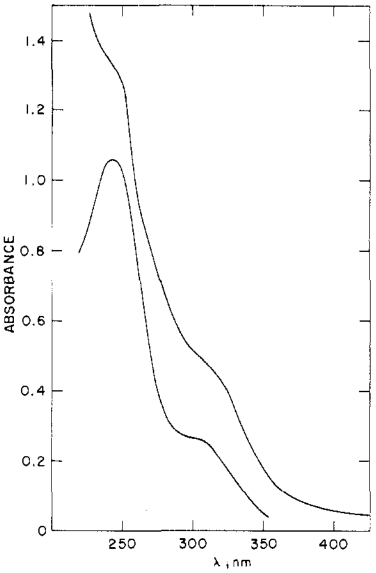

Figure 6. Absorption spectra of product mixtures from the photoinduced oxygenation in aerated 0.1 M $HClO_4$. Initial substrate composition: upper curve, 1.01×10^{-3} M $Rh(NH_3)_4(OH_2)H^{2+}$ *and* 1.2×10^{-3} M $Rh(NH_3)_4(OH_2)C_2H_5^{2+}$; lower curve, 1.01×10^{-3} M $Rh(NH_3)_4(OH_2)H^{2+}$. The ethyl complex exhibits a very strong absorbance for $\lambda < 225$ nm.

in Figure 2, a new species, strongly absorbing at ~240 nm, was generated over a period of several minutes after the irradiation had stopped. The dark reaction occurred with similar efficiency even in 1.7 M 2-propanol and was not very sensitive to pH. The rate of growth of the 240-nm species was a function of concentration of substrate and the number of quanta absorbed (Tables S-I and S-II;[31] Figures 3–5). The initial stage of the thermal reaction was a relatively rapid rise in the 240-nm absorbance followed by a much slower decay of the initial product into a more stable species absorbing in the visible. The amount of initial product did not depend significantly on $[Rh(NH_3)_4(OH_2)H^{2+}]$ (Figure 3), but it was proportional to $[O_2]$. We found the average absorptivity of the initial product to be ϵ_{240} 4025 $M^{-1}\ cm^{-1}$ based on total consumption of O_2. This may be compared to the value of ϵ_{237} 3800 $M^{-1}\ cm^{-1}$ reported by Johnston and Page for $Rh(NH_3)_4(OH_2)O_2H^{2+}$.[14] The rate of formation of the initial product appeared to be zero order in $[O_2]$ but was directly proportional to $[Rh(NH_3)_4(OH_2)H^{2+}]$ (Figure 4, Table S-I) with $dA(240\ nm)/dt = (0.58 \pm 0.05)[Rh(NH_3)_4(OH_2)H^{2+}]$. For reasonably large flash intensities, this rate was also directly proportional to the incident pulse intensity with $dA(240\ nm)/dt = (1.2 \pm 0.1) \times 10^{-20}Q$, where Q is the relative intensity per flash as defined in Figure 1. Since we used a white flash for excitation, and since the absoption profiles of $Fe(C_2O_4)_3^{3-}$ and $Rh(NH_3)_4(OH_2)H^{2+}$ are vastly different, this is only a relative intensity dependence; however, our concentations were such that much more light was absorbed by $Fe(C_2O_4)_3^{3-}$ than by $Rh(NH_3)_4(OH_2)H^{2+}$ so that the implied quantum yields are much greater than 1 as expected for a chain reaction. We were working in a concentration region where absorption intensity (I_a) did vary with concentration, but an approximate correction for these variations did not significantly affect the apparent first-order dependence of the thermal reaction on $Rh(NH_3)_4(OH_2)H^{2+}$ (Figure 4); this "correction" would reduce the pseudo-zero-order rate constant by 10%. At the very lowest intensities used (cell-to-lamp distances of 6–10 cm) plots of A(240 nm) vs. time exhibited positive curvature (Figure 5). Introduction of small amounts of H_2O_2 into $Rh(NH_3)_4(OH_2)H^{2+}$ generated qualitatively similar effects (Figure 5). Efforts to obtain quantitative data from continuous photolyses (i.e., quantum yields, threshold energies, etc.) were frustrated by the efficiency of the thermal chain reaction and by secondary photolysis of the very strongly absorbing product species.

The initial oxygenation product (λ_{max} 240 nm) decayed over the period of many hours into a purple paramagnetic product (λ_{max} at 355 and 565 nm).

Irradiation of $Rh(NH_3)_4(OH_2)H^{2+}$ solutions containing $Rh(NH_3)_5Cl^{2+}$ resulted in a diminution of the rate formation of $Rh(NH_3)_4(OH_2)O_2H^{2+}$, presumably due to an inner filter effect. In contrast, irradiation of solutions containing $Rh(NH_3)_4(OH_2)C_2H_5^{2+}$ resulted in an increase in the rate of formation of the hydroperoxo product (Table I, Figure 6).

Discussion

Photohomolytic processes in organocobalt[6,22,31] and organorhodium[23] complexes tend to be thermally reversible (e.g., as in eq 1 and 2) in the absence of radical scavengers

$$H_2OML_4R + h\nu \rightarrow H_2OML_4 + \cdot R \qquad (1)$$

$$\cdot R + H_2OML_4 \rightarrow H_2OML_4R \qquad (2)$$

Table I. Variations in the Rates of Product Formation with Concentration of $Rh(NH_3)_4(OH_2)C_2H_5^{2+}$

$10^3[Rh(NH_3)_4(OH_2)H^{2+}]$,[a] M	$10^3[Rh(NH_3)_4(OH_2)C_2H_5^{2+}]$, M	pseudo-zero-order rate, $10^4 dA(240\ nm)/dt$
1.01	0	3.6
1.01	0.35	3.11
1.01	1.18	4.1
1.01	2.2	7.3
1.01	2.75	8.5

[a] Initial concentrations. All solutions in 0.10 M $HClO_4$. Cell-to-sample distance = 3.65 cm; the smaller rates obtained here than in Table S-II are attributed to a decrease in the ultraviolet intensity of the lamp in the one-year interval between the sets of experiments.

since the photostationary-state concentration of the H_2OML_4 fragment quickly becomes large enough that (2) becomes the predominant observed reaction of the radicals, ·R. Oxygen has been a frequently employed and very useful scavenger for alkyl radicals in these systems.

There are many chemical similarities in the behavior of hydrogen atoms (·H) and alkyl radicals, including the efficient oxygen-scavenging reactions. However, ultraviolet irradiations of aerated aqueous solutions of $Rh(NH_3)_4(OH_2)H^{2+}$ initiate processes which result in the "insertion" of O_2 in the Rh–H bond, forming $Rh(NH_3)_5(OH_2)O_2H^{2+}$ as the initial observed product. The hydroperoxo complex decays very slowly, into a colored species similar to those previously identified as superoxo complexes.[15,33] Once initiated, the reaction producing the hydroperoxo complex proceeds in the dark until all of the oxygen is consumed. "Quantum yields" calculated for this process can be astronomical at very low light levels and are always greater than 1.0. In addition, the rate of formation of hydroperoxo complex is zero order in $[O_2]$ but first order in $[Rh(NH_3)_4(OH_2)H^{2+}]$ and in the number of incident photons. These observations strongly implicate a simple free-radical mechanism with $Rh(NH_3)_4^{2+}(aq)$[34-36] as the chain carrier, eq 3–7. If we assume that $[Rh(NH_3)_4^{2+}(aq)]$ + $[Rh(NH_3)_4(OH_2)O_2^{2+}] = 2Q_a = 2\int_0^\infty\int_0^\infty \phi(I_a)\, d\nu\, dt$ (i.e., the total number of moles per liter of primary products), the rate of formation of $Rh(NH_3)_4(OH_2)O_2H^{2+}$ is given by (8). For most experimental conditions we find $k_{obsd} \simeq k[Rh(NH_3)_4(OH_2)H^{2+}]Q_a$, which implies that $k_4[O_2] > (k_{-4} + k_5[Rh(NH_3)_4(OH_2)H^{2+}])$. It has previously been shown that $k_4 \simeq 2 \times 10^8\ M^{-1}\ s^{-1}$,[36] so k_5 must be less than $\sim 4 \times 10^7\ M^{-1}\ s^{-1}$. These parameters also indicate that $5 \times 10^{-8}\ M >> Q_a \geq 4 \times 10^{-12}$ M for the data in Figure 3. This is quite reasonable as the intensity of the xenon flash lamp falls off in the ultraviolet where the substrate absorbs, and since $\phi \leq 1$.

$$Rh(NH_3)_5(OH_2)H^{2+} + h\nu \rightarrow Rh(NH_3)_4^{2+}(aq) + \cdot H \qquad \phi(I_a) \quad (3)$$

$$\cdot H + O_2 \rightarrow HO_2 \quad (4)$$

$$HO_2 + Rh(NH_3)_4(OH_2)H^{2+} \rightarrow H_2O_2 + Rh(NH_3)_4^{2+}(aq) \quad (5)$$

$$Rh(NH_3)_4^{2+}(aq) + O_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Rh(NH_3)_4(OH_2)O_2^{2+} \quad (6)$$

$$Rh(NH_3)_4(OH_2)O_2^{2+} + Rh(NH_3)_4(OH_2)H^{2+} \xrightarrow{k_5} Rh(NH_3)_4(OH_2)O_2H^{2+} + Rh(NH_3)_4^{2+}(aq) \quad (7)$$

$$\frac{d[Rh(NH_3)_4(OH_2)O_2H^{2+}]}{dt} = \frac{2k_4k_5[Rh(NH_3)_4(OH_2)H^{2+}][O_2]Q_a}{k_4[O_2] + k_{-4} + k_5[Rh(NH_3)_4(OH_2)H^{2+}]} \quad (8)$$

It is to be noted that the proposed mechanism takes account of the observed efficient formation of $Rh(NH_3)_4(OH_2)O_2H^{2+}$ and the previously established efficiency of $Rh(NH_3)_4^{2+}$ for scavenging O_2.[36] Other alternatives, involving outer-sphere oxidations of $Rh(NH_3)_4^{2+}$, would lead to substitution-inert rhodium(III) species and would not readily account for the observation of nearly quantitative formation of the hydroperoxide as an initial product.

The enhancement of the rate of production of $Rh(NH_3)_4(OH_2)O_2H^{2+}$ found for irradiations of solutions containing both $Rh(NH_3)_4(OH_2)H^{2+}$ and $Rh(NH_3)_4(OH_2)C_2H_5^{2+}$ as the latter becomes the principle absorbing species[37] lends qualitative support to the proposed chain mechanism since the efficient rhodium–alkyl homolysis would result in an increase of the amount of chain carrier. Our results (Figure 6) also indicate that the thermal chain reactions do not involve $Rh(NH_3)_4(OH_2)C_2H_5^{2+}$, consistent with the previously noted thermal stability of photolyzed solutions of this substrate.[23]

Given the very small number of photons actually absorbed by the substrate, we attribute the complex kinetic behavior exhibited at very low light intensities to other species (e.g., H_2O_2) which become significant contributing sources of the $Rh(NH_3)_4^{2+}(aq)$ chain carrier through relatively slow thermal reactions. Under these conditions one observes an induction period characteristic of the slow generation of the chain carrier. The "dark" reaction of $Rh(NH_3)_4(OH_2)H^{2+}$ in aerated solutions exhibits qualitatively similar features, suggesting that very small concentrations of oxidizing contaminants (or O_2) can generate enough $Rh(NH_3)_4^{2+}(aq)$ to set off the chain reaction. In fact the very small photonic requirements of the photoinduced oxygenation reaction lead us to suspect that the "dark" reactions occur as a consequence of limited exposure of the sample to light (e.g., in the spectrophotometer).

Equations 3–7 describe chain-initiation and propagation steps in terms of reactions of predominant solution species (i.e., O_2 and $Rh(NH_3)_4(OH_2)H^{2+}$). The chain-termination step (or steps) must be higher order in transient species; e.g., as in (9).

$$Rh(NH_3)_4^{2+}(aq) + Rh(NH_3)_4(OH_2)O_2^{2+} \rightarrow [Rh(NH_3)_4OH_2]_2O_2^{4+} \quad (9)$$

The photoinduced oxygenation of $Rh(NH_3)_4(OH_2)H^{2+}$ has been found to be a remarkably efficient chain reaction. This efficiency arises because the chain carrier, $Rh(NH_3)_4^{2+}(aq)$, is a relatively discriminating "radical" species, and very few side reactions seem to complicate the process. Processes of this type could constitute a serious problem in the utilization of hydrido complexes in schemes for the photochemical cleavage of water. It will be of some interest to further explore the extent to which low-spin d^7 metal complexes can be the active participants in radical reaction processes.

It is interesting that the coordinated dioxygen molecule is appreciably more reactive than the molecular oxygen. However, there can be little doubt that the reason (7) occurs orders of magnitude more rapidly than (10) is due to the relative stability of hydroperoxide compared to perhydroxyl.

$$O_2 + Rh(NH_3)_4(OH_2)H^{2+} \rightarrow HO_2\cdot + Rh(NH_3)_4^{2+}(aq) \quad (10)$$

In this instance, at least, the process of "activation" of molecular oxygen simply corresponds to formation of a complex in which coordinated O_2 can function as a superoxo species. This kind of reactivity is observed in many dioxygen adducts of low-spin d^7 species.[38]

Registry No. *trans*-$Rh(NH_3)_4(OH_2)H^{2+}$, 44469-95-6; $Rh(NH_3)_4(OH_2)O_2H^{2+}$, 68492-49-9; $Rh(NH_3)_4(OH_2)C_2H_5^{2+}$, 68539-08-2; $[Rh(NH_3)_5H]SO_4$, 19440-32-5.

Supplementary Material Available: Tables S-I (kinetic data) and S-II (variations of kinetic parameters with light intensity) (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Partial support of this research by the National Science Foundation and the National Institutes of Health is gratefully acknowledged. (b) UNESCO Fellow during September 1976.

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Kinetic Study on the Disproportionation Equilibrium of μ-Oxo-bis[oxobis(*N*,*N*-diethyldichalcogenocarbamato)molybdenum(V)]

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μ-Oxo-bis[oxobis(*N*,*N*-diethylthioseleno- and -diselenocarbamato)molybdenum(V)], $Mo^{V}{}_2O_3(XYCNEt_2)_4$ (XY = SSe, SeSe), were prepared. These compounds undergo a disproportionation reaction in solution to exist as an equilibrium mixture with $Mo^{IV}O(XYCNEt_2)_2$ and $Mo^{VI}O_2(XYCNEt_2)_2$, as reported for the dithiocarbamato analogue, $Mo^{V}{}_2O_3(S_2CNEt_2)_4$. Rates of the equilibration for these three systems were determined by the concentration-jump relaxation technique in 1,2-dichloroethane. The rate of disproportionation of the Mo(V) complexes increases in the order of XY = SS < SSe < SeSe, while that of the coupling reaction of the Mo(IV) complex with the Mo(VI) complex shows a reverse tendency. Activation parameters for the disproportionation and the coupling reaction of these systems suggest that the Mo–O–Mo linkage in the transition state of the disproportionation is greatly weakened. Enthalpy and entropy changes in the disproportionation were also obtained; the values in the diseleno complex are fairly smaller than those of the dithio and thioseleno analogues. A possible explanation for this is presented in terms of marked differences of the absorption intensity in their visible spectra.

Introduction

In recent years, much attention has been paid to molybdenum complexes containing sulfur ligands as model compounds for molybdenum-containing enzymes.[1,2] In this connection, dimeric μ-oxo-molybdenum(V) complexes of the $Mo_2O_3L_4$ type (L = dialkyldithiocarbamate, 1-piperidinecarbodithioate, diphenylphosphinodithioate, and related ligands) are well-known to undergo disproportionation in solution to exist as an equilibrium mixture with oxomolybdenum(IV), $MoOL_2$, and dioxomolybdenum(VI) complexes, MoO_2L_2, as follows:[3,4]

$$Mo_2O_3L_4 \overset{K}{\rightleftharpoons} MoOL_2 + MoO_2L_2$$

The equilibrium constant K for L = n-Pr_2NCS_2 was determined as 4×10^{-3} mol/L in chlorobenzene at 41 °C.[5] Newton and his co-workers have suggested that this sort of equilibrium

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