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Redox-Catalyzed Aquation of Nitrosylpentaammineruthenium(3+) Ion[1]

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The reaction of 1 equiv of $Ru(NH_3)_5NO^{3+}$ with 0.02–0.1 equiv of the one-electron reducing radicals CO_2^- ($k_1 = 3.1 \times 10^9$ M^{-1} s^{-1}) and $(CH_3)_2\dot{C}OH$ ($k_2 = 5.5 \times 10^8$ M^{-1} s^{-1}), produced by radiation chemical techniques in neutral aqueous solution, generates nearly 1 equiv each of *trans*-$Ru(NH_3)_4NO(OH)^{2+}$ and NH_3. The initially produced one-electron reduced species $Ru(NH_3)_5\dot{N}O^{2+}$ undergoes trans-NH_3 detachment and aquation to form the catalyst for the reduction of unreacted substrate; O_2 quenches the catalyzed aquation by scavenging $Ru(NH_3)_5\dot{N}O^{2+}$ ($k = 7.6 \times 10^6$ M^{-1} s^{-1}). The formation of *trans*-$Ru(NH_3)_4NO(OH)^{2+}$ proceeds via zero-order kinetics with a rate constant that is independent of $[Ru(NH_3)_5NO^{3+}]$ but linearly dependent on $[Ru(NH_3)_5\dot{N}O^{2+}]$ initially produced by the radical reduction. Kinetic analysis shows that $k_3 = 1.8 \times 10^{-2}$ s^{-1} and $k_4 = 8$ M^{-1} s^{-1}. In acidic solution, without the driving force of reaction 5, the overall reaction does not go to completion.

$$Ru(NH_3)_5\dot{N}O^{2+} \xrightarrow{H_2O} trans\text{-}Ru(NH_3)_4\dot{N}O(OH_2)^{2+} + NH_3 \qquad (3)$$

$$trans\text{-}Ru(NH_3)_4\dot{N}O(OH_2)^{2+} + Ru(NH_3)_5NO^{3+} \rightleftarrows trans\text{-}Ru(NH_3)_4NO(OH_2)^{3+} + Ru(NH_3)_5\dot{N}O^{2+} \qquad (4)$$

$$trans\text{-}Ru(NH_3)_4NO(OH_2)^{3+} \rightleftarrows trans\text{-}Ru(NH_3)_4NO(OH)^{2+} + H^+ \qquad (5)$$

Introduction

Ruthenium–nitrosyl complexes of the form $Ru^{II}–NO^+$ undergo facile reversible electron transfer in which the added electron is localized mainly on the nitrosyl ligand yielding a coordinated nitric oxide complex of the form $Ru^{II}–\dot{N}O$.[2] Such species may be important intermediates in the multistep reduction of nitrosyl complexes[3,4] and in the oxidation of coordinated NO^-; linear NO^+ and bent NO^- show contrasting properties of chemical reactivity which depend upon the particular bonding mode of the ligand and the overall geometry of the complex.[5] The one-electron reduction of *cis*-$Ru(bpy)_2NO(X)^{n+}$ complexes ($X = N_3^-, Cl^-, NO_2^-$ ($n = 2$); $X = NH_3$, pyridine, CH_3CN ($n = 3$)), results in characterizable air-sensitive compounds in which the integrity of the ligands has been maintained.[6] On the other hand, the one-electron reduction of $Fe(CN)_5NO^{2-}$ results in the reversible loss of trans CN^- to yield an equilibrium mixture of $Fe(CN)_5\dot{N}O^{3-}$ and $Fe(CN)_4NO^{2-}$.[7]

In previous studies involving the free-radical and cyclic voltammetric reduction of $Ru(NH_3)_5NO^{3+}$,[2] it was observed that the initially produced $Ru(NH_3)_5\dot{N}O^{2+}$ was unstable in aqueous solution in the time frame of tens of seconds as evidenced by time-dependent changes in its spectrum and irreversible cyclic voltammetric waves at slow scan rates. In this paper, an examination is made of the irreversible detachment of the trans ligand and the electron-transfer reactions of the resulting reduced complex.

Experimental Section

Materials. All reagents were of the highest obtainable quality and were used without further purification unless otherwise stated. Solutions were prepared from distilled water that had been passed through a Millipore purification train and were buffered with phosphate and NaOH. Nitrous oxide (Matheson) was scrubbed with consecutive towers of fresh Cr_{aq}^{2+} and 0.1 M NaCl in an all-glass flow system to remove traces of O_2 and was introduced into the solutions via Pt or stainless steel needles or glass capillaries. Trifluoromethylsulfonic acid (3 M) was distilled and stored as previously described.[8] The sodium salt (NaTFMS) was prepared by the method of Scott.[9]

$[Ru(NH_3)_5NO]Cl_3$ was prepared by the reaction of $Ru(NH_3)_6^{3+}$ with NO(g)[10] or by the method of Gleu.[11] The $TFMS^-$ salt was prepared as previously described.[4] Both the Cl^- and $TFMS^-$ salts gave identical results in this study. The preparation of *trans*-$[Ru(NH_3)_4NO(OH)]Cl_2$ has been described before.[11] Solutions of the Ru complexes containing HCO_2^- as the only anion were prepared from the Cl^- salts using ion-exchange techniques.

Separations. Sephadex-C25 100–200 mesh (Pharmacia) cation-exchange resin was used without further purification. Previous experience with this resin[4] indicated that 1+, 2+, and 3+ charged monomeric Ru–ammine complexes are eluted with 0.25, 0.5, and 1.0 M NaCl solutions, respectively, and move more rapidly with KBr solutions than with NaCl.

Analyses. The free NH_3 concentration was measured with an ammonia electrode (Orion Model 95-10) coupled to an ion analyzer (Orion Model 801) which was equipped with digital printer (Orion Model 751). Calibration plots of log $[NH_3]$ vs. mV were made daily from fresh standard NH_4Cl solutions. The presence of Ru complexes at pH 13 did not interfere with the NH_3 analysis; unirradiated complexes gave residual $[NH_3] < 5 \times 10^{-6}$ M. Using the modified procedure of Woodhead and Fletcher,[8,12] [Ru] was determined spectrophotometrically at the ruthenate–perruthenate isosbestic point (ϵ_{415} 1050 M^{-1} cm^{-1}).

All UV–vis spectra and slow kinetic data were obtained with a Cary 118 or 15 recording spectrophotometer. IR spectra were obtained with a Beckman IR 9 spectrophotometer from samples suspended in a KBr matrix. The pH of all solutions was determined with Beckman SS-2, Orion 801, or Corning 112 pH meters calibrated with certified buffers (Fisher).

Radiolysis Procedures. Pulse radiolyses with optical absorption detection were performed at the U.S. Army Natick Research and Development Command with instrumentation previously described.[13] The radiation dose per pulse was established by SCN^- dosimetry.[14] Continuous radiolyses were performed with ^{60}Co γ sources with dose rates in water of 9.5×10^{17} eV mL^{-1} min^{-1} (15.3 krd min^{-1}) and 6.2×10^{17} eV mL^{-1} min^{-1} (10.0 krd min^{-1}) as determined by the Fricke dosimeter.[15] Solutions to be irradiated continuously were purged with N_2O for at least 15 min to ensure saturation (2.5×10^{-2} M) in 1-cm spectrophotometer cells fitted with a glass extension allowing them to be tightly septum capped. For kinetic determinations, the cells were equilibrated for 30 min in the same thermostated circulating water bath used to maintain the spectrophotometer cell compartment at the constant desired temperature. The solutions were then irradiated while thermostated. Following irradiation, solutions were returned to the spectrophotometer in less than 1 min for kinetic measurements. Despite the sensitivity of the solutions toward O_2[2] and the low concentrations of reactants and products, the changes in the concentrations of radiolytically reduced products yielded rate constants of reactions that were reproducible within 10%. Kinetic trends were established from experiments conducted under exactly the same conditions on the same day. Larger volume solutions for product analysis, which had been previously saturated with N_2O, were continuously irradiated in tightly stoppered volumetric flasks.

Generation of Radicals. As has been outlined in detail previously,[7] radiolysis of N_2O-saturated aqueous solutions containing HCO_2^- and 2-propanol generates the one-electron reducing radicals, CO_2^- and $(CH_3)_2\dot{C}OH$, with yields of 6.2 and 5.6 radicals per 100 eV of energy

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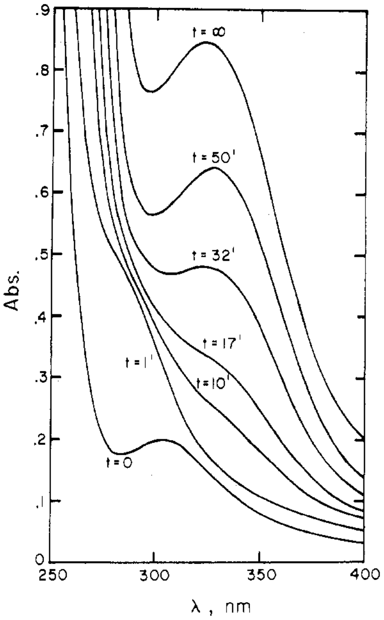

Figure 1. Spectral changes following the 11.0-krd irradiation of an N_2O-saturated solution containing 3.2×10^{-3} M $Ru(NH_3)_5NO^{3+}$ and 0.2 M HCO_2^- at pH 7.1.

absorbed, respectively. In the case of 2-propanol scavenging, 0.6 radicals per 100 eV of energy absorbed resulting from β-hydrogen abstraction, $\cdot CH_2C(CH_3)HOH$, are generated;[16] the β radicals are weaker reducing agents than are the α radicals.[17]

Results and Discussion

Free-Radical Reduction. As previously reported,[2] CO_2^- and $(CH_3)_2\dot{C}OH$ radicals react rapidly with $Ru(NH_3)_5NO^{3+}$ to yield $Ru(NH_3)_5\dot{N}O^{2+}$ ($k_1 = 3.1 \times 10^9$ M^{-1} s^{-1}; $k_2 = 5.5 \times 10^8$ M^{-1} s^{-1}) which exhibits a characteristic absorption spectrum

$$CO_2^- + Ru(NH_3)_5NO^{3+} \rightarrow Ru(NH_3)_5\dot{N}O^{2+} + CO_2 \qquad (1)$$

$$(CH_3)_2\dot{C}OH + Ru(NH_3)_5NO^{3+} \rightarrow Ru(NH_3)_5\dot{N}O^{2+} + (CH_3)_2CO + H^+ \qquad (2)$$

(λ_{max} 350, 280 nm; ϵ_{max} 750, 3700 M^{-1} cm^{-1}). $Ru(NH_3)_5\dot{N}O^{2+}$ reacts with O_2 ($k = 7.6 \times 10^6$ M^{-1} s^{-1}) to regenerate the parent complex and combines with $\cdot CH_2C(CH_3)_2OH$ radicals ($k = 7.4 \times 10^8$ M^{-1} s^{-1}) to yield a stable, air-insensitive green alkyl nitroso complex.[2,8]

Figure 1 shows typical spectral changes in an N_2O-saturated solution of 3.2×10^{-3} M $Ru(NH_3)_5NO^{3+}$ in 0.2 M HCO_2^- at pH 7.0 which has been irradiated with 11.0 krd corresponding to the reduction of only ~2% of the complex. Immediately after irradiation is complete (1.0 min after the 60-s exposure), the spectrum contains elements of $Ru(NH_3)_5\dot{N}O^{2+}$. Without further irradiation, the absorption gradually increases until the final spectrum shows a maximum at 325–330 nm with a strong end absorption in the UV. Over the course of the postirradiation reaction, solutions change from the orange of $Ru(NH_3)_5NO^{3+}$ to bright yellow. Identical spectral changes are observed irrespective of whether $(CH_3)_2\dot{C}OH$ or CO_2^- is the reducing radical.

After the reaction is complete, no further spectral changes are observed upon saturation of the solution with O_2. However, the addition of O_2(g) or O_2-saturated water at any time prior to the completion of the reaction immediately quenches any further reaction with a concomitant decrease in the absorption of $Ru(NH_3)_5\dot{N}O^{2+}$ at 280 and 350 nm.

After completion of the reaction in the absence of O_2, ion-exchange separation reveals primarily a yellow band that can be eluted with neutral 0.5 M NaCl, indicative of a 2+ charged complex. A narrow brown band containing a highly charged complex or solid remains at the top of the column and cannot be removed with 2 M NaCl. In the event of addition of O_2 prior to the completion of reaction, conversion to the yellow product is incomplete; it elutes prior to orange $Ru(NH_3)_5NO^{3+}$ (λ_{max} 305 nm; ϵ_{max} 56 M^{-1} cm^{-1})[18] with little or no brown product evident.

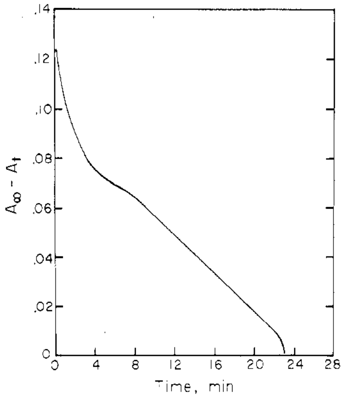

Figure 2. Plot of the change in the absorbance at 315 nm following the 9.5-krd irradiation of an N_2O-saturated solution containing 1.7×10^{-3} M $Ru(NH_3)_5NO^{3+}$ and 0.4 M HCO_2^- at pH 7.1 and 25.0 °C.

The UV–vis spectrum of the ion-exchanged yellow product has absorption maxima at ~420, 330, and 233 nm with ϵ_{max} 28, 200, and 5500 M^{-1} cm^{-1}, respectively, based on the standard ruthenium analysis. The IR spectrum in a KBr matrix of the rotoevaporated yellow solution shows the characteristic ν_{NO} at 1845 cm^{-1} and ν_{Ru-NO} at 630 cm^{-1}. These spectra are identical with those of authentic *trans*-$Ru(NH_3)_4NO(OH)^{2+}$.[18,19] Ammonia analysis of the irradiated solutions following completion of the postirradiation reaction yields 1.0 ± 0.1 equiv of free NH_3/equiv of $Ru(NH_3)_5NO^{3+}$ destroyed; the pH of unbuffered solutions irradiated at pH 7.2 increases as the final product is generated. These facts indicate that the reaction of 1 equiv of $Ru(NH_3)_5NO^{3+}$ with 0.02–0.1 equivalent of one-electron reducing radicals in neutral solution to form initially $Ru(NH_3)_5\dot{N}O^{2+}$ results in the formation of nearly 1 equiv each of *trans*-$Ru(NH_3)_4NO(OH)^{2+}$ and NH_3 via secondary thermal reactions.

In contrast, irradiation (16 krd) of 2.0×10^{-3} M $Ru(NH_3)_5NO^{3+}$ in 0.5 M 2-propanol at pH 1 (N_2O saturated) results in very little change in the spectrum of the solution. This is not unexpected inasmuch as $Ru(NH_3)_5NO^{3+}$ and the anticipated product, *trans*-$Ru(NH_3)_4NO(OH_2)^{3+}$, absorb in the same spectral regions with very similar molar absorptivities. Therefore, the irradiated solutions at pH 1 were left overnight to ensure as great an extent of postirradiation reaction as possible. They were then ion exchanged as described above with *neutral* eluents. Three bands were discernible: *trans*-$Ru(NH_3)_4NO(OH)^{2+}$, $Ru(NH_3)_5NO^{3+}$, and highly charged brown material. The amount of *trans*-$Ru(NH_3)_4NO(OH)^{2+}$ recovered corresponds to the formation of 0.25 equiv from ~0.03 equiv of reducing radicals.

Kinetics. Figure 2 shows a typical plot obtained by monitoring the change in absorbance at 315 nm immediately following the 9.5-krd irradiation of an N_2O-saturated solution containing 1.7×10^{-3} M $Ru(NH_3)_5NO^{3+}$ and 0.4 M HCO_2^- at pH 7.1 and 25.0 °C. Although the graph is linear for over 80% of reaction, it is apparent that there are three distinct regions. The initial portion of the reaction displays first-order kinetics with the same rate constant as obtained using the pulse-radiolysis technique ($k = (1.8 \pm 0.3) \times 10^{-2}$ s^{-1}; Figure 3). Although the extent of these initial absorbance changes is dependent upon the radiation dose delivered to the solution, the rate constant is independent of dose and the initial concentration of the substrate, $[Ru(NH_3)_5NO^{3+}]_0$.

The second stage of the reaction follows zero-order kinetics with the observed rate constant k_{obsd} linearly dependent on the

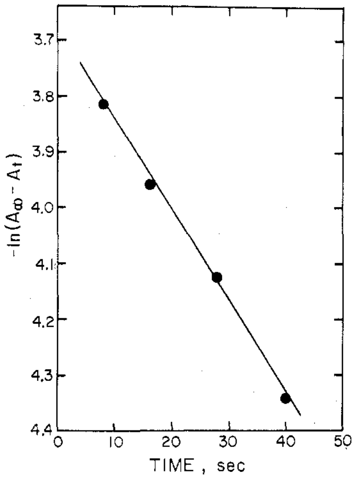

Figure 3. First-order plot for the initial change in absorbance at 315 nm following the pulse radiolysis of an N_2O-saturated solution containing 5×10^{-4} M $Ru(NH_3)_5NO^{3+}$ and 0.2 M HCO_2^- at pH 7.1; optical path length 2 cm, dose/pulse = 4.0 krd.

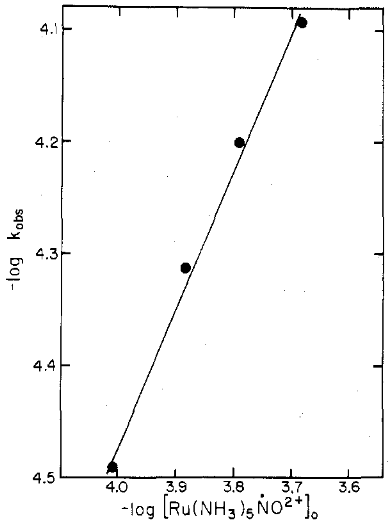

Figure 4. Plot of log k_{obsd} (expressed in units of M min^{-1}) vs. log $[Ru(NH_3)_5\dot{N}O^{2+}]_0$.

radiation dose and, hence, the concentration of $Ru(NH_3)_5\dot{N}O^{2+}$ generated in reaction 1, $[Ru(NH_3)_5\dot{N}O^{2+}]_0$. The slope of the plot of log k_{obsd} vs. log $[Ru(NH_3)_5\dot{N}O^{2+}]_0$ (Figure 4) is 1.2 ± 0.1 establishing that the second stage of the reaction is first order in the reduced complex; the overall zero-order kinetics requires that the concentration of $Ru(NH_3)_5\dot{N}O^{2+}$ not change during the formation of *trans*-$Ru(NH_3)_4NO(OH)^{2+}$. Figure 5 shows the dependence of k_{obsd} on temperature which permits the following activation parameters (and standard deviations) to be derived: $\Delta H^{\ddagger} = 23.7\ (\pm 0.2)$ kcal mol^{-1}, $\Delta S^{\ddagger} = 10.8\ (\pm 0.6)$ cal deg^{-1} mol^{-1}.

The final stage of the reaction occurs within 10% of completion and does not lend itself to simple kinetic analysis. As discussed below, it seems to be associated with the generation of the brown material involving the final reactions of the intermediates.

Reaction Mechanism. Following reaction 1 (or reaction 2), the initial first-order increase in absorbance at 315 nm with a rate constant that is independent of radiation dose, and hence $[Ru(NH_3)_5\dot{N}O^{2+}]_0$, is attributed to the labilization of trans NH_3 to yield *trans*-$Ru(NH_3)_4\dot{N}O(OH_2)^{2+}$ according to reaction 3 for which $k_3 = (1.8 \pm 0.3) \times 10^{-2}$ s^{-1}. Given the

$$Ru(NH_3)_5\dot{N}O^{2+} \xrightarrow{H_2O} trans\text{-}Ru(NH_3)_4\dot{N}O(OH_2)^{2+} + NH_3 \qquad (3)$$

identity of the final product and the fact that reaction 3

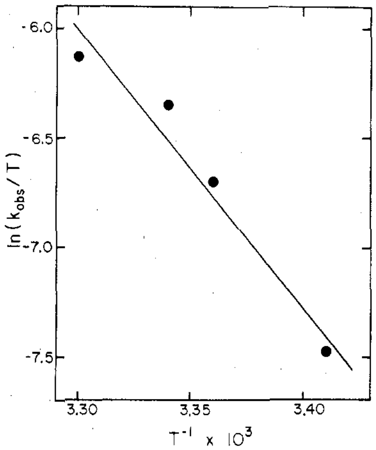

Figure 5. Temperature dependence of k_{obsd}; $[Ru(NH_3)_5NO^{3+}]_0 = 2.0 \times 10^{-3}$ M, pH 7.1, $\mu = 0.4$ M.

precedes the zero-order reaction, the conclusion is reached that *trans*-$Ru(NH_3)_4\dot{N}O(OH_2)^{2+}$ serves as a catalyst by perpetuating the formation of $Ru(NH_3)_5\dot{N}O^{2+}$ via electron-transfer reaction 4. The observed catalytic zero-order reaction

$$trans\text{-}Ru(NH_3)_4\dot{N}O(OH_2)^{2+} + Ru(NH_3)_5NO^{3+} \rightleftarrows trans\text{-}Ru(NH_3)_4NO(OH_2)^{3+} + Ru(NH_3)_5\dot{N}O^{2+} \qquad (4)$$

constitutes the cyclic repetition of reactions 3 and 4. In neutral solution, the rapid deprotonation of *trans*-$Ru(NH_3)_4NO(OH_2)^{3+}$ ($pK_a \approx 2$)[20] occurs to yield the final product.

$$trans\text{-}Ru(NH_3)_4NO(OH_2)^{3+} \rightleftarrows trans\text{-}Ru(NH_3)_4NO(OH)^{2+} + H^+ \qquad (5)$$

Assuming that reactions 3 and 4 constitute the rate-determining steps and that $Ru(NH_3)_5\dot{N}O^{2+}$ achieves a steady-state (constant) concentration, it is easily shown that $k_{obsd} = k_3[Ru(NH_3)_5\dot{N}O^{2+}]_{ss}$ with $d[trans\text{-}Ru(NH_3)_4NO(OH)^{2+}]/dt = k_{obsd}$ for the overall zero-order formation of the product. As long as reaction 4 is fast compared to other modes of reaction of *trans*-$Ru(NH_3)_4\dot{N}O(OH_2)^{2+}$, this catalytic species will also achieve a steady-state (constant) concentration such that $[trans\text{-}Ru(NH_3)_4\dot{N}O(OH_2)^{2+}]_{ss} + [Ru(NH_3)_5\dot{N}O^{2+}]_{ss} = [Ru(NH_3)_5\dot{N}O^{2+}]_0$. Now, $[Ru(NH_3)_5\dot{N}O^{2+}]_0$ is given from the knowledge of the radiation dose and the *G* values for the formation of the reactive radicals. Inasmuch as $[trans\text{-}Ru(NH_3)_4\dot{N}O(OH_2)^{2+}]_{ss} = k_3[Ru(NH_3)_5\dot{N}O^{2+}]_{ss}/k_4[Ru(NH_3)_5NO^{3+}]_0$, it can be further shown that $[Ru(NH_3)_5\dot{N}O^{2+}]_{ss} = k_4[Ru(NH_3)_5NO^{3+}]_0[Ru(NH_3)_5\dot{N}O^{2+}]_0/(k_4[Ru(NH_3)_5NO^{3+}]_0 + k_3)$. This treatment predicts that a plot of k_{obsd} vs. $[Ru(NH_3)_5\dot{N}O^{2+}]_0$ at constant $[Ru(NH_3)_5NO^{3+}]_0$ be a straight line. Figure 6 demonstrates such a plot with a slope (k') of 8.8×10^{-3} s^{-1}. Inasmuch as $k_4 = k_3k'/(k_3 - k')[Ru(NH_3)_5NO^{3+}]_0$, the value of k_4 is evaluated as 8 M^{-1} s^{-1} (ionic strength established by 0.4 M $NaHCO_2$).

With regard to the temperature dependence of k_{obsd}, the value of $[Ru(NH_3)_5\dot{N}O^{2+}]_{ss}$ as seen above is mainly dictated by the radiation dose and therefore is not very sensitive to temperature. Thus, the activation parameters refer, in the main, to k_3.

The results at pH 1 imply that deprotonation reaction 5 constitutes a large and, perhaps, the major component of the overall driving force of reaction 4. Thus, in neutral solution, reaction 4 is driven to completion via reaction 5 while in acidic medium reaction 4 reaches some state of equilibrium. An investigation of the one-electron reduction of *trans*-$Ru(NH_3)_4NO(OH_2)^{3+}$ and *trans*-$Ru(NH_3)_4NO(OH)^{2+}$ will be reported separately.[20]

Disquisition. The catalyzed aquation of $Ru(NH_3)_5NO^{3+}$ is made possible by the facile labilization of the trans NH_3

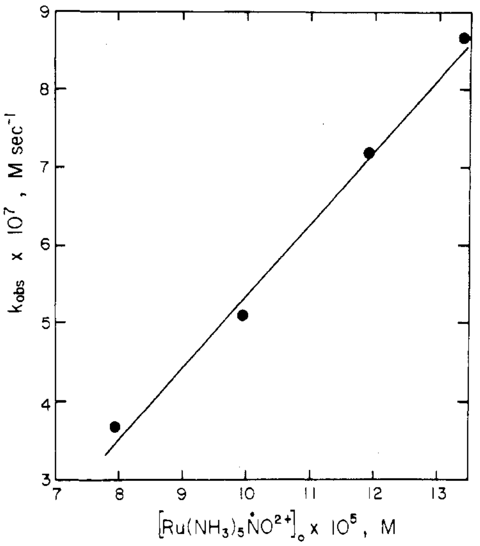

Figure 6. Dependence of the observed zero-order rate constant, k_{obsd}, on the concentration of $Ru(NH_3)_5\dot{N}O^{2+}$ formed initially by the radical reduction in the irradiation of N_2O-saturated solutions containing 2.0×10^{-3} M $Ru(NH_3)_5NO^{3+}$ and 0.4 M HCO_2^- at pH 7.5 and 26.0 °C.

of $Ru(NH_3)_5\dot{N}O^{2+}$. This lability is in direct contrast to that of $Ru(NH_3)_5NO^{3+}$ which is stable toward substitution even in boiling mineral acid. The inertness of $Ru(NH_3)_5NO^{3+}$, which formally contains the linear Ru^{II}–NO^+ entity, is explained in terms of back-donation between the metal $d\pi$ electrons and the strong π-acid ligand. Isied and Taube[21] have found that the lability of H_2O in *trans*-$Ru^{II}(NH_3)_4(H_2O)L$ complexes follows the increasing order for L of CO = N_2 < isonicotinamide < pyridine < N-bound imidazole $\approx$ NH_3 < OH^- < CN^- < SO_3^{2-} < C-bound imidazole; π-acid ligands impart the greatest stability toward trans labilization. Though presently more limited in scope, a similar trend for L is evolving for the labilization of trans NH_3 from $Ru^{II}(NH_3)_5L$ complexes: NH_3 << CN^- < SO_3^{2-}.[22,23] Compared to these ligands, the strongest trans-labilization influence is exhibited by L = $\dot{N}O$.

The large trans effect in $Ru(NH_3)_5\dot{N}O^{2+}$ can be rationalized in terms of the modifications that take place in the initially linear nitrosyl ligand as a result of the localization of the added electron mainly, but not entirely, in the π^* orbital of the ligand. EPR measurements on the analogous reduced complex, $Fe(CN)_5\dot{N}O^{3-}$, show that appreciable (~25%) electron density is localized in the d_{z^2} orbital of the metal center.[24] In aqueous solution, $Fe(CN)_5\dot{N}O^{3-}$ undergoes reversible detachment of trans CN^- ($k = 2.8 \times 10^2$ s^{-1}) which seems to be coupled with intramolecular electron transfer from the NO ligand to the metal d_{z^2} orbital to yield $Fe(CN)_4NO^{2-}$; this complex has the formal configuration $[Fe^I$–$NO^+]$.[7] While there is no evidence here for the formation of Ru(I), the high reactivity of $Ru(NH_3)_5\dot{N}O^{2+}$ towards trans-ligand detachment suggests that some slight increase in the electron density on the metal center may occur.

The redox step, reaction 4 in the mechanism, demonstrates the ability of the nitrosyl complexes and their reduction products to undergo reversible electron transfer. $Ru(NH_3)_5NO^{3+}$ and *trans*-$Ru(NH_3)_4NO(OH_2)^{3+}$ exhibit reversible CV waves with $E_{1/2}$ values of −0.12 and −0.10 V, respectively.[2,20] Taking k_4 (i.e., k_{12}) = 8 M^{-1} s^{-1} and K_4 (i.e., K_{12}) = 0.7 from the $E_{1/2}$ values, the Marcus cross-reaction equation, $k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$,[25] can be used to estimate the rate constants (k_{11} and k_{22}) of the self-exchange for the couples $Ru(NH_3)_4NO(OH_2)^{3+/2+}$ and $Ru(NH_3)_5NO^{3+/2+}$. Assuming $k_{11} \approx k_{22}$ and taking the f factor as unity,[25] a value of $k_{11} \approx k_{22} \approx 10$ M^{-1} s^{-1} is obtained. This value is within the range of values estimated for *cis*-$Ru(bpy)_2NO(X)^{n+}$ complexes.[6] It should be noted that in neutral solution, the final product, *trans*-$Ru(NH_3)_4NO(OH)^{2+}$, is stable toward further reaction inasmuch as its reduction potential is more negative than −0.3 V.[20]

The value of $\Delta H^{\ddagger}$ for reaction 3 is of the magnitude of other ligand substitution reactions.[26] The large positive value of $\Delta S^{\ddagger}$ suggests that the activated complex of reaction 3 reflects a rather large amount of trans-NH_3 bond breakage and may approximate a five-coordinate species; in an analogous manner, the trans-CN^- detachment of $Fe(CN)_5\dot{N}O^{3-}$ produces $Fe(CN)_4NO^{2-}$.[7]

Registry No. $Ru(NH_3)_5NO^{3+}$, 37874-79-6; $Ru(NH_3)_5NO^{2+}$, 53011-05-5; *trans*-$Ru(NH_3)_4NO(OH)^{2+}$, 52720-69-1.

References and Notes

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