

The Photosubstitution Reactions of Rhodium(III) Ammine Complexes

A Case Study

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Preceding articles in this issue (Porter, Crosby, Adamson, Endicott) have described the types of excited states of different transition metal complexes and have illustrated reaction modes which might be expected as the result of populating such states. The goal of the present article is to review, as a case study, investigations focused on elucidating the photosubstitution mechanisms of the ammine complexes of rhodium(III) in solution. A typical reaction is illustrated in eqn. (1)



The ground state complexes of rhodium(III) have low-spin d^6 electronic configurations and are slow in their thermal substitution reactions in ambient temperature solutions. As a result, the photosubstitutions are relatively convenient to study using conventional continuous photolysis techniques. The ammine complexes are of particular interest since, in most cases, the lower energy absorption bands (in the near UV) and the excited state luminescence (when observable) involve electronic transitions between the ground state and the ligand field (LF, i.e., $d-d$) excited states. Thus, the photoreaction behavior of these Rh(III) complexes can serve as a prototype for the ligand field excited state chemistry of other complexes having the very important d^6 configuration including complexes of iridium(III), cobalt(III), iron(II), osmium(II), and platinum(IV), as well as the extensively studied complexes of ruthenium(II) (1).

Upon initiating a mechanistic photochemical study, it is important to have a framework of questions to ask in order to design a logical scheme for the investigation. In our laboratory such questions would be:

- 1) What excited states are initially populated by the exciting light?
- 2) From which excited state or states does reaction to products and/or deactivation to the ground electronic state occur?
- 3) What are the dynamics and mechanisms of these excited state reactions and of other deactivation (radiative and nonradiative) processes?
- 4) What are the intermediates formed by the excited state reactions and what are their chemical fates?

It should be obvious that addressing all these questions in detail would be a major enterprise. This article will summarize such an endeavor.

Identifying the Relevant Excited States

The first question noted above is answered by theoretical analysis of the absorption bands characteristic to the complex at the wavelength of the exciting light. For the Rh(III) complex ions such as $\text{Rh}(\text{NH}_3)_6^{3+}$, $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$, or $\text{Rh}(\text{NH}_3)_5\text{py}^{3+}$ (py = pyridine), the lowest energy electronic absorption bands of significant intensity are the spin-allowed, singlet-to-singlet LF transitions. Although ligand-to-metal charge transfer (LMCT) bands and intraligand (IL) $\pi-\pi^*$ bands are prominent in the spectra of complexes such as $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ and $\text{Rh}(\text{NH}_3)_5\text{py}^{3+}$, respectively, the lowest absorptions of these complexes remain LF in character. Figure 1 shows the absorption and emission spectra of one example, the octahedral $\text{Rh}(\text{NH}_3)_6^{3+}$ ion. The UV absorptions have been assigned as the $^1T_{1g} \leftarrow ^1A_{1g}$ (306 nm) and $^1T_{2g} \leftarrow ^1A_{1g}$ (255 nm) transitions. The state from which the emission originates has been assigned as the lowest energy excited state, the LF triplet $^3T_{1g}$. This observation immediately illustrates the point raised by question 2. The states initially populated by

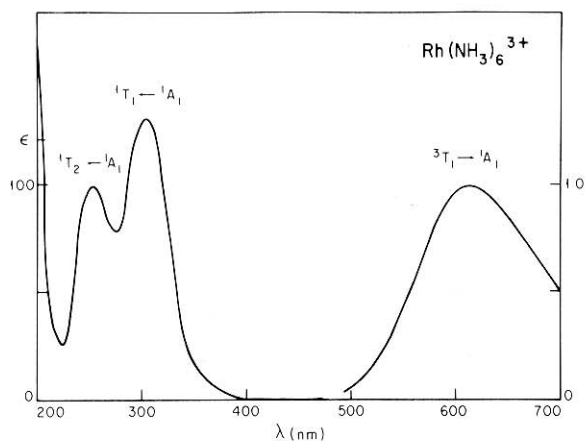
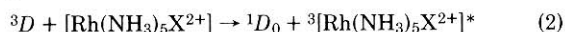


Figure 1. Absorption spectrum of $\text{Rh}(\text{NH}_3)_6^{3+}$ in aqueous solution at 298 K (on left). Emission spectrum in an alcoholic glass at 77 K (on right).

excitation in the near-UV are LF singlets, but emission occurs from a different state, a LF triplet. Although there is some evidence suggesting fluorescence from certain Rh(III) complexes (2), it is generally concluded that the large majority of the excited molecules initially formed as singlet states undergo efficient internal conversion/intersystem crossing to the lower energy triplet LF states. Figure 2 illustrates such a situation, where k_{isc} is the dominant pathway for deactivation of the singlet states and the photochemistry largely reflects the reactivity of the triplet LF states.

What is the evidence which has led to the conclusion that photoexcitation into the Rh(III) singlet states is followed by rapid, efficient interconversion to the lower energy triplets? One example is that the quantitative photochemistry of many rhodium(III) complexes is insensitive to the excitation wavelength (λ_{irr}) when that wavelength is confined to the LF absorptions (1). This observation suggests that reaction occurs from a common state or collection of states, the lowest energy excited state formed by direct excitation or one at lower energy. That such were triplets was first indicated by sensitization experiments which demonstrated that triplets of the halopentaamminerhodium(III) ions formed by energy transfer from organic sensitizers (3)



demonstrated the same quantitative photochemistry as complexes excited directly into the LF singlet absorptions. Later it was shown in our laboratory using ns pulse laser techniques that the LF triplet state lifetimes of these same ions in fluid aqueous solution could be directly correlated to the quantum yields of product formation (4) and, in another laboratory, that quenching of the triplet state by Brønsted bases led to the quenching of most photosubstitutions (5).

Conclusions about excited state behavior similar to that shown in Figure 2 have been used to interpret the LF photochemical reactions of iridium(III) ammine complexes such as $\text{Ir}(\text{NH}_3)_6^{3+}$ and the polycyano complexes of cobalt(III), e.g., $\text{Co}(\text{CN})_6^{3-}$. However, as caveats, I should emphasize that LMCT photoexcitation of Rh(III) complexes at higher energies leads to entirely different photochemistry (see below) and that even for LF excitation of the Rh(III) amines there is some evidence that minor reaction pathways may occur from higher energy excited states in competition with internal conversion to the lowest energy triplet state(s).

Excited State Reaction Mechanisms and Dynamics

Question 3 relates to the dynamics and mechanisms of various excited state processes. From the chemist's perspective the most interesting of these is reactive deactivation, the formation of new molecular species from the excited state. For

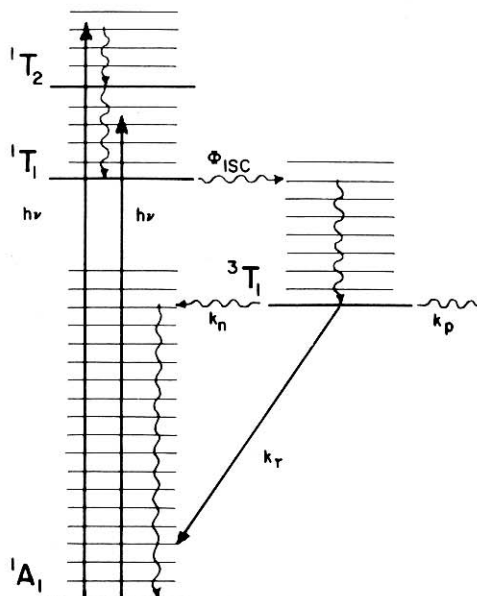
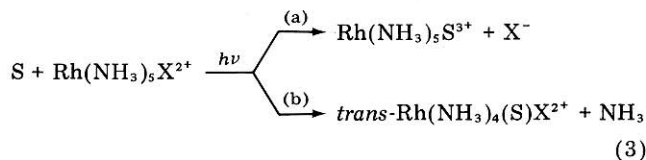


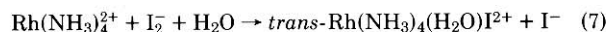
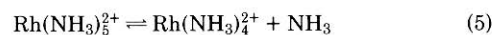
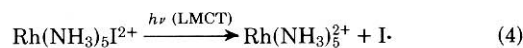
Figure 2. Jablonski diagram for $\text{Rh}(\text{NH}_3)_6^{3+}$. Φ_{ISC} is the efficiency of the internal conversion/intersystem crossing from singlet states (initially formed by excitation) to lower energy triplet states. The rate constants k_n , k_r , and k_p represent nonradiative and radiative deactivation to ground state and reactive deactivation to products, respectively.

the halopentaamminerhodium(III) complexes in solution, both halide and ammine photosubstitution is seen (eqn. (3)) but the actual mechanism of this process is sharply dependent on the nature of the reactive excited states.



Charge Transfer States

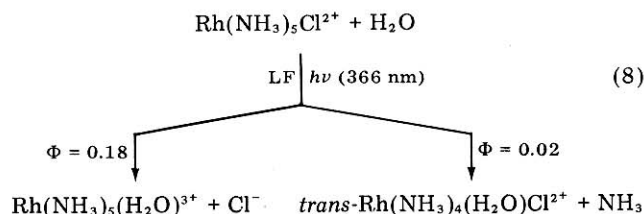
For $\text{X}^- = \text{I}^-$, LMCT bands are prominent in the UV spectrum at energies above the lowest LF bands. Photolysis into the LF bands (385–470 nm) gives high yields ($\Phi = 0.85$) of reaction (3b) but significantly lower yields (0.42) of the same reaction are found with higher energy (214–254 nm) irradiations of LMCT bands (6). This result immediately tells one that the LMCT state can undergo deactivation to the ground state by a mechanism other than interconversion to the lower energy LF states. Furthermore, when solutions of aqueous $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ with traces of I^- are subjected to flash photolysis, I_2^- was detected in the LMCT spectral region. This observation was cited as evidence for an electron transfer step as the primary photochemical event. Thus, although the net photoreaction is NH_3 substitution to give the Rh(III) product $\text{trans-Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$, the intimate mechanism in this case involves an intermediate resulting from photoredox processes.



Ligand Field States

Entirely different mechanisms are extant for the substitution induced by exciting the lower energy ligand field bands since there is no evidence for redox reactions in these cases.

For $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ in 25°C aqueous solution, the principal photoreaction is Cl^- aquation although modest NH_3 aquation is also seen. The latter reaction is "anti-thermal" since the solution phase aquations of the $\text{Rh}(\text{III})$ halopentaammines appear to involve labilization of the halides exclusively.



For $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ the antithermal pathway is predominant in aqueous solution.

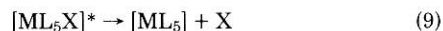
It was shown above that LF excitation leads to efficient internal conversion/intersystem crossing to the lowest energy triplets. How really efficient is "efficient" in these cases given the relative uncertainties in the various kinds of measurements used to support this conclusion? This question remains yet to be answered exactly, but while there are some indications that a small fraction of the emission (2) and photochemistry (5) may originate from upper states, perhaps singlet states, the bulk of the reactions occur subsequent to relaxation to the thermally equilibrated lowest energy LF state.

For the $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$ ions where X^- is a halide, the lowest energy LF state is 3E , which can be represented with the one electron configuration $(d_{xy})^2(d_{xz,yz})^3(d_{z^2})^1(d_{x^2-y^2})^0$ (i.e., $(b_2)^2(e)^3(a_1)^1(b_1)^0$). Although such a representation is certainly simplistic given configuration interaction with the higher energy 3E LF state, it does provide a reasonable guideline for the types of photoreaction activity to be expected. Population of the sigma antibonding d_{z^2} orbital might be expected to weaken the sigma component of all metal-ligand bonds with the major distortion occurring along the unique z -axis. In contrast, the π component of the $\text{Rh}-\text{X}$ bond would be somewhat enhanced owing to the π^* nature of the excited orbitals. The extent of these changes has been summarized by Vanquickenborne and Cuelemans (7), who used an additive angular overlap model and spectroscopic σ and π parameters for ligands to calculate bond indices $I^*(\text{ML})$ for the LF excited state. These indices constitute the contribution made to the $\text{M}-\text{L}$ bond energy owing to d -orbital interactions. These authors argued that the $I^*(\text{ML})$ values provide a comparative measure of the different metal-ligand bond strengths in a particular excited state and the ligand with the smallest $I^*(\text{ML})$ would be the one likely to be labilized in the dominant photosubstitution. For the $\text{Rh}(\text{III})$ complexes, a problem with this treatment is that accurate σ and π ligand parameters have not been determined for the heavier transition metals, thus, parameters derived for $\text{Cr}(\text{III})$ are used. Furthermore, such treatments, based solely on evaluating changes in the metal-ligand bonding as the result of electronic excitation, cannot deal with the intimate details of the actual mechanisms (such as the role of the solvent) (4b) although dissociative behavior is implicitly assumed. However, despite such concerns, the theoretical model does provide easily implemented guidelines regarding which ligands should be the more susceptible to photolabilization.

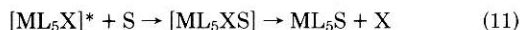
For $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ in the lowest 3E LF excited state, this theoretical model indicates that both ligands on the z -axis, Cl^- and the *trans*- NH_3 , should be considerably more labile than the NH_3 's lying on the x - and y -axes. This is consistent with the primary reaction mode being Cl^- loss in aqueous solution. For the cyano complex $\text{Rh}(\text{NH}_3)_5\text{CN}^{2+}$, the 3A_2 state is the lowest LF excited state, and the smallest $I^*(\text{ML})$ values involve the equatorial amines. Again, the model correctly predicts formation of *cis*- $\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$ as the sole photoproduct, but as we will see below, the stereochemistry

of the product may not be diagnostic of the origin of the labilized ligand.

The implicit assumption of this model is that the reaction occurs from the LF excited state rather than a vibrationally "hot" ground electronic state produced in the course of non-radiative deactivation. It also assumes that the weakest bonds of the excited state molecule will be the ones labilized, a conclusion most consistent with a limiting dissociative mechanism for ligand substitution



However, the radial transition of electron density from " t_{2g} -like" orbitals to " e_g -like" orbitals should also make the complexes more receptive to attack of solvent at the octahedral faces in an associative (e.g., eqn. (11)) or interchange mechanism. Given evidence that the ground state substitutions follow associative pathways, these certainly need to be considered seriously.



How does one investigate the intimate reaction mechanisms of a chemical species with but a fleeting existence? Historically, such interpretations have been based on comparing products and quantum yields for homologous complexes and for systematic variation of reaction conditions. However, even for reactions which originate from a single, thermally relaxed excited state as indicated in Figure 2, the Φ values represent ratios of several terms, each of which may be affected by variations in the conditions or the nature of the coordination sphere of the complexes (8)

$$\Phi_p = \Phi_{\text{isc}} k_p / (k_p + k_n + k_r) \quad (12)$$

A far more convincing parameter to examine for mechanistic significance is the rate constant k_p for the excited state reaction itself. Given the conclusion that $\Phi_{\text{isc}} \approx 1$ and the relationship between the excited state lifetime and the rate constants for deactivation of that state

$$\tau = (k_p + k_n + k_r)^{-1} \quad (13)$$

Equation (12) can be rewritten as

$$\Phi_p = k_p \tau \quad (14)$$

Thus, if the quantum yield Φ_i of a particular process and the lifetime τ of the relevant state can be measured under identical conditions, the rate constants of interest can be determined according to the equation

$$k_i = \Phi_i \tau^{-1} \quad (15)$$

It was to address precisely this goal that we began pulse laser experiments with the halopentaamminerhodium(III) complexes. Luminescence is observable in fluid aqueous solution with lifetimes in the 10–40 ns range, and the emission spectrum is the same as that found in low temperature glasses. For several examples, the lifetimes measured under the photochemically significant conditions are summarized in the table. The quantum yields for the substitution reactions and for emission combined with the lifetimes give the rate constants also summarized in this table.

From these data the following conclusions can be drawn. First, there is a relatively close correlation between Φ_p , Φ_r , and τ for the perdeuterated complexes $\text{Rh}(\text{ND}_3)_5\text{X}^{2+}$ relative to the perprotio complexes. This demonstrates that the ligand labilization reactions are from the luminescing state (3E), not from vibrationally "hot" molecules formed in the course of nonradiative deactivation to the ground state. Second, the rate of ligand substitution from these LF states is tremendously faster than those of the comparable thermal reactions. For example, loss of Cl^- from $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ ($k_p = 1.3 \times 10^7 \text{ s}^{-1}$) is about fourteen orders of magnitude faster than the comparable thermal reaction. The activation energy for this photo-

Quantum Yields, Luminescence Lifetimes, and Calculated Rate Constants Related to the Photochemistry of Chloropentaamminerhodium(III) in Solution^a

| Complex | Solvent | $\Phi_{\text{Cl}^-}^b$ | Φ_A^c | Φ_t^d | τ (ns) | $k_{\text{Cl}^-}^e$ | k_A^f | k_r^g | k_n^h |
|--|--------------------|------------------------|--------------|----------------------|-------------|---------------------|----------------------|-------------------|-------------------|
| Rh(NH ₃) ₅ Cl ²⁺ | H ₂ O | 0.18 | 0.02 | 3.2×10^{-5} | 14.2 | 1.3×10^7 | 1.5×10^6 | 2.3×10^3 | 5.6×10^7 |
| Rh(ND ₃) ₅ Cl ²⁺ | D ₂ O | 0.28 | ≤ 0.05 | 6.6×10^{-5} | 27.3 | 1.0×10^7 | $\leq 2 \times 10^6$ | 1.9×10^3 | 1.9×10^7 |
| Rh(NH ₃) ₅ Cl ²⁺ | HCONH ₂ | 0.057 | ~ 0.011 | $< 10^{-4}$ | 22.4 | 2.5×10^6 | $\sim 5 \times 10^6$ | — | 4.5×10^7 |
| Rh(NH ₃) ₅ Cl ²⁺ | DMF ⁱ | 0.004 | 0.070 | $< 10^{-4}$ | 32.4 | 1.2×10^5 | 2.2×10^6 | — | 3.1×10^7 |
| Rh(NH ₃) ₅ Cl ²⁺ | DMSO ^j | < 0.006 | 0.029 | $< 10^{-4}$ | 35.1 | $< 1.7 \times 10^5$ | 0.8×10^6 | — | 2.8×10^7 |

^a Photolysis carried out at 366 nm in 25°C solution, data from Reference (4).

^b Moles/einstein.

^c Quantum yield for ammine loss in moles/einstein.

^d Quantum yield for emission in einstein/einstein.

^e Excited state rate constant for Cl⁻ substitution in s⁻¹.

^f Excited state rate constant for ammine substitution in s⁻¹.

^g Excited state rate constant for radiative decay in s⁻¹.

^h Excited state rate constant for nonradiative decay in s⁻¹.

ⁱ Dimethyl formamide.

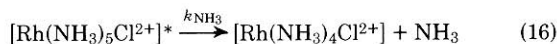
^j Dimethyl sulfoxide.

substitution (~ 7 kcal/mole) indicates that this reaction occurs from a bound electronic state although this E_a value is much smaller than that for thermal aquation (~ 25 kcal/mole).

The table also includes photoreaction quantum yield and kinetics data for Rh(NH₃)₅Cl²⁺ in different solvent media. For this complex, the LF absorption and emission spectra appear little affected by the solvent, but the quantitative photoreaction behavior is dramatically perturbed. For example, in water and formamide, Cl⁻ labilization is the major photoreaction, but in DMSO and DMF, Φ_{NH_3} is much larger than Φ_{Cl^-} . Examination of the excited state rate constants tells us that the main reason for this turnabout is the marked sensitivity of k_{Cl^-} to the medium, with values about two orders of magnitude smaller in the latter solvents than in H₂O. The k_{Cl^-} values qualitatively parallel the free energies of solvation for this ion, suggesting that there is considerable charge separation in the Rh(III)—Cl⁻ bond in the transition state of the excited state reaction.

In search of mechanistic information more specifically directed toward differentiating the associative or dissociative character of the excited state reactions, we, in collaboration with others, initiated an investigation of pressure effects on the excited state kinetics (9). This was accomplished by measuring photoreaction quantum yields as a function of pressure to 2 kbar while measuring luminescence lifetimes under identical conditions. From these data, volumes of activation ΔV^\ddagger were determined for the Cl⁻ and NH₃ aquation rates giving the values -8.6 and $+9.3$ cm³/mole, respectively. Analogous experiments for Rh(NH₃)₅Br²⁺ also gave similar ΔV^\ddagger values for the respective photoaquation pathways.

At first glance, the opposite signs of the $\Delta V_{\text{Cl}^-}^\ddagger$ and $\Delta V_{\text{NH}_3}^\ddagger$ values would appear to imply that the two excited state reactions proceed by different mechanisms, the Cl⁻ aquation having a substantially associative character, NH₃ aquation having a substantially dissociative character. The NH₃ aquation from the excited state is the easier to interpret since the ligand labilized is uncharged. For a limiting dissociative mechanism, the volume difference between the excited state and the transition state of the reaction



would be the ΔV^\ddagger . Estimates of the volumes of the excited state and of the pentacoordinate Rh(NH₃)₄Cl²⁺ intermediate suggest that the $+9.3$ cm³/mole measured for NH₃ loss from the excited state would be a reasonable value for a limiting dissociative mechanism, especially if one considers that the transition state of this very rapid reaction is likely to occur rather early along the reaction coordinate. The large difference in magnitude between the $\Delta V_{\text{Cl}^-}^\ddagger$ and $\Delta V_{\text{NH}_3}^\ddagger$ values also points to a dissociative mechanism since the volume change for the dissociation of Cl⁻



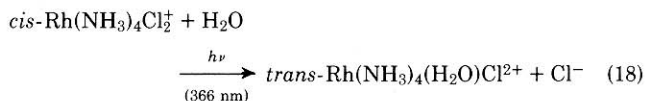
should be much smaller than for eqn. (16) given the creation

of charge in eqn. (17) (dissociation of a +2 ion to give a -1 ion plus a +3 ion). The solvent collapse to facilitate such charge creation appears to be the factor dominating volume changes to achieve the transition state for aquation of the anion from the hexacoordinate excited state and parallels the marked effects of solvent on the reaction pathways noted above.

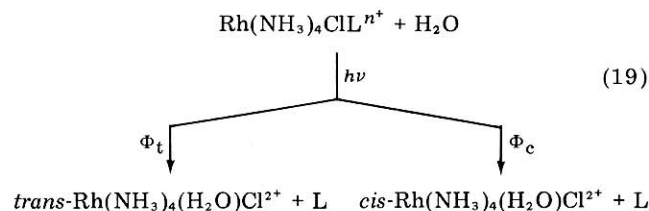
In summary, the evidence noted in this section points to a dissociative character for the excited state substitution mechanisms. However, the data require a rather involved interpretation. A more convincing case will be made in the next section.

The Fate of Intermediates

If the limiting dissociative mechanisms illustrated in eqns. (16) and (17) are in operation for the excited state substitutions, pentacoordinate species such as Rh(NH₃)₅³⁺ and Rh(NH₃)₄X²⁺ are intermediates in the course of forming the products. Unlike the well studied metal carbonyls for which pentacoordinate intermediates have been generated and directly observed spectrally in matrix isolation experiments, there are no examples for the direct observation of such dissociated intermediates in the photochemistry of d⁶ metal ammine complexes. However, strong circumstantial evidence for the limiting dissociative mechanism is provided by the photostereochemistry of these complexes (10, 11). One early example was the observation that irradiation of *cis*-Rh(NH₃)₄Cl₂⁺ in aqueous solution led to concomitant photosubstitution/photoisomerization



The analogous thermal aquations are stereoretentive as is the photoaquation of *trans*-Rh(NH₃)₄Cl₂⁺. Initially, it was thought that for the *cis* isomer $\Phi(\text{isomerization}) = \Phi(\text{aquation})$; however, very careful reexamination (12) indicated that a minor but measurable second reaction is photolabilization without isomerization



Since *cis*-Rh(NH₃)₄(H₂O)Cl²⁺ itself is quite photoactive (undergoing *cis*-to-*trans* isomerization), only a small concentration builds up during the course of the *cis*-Rh(NH₃)₄Cl₂⁺ photolysis experiment (Fig. 3). The key observation is that for reaction (19) the ratio of Φ_t/Φ_c is 0.46/0.10 = 4.6 for L = H₂¹⁸O, within experimental uncertainty of the Φ_t/Φ_c ratio (0.35/0.07 = 5.0) found for L = Cl⁻. This suggests that the photoreac-

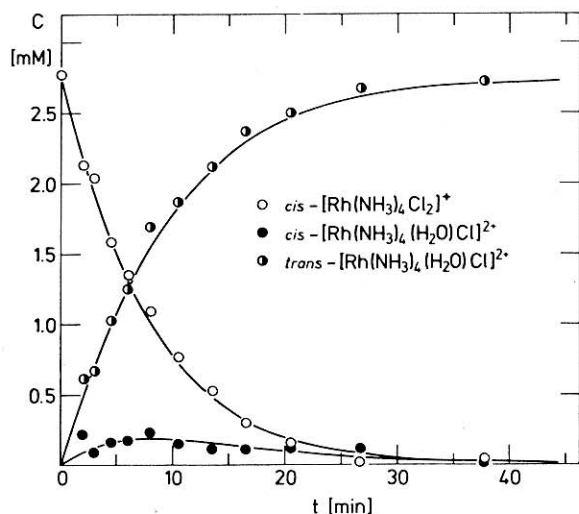


Figure 3. Concentrations of initial reactant $cis\text{-Rh}(\text{NH}_3)_4\text{Cl}_2^+$ and products $cis\text{-Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$ and $trans\text{-Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$ as functions of time when irradiated at 366 nm in 25°C aqueous solution (pH 3). Data from Reference (12).

tions proceed through a common intermediate, that is, the pentacoordinate $[\text{Rh}(\text{NH}_3)_4\text{Cl}]^+$ generated by L dissociation from the $[cis\text{-Rh}(\text{NH}_3)_4\text{ClL}]^+$ LF excited state.

The theoretical model (10, 11) proposed to interpret the stereochemical lability associated with the photosubstitution reactions of such d^6 complexes is illustrated in Figure 4. The key feature of this model is that the thermally relaxed LF triplet state dissociates one ligand to give a square pyramidal pentacoordinate intermediate remaining in an excited electronic state, i.e., the lowest energy LF triplet. Electronic deactivation of the pentacoordinate intermediate followed by trapping by solvent would give the product with stereochemistry identical to the initial reactant while isomerization to the other square pyramidal intermediate (eqn. (20)) and subsequent deactivation and trapping would give the other geometric isomer



Thus the ratios of isomers produced are functions of the relative energies of SP_a^* and SP_b^* and of the relative rates of interconversion between the two isomers versus deactivation and trapping by solvent.

This model was shown to have predictive value in the sense that, according to a qualitative molecular orbital analysis, the more stable of these two excited state intermediates would be the one with the weaker σ -donor in the unique apical site. Thus, when L = NH_3 , and X is a weaker σ -donor such as Cl^- or Br^- , photoisomerization cis -to- $trans$ is favored because SP_a^* has the lower energy. However, when X is a strong sigma donor such as OH^- or CN^- , $trans$ to cis isomerization is associated with the photolabilization (13), e.g.,

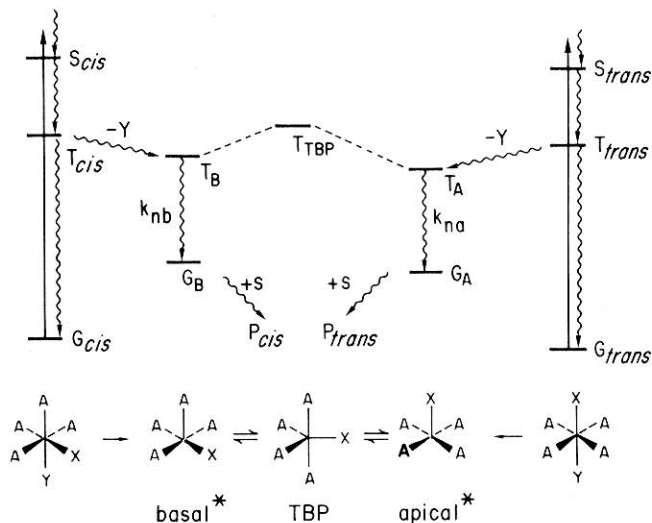
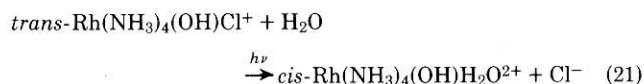


Figure 4. A graphical illustration of the theoretical model for the photoisomerization of d^6 complexes of the type MA_4XY . S = singlet, T = triplet, G = ground electronic state for particular geometries shown. P represents the product MA_4XS .

The success of the model for interpreting these stereochemical results provides convincing circumstantial evidence for the existence of these excited state pentacoordinate intermediates formed as the result of a limiting dissociative labilization of one ligand from the hexacoordinate LF excited state.

Concluding Remarks

In summary, the above discussion has illustrated in-depth investigations of the ligand field photosubstitution chemistry of the d^6 rhodium(III) ammine complexes. The conclusions from these investigations are that most of this photochemistry occurs from the lowest energy excited states of such complexes, the LF triplets. These states are sufficiently long-lived to be considered new chemical species, the reactions of which can be subjected to kinetic and mechanistic analysis. Ligand labilization occurs at rates $>10^{14}$ times more rapid from the LF excited state than from the ground state, and both the ligand labilized and the product stereochemistry are often different from the thermal reactions. Analysis of the quantum yields, solvent rate effects, pressure effects, and stereochemistry points to a limiting dissociative mechanism for the prevalent pathway of the observed photoreactions.

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