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THE LIGAND FIELD PHOTOSUBSTITUTION REACTIONS OF d^6 HEXACOORDINATE METAL COMPLEXES

PETER C. FORD *

Department I, Inorganic Chemistry, H.C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø (Denmark)

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CONTENTS

ABBREVIATIONS

bpy	2,2′-bipyridine
en	ethylenediamine
LEES	lowest energy excited state
LF	ligand field
MLCT	metal to ligand charge transfer
phen	*o*-phenanthroline
SP	square pyramidal (or square pyramid)
TBP	trigonal bipyramidal (or trigonal bipyramid)
trien	triethylenetetraamine

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* Address correspondence to: The Department of Chemistry, University of California, Santa Barbara, CA 93106, U.S.A.

A. INTRODUCTION

The transition elements are those having chemically significant oxidation states for which a *d*-electron subshell is but partially filled. Coordination of the metal ion or atom in a non-spherically symmetric environment, i.e. a ligand field, differentiates the energies of the *d*-orbitals. (In a molecular orbital sense, the mixing of metal *d*-orbitals with ligand σ- and π-orbitals leads to the formation of partially filled frontier MOs of differing energies which are largely metal *d*-orbitals in character.) For example a hexacoordinate d^6 complex with a strong octahedral (O_h) ligand field will show the following pattern of orbital splitting

$$- - e_g(d_{x^2-y^2}, d_{z^2})$$

$$\overset{\uparrow\downarrow}{-}\ \overset{\uparrow\downarrow}{-}\ \overset{\uparrow\downarrow}{-}\ t_{2g}(d_{xy}, d_{yz}, d_{xz})$$

Electronic transitions between such orbitals are termed ligand field (LF) transitions and Fig. 1 illustrates how the energies of resulting lower energy excited states are a function of the ligand field strength Δ.

Both redox and ligand substitution reactions have been noted for ligand field excited states; however, the more common of these chemical deactiva-

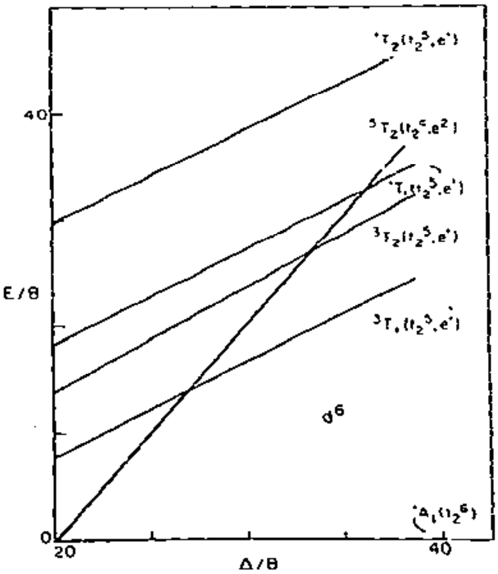

Fig. 1. A Tanabe–Sugano type diagram indicating qualitatively the relative positions of the lower energy ligand field excited states of an octahedral complex ML_6 with a d^6 electronic configuration.

tion pathways for the LF states of d^6 complexes in solution is the labilization of one coordinated ligand toward substitution by another nucleophile (eqn. 1). The mechanisms of this fundamental reaction are the subject of

$$ML_6 + Y \xrightarrow{h\nu} ML_5Y + L \quad \text{(where Y is commonly the solvent)} \qquad (1)$$

much renewed interest owing in large part to the opportunity to employ new experimental techniques, principally based on the use of pulse lasers, to study directly excited state properties and reaction dynamics. (It is also not of inconsequential interest that ligand photosubstitutions are degradation processes for certain complexes considered potential catalysts for solar energy conversion mechanisms.)

The following questions need to be addressed in order to understand the chemical consequences of electronic excitation of metal complexes:

(1) What excited states are formed in the excitation?

(2) After electronic excitation to a Franck–Condon state, do chemical processes (e.g. ligand labilization, isomerization, redox reactions) and other physical processes (nonradiative or radiative deactivation to ground state, and interconversion to other excited states) compete with vibrational relaxation of the initial state?

(3) Do chemical and other physical processes compete significantly with internal conversion within manifolds of excited states with the same multiplicity and similar orbital parentages?

(4) What are the roles of states of different multiplicities and/or different orbital parentages?

(5) What are the dynamics and mechanisms of the various radiative, nonradiative and reactive modes for excited state deactivation?

(6) What are the natures of and chemical fates of those intermediates produced initially by the reactions of relevant excited states?

Answering each of these questions with thoroughness is obviously a major, if not monumental, task. For example, in condensed phase vibrational relaxation within a single electronic state can be expected to occur within the picosecond time regime; thus, direct observations of these processes requires picosecond or sub-picosecond time resolution. Such experiments are now accessible using pulse laser techniques but are not routinely applied to the study of transition metal complex photoreactions. However, one such study by Pyke and Windsor [1] on d^3 Cr(III) complexes indicates rise times for the formation of doublet states after excitation into a quartet absorption band to occur within picoseconds! Several different interpretations for this phenomenon have been offered; however, it is clear from these studies that very soon after excitation it is possible for states to be populated other than those which might be conventionally assigned from the absorption spectrum.

B. EXCITED STATES

Figure 2 shows the absorption and emission spectra of the hexaamminerhodium(III) ion, $Rh(NH_3)_6^{3+}$, which has O_h symmetry if one neglects the NH_3 hydrogens. The absorption spectrum in aqueous solution shows but two well defined bands, both of relatively low intensity ($\epsilon \sim 10^2$ M^{-1} cm^{-1}) which are typically assigned to the multiplicity allowed, Laporte forbidden ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{2g} \leftarrow {}^1A_{1g}$ transitions. The Tanabe–Sugano diagram (Fig. 1) indicates the presence of at least three other low energy states, two triplets (${}^3T_{1g}$ and ${}^3T_{2g}$) and a quintet (${}^5T_{2g}$). Transitions to these are also multiplicity forbidden and there are no clear indications of such bands in the aqueous solution absorption spectra of $Co(NH_3)_6^{3+}$ or $Rh(NH_3)_6^{3+}$. In contrast, the absorption spectrum of $Ir(NH_3)_6^{3+}$ shows a long wavelength tail on the first singlet absorption which has been assigned to the ${}^3T_{1g} \leftarrow {}^1A_{1g}$ transition [2].

The quintet state ${}^5T_2$ has a $(t_{2g})^4(e_g)^2$ configuration (compared to the $(t_{2g})^5(e_g)^1$ configuration of the low energy singlet and triplet excited states) making this especially sensitive to the strength of the ligand field. As a consequence, it is generally agreed that the lowest energy excited state (LEES) for the Rh(III) and Ir(III) amines as well as the stronger field complexes of Co(III) such as $Co(CN)_6^{3-}$ is the triplet ${}^3T_{1g}$ [3,4]. However, for complexes with lower or intermediate field strengths, it is clear from Fig. 1 that the quintet may be the LEES (or even the ground state for sufficiently weak a field) or close to the LEES energetically. For example, recent studies by Wilson and Solomon [4] on the single crystal spectra of

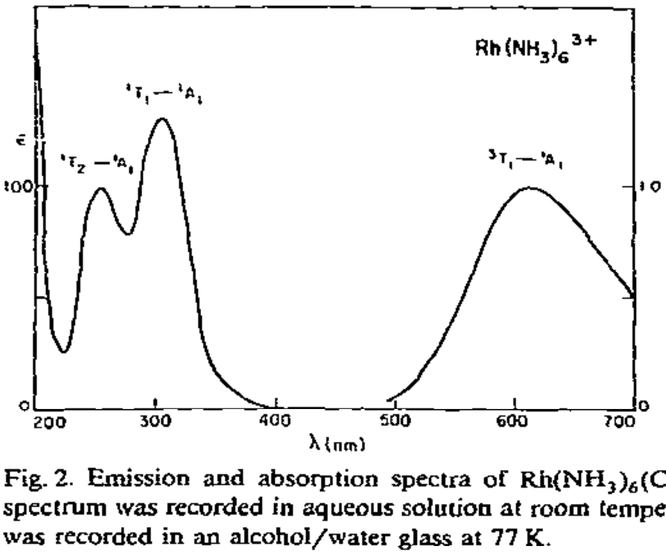

Fig. 2. Emission and absorption spectra of $Rh(NH_3)_6(ClO_4)_3$ in solution. The absorption spectrum was recorded in aqueous solution at room temperature while the emission spectrum was recorded in an alcohol/water glass at 77 K.

$[Co(NH_3)_6](ClO_4)_2Cl \cdot KCl$ have led to results interpreted by those workers in terms of the $^5T_{2g}$ state being the probable LEES for the $Co(NH_3)_6^{3+}$ ion. This work is especially notable given the marked differences between the photochemical reaction patterns resulting from the LF excitation of Co(III) amine complexes and those of the Rh(III) and Ir(III) homologs under similar conditions (vide infra).

Figure 2 also illustrates the emission spectrum of $Rh(NH_3)_6^{3+}$ in a low temperature alcohol/water glass. A single broad, gaussian shaped band is observed, and assignment as the $^3T_{1g} \rightarrow {}^1A_{1g}$ phosphorescence has been made [3]. Emission bands given analogous assignments have been observed for a number of other Rh(III) and Ir(III) complexes of saturated amines as well as for $Co(CN)_6^{3-}$, but no comparable emissions have been seen for the Co(III) amines. Given the relative independence of these emissions with regard to the excitation wavelength, it has been concluded that the luminescence originates from the LEES of these complexes, the $^3T_{1g}$ state for O_h symmetry or a component split out of this at lower symmetry [3]. The Jablonski diagram in Fig. 3 illustrates this point. However, it should be noted that, while it is often assumed that emission will occur from the LEES or a state

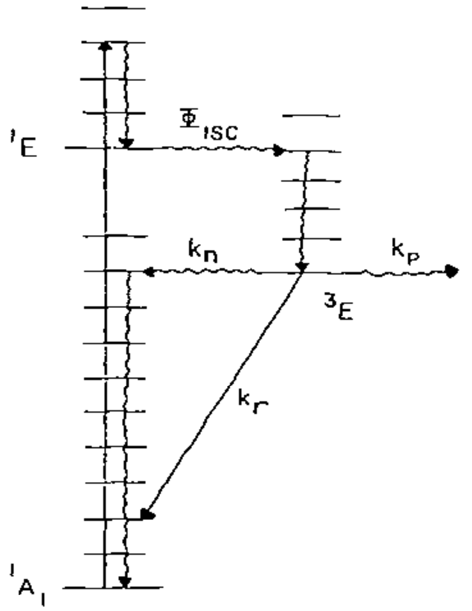

Fig. 3. A Jablonski type diagram for the lowest states of a d^6 complex such as $Rh(NH_3)_5Cl^{2+}$. k_s represents ligand substitution from the excited state, k_r and k_n represent radiative and nonradiative deactivation to the ground state respectively, and Φ_{ISC} represents the efficiency of internal conversion/intersystem crossing from states initially populated to the lowest energy LF state ^3E.

in equilibrium with the LEES [5] and this assumption appears valid for the simple ammine or cyano complexes, the same cannot be said for certain complexes such as $Ir(phen)_2Cl_2^+$ having several low energy excited states with different orbital parentages [6]. In such cases dual emissions may occur from nonequilibrated states, potentially confusing assignment of the LEES [6].

C. PHOTOREACTIONS

Ligand field excitation of $Rh(NH_3)_6^{3+}$ in aqueous solution labilizes NH_3 (eqn. 2) with a moderate quantum yield Φ_s which is essentially independent

$$M(NH_3)_6^{3+} + H_2O \xrightarrow{h\nu} M(NH_3)_5H_2O^{3+} + NH_3 \tag{2}$$

of the excitation energy (Table 1). Similar behavior is seen for $Ir(NH_3)_6^{3+}$ including for excitation wavelengths (λ_{irr}) corresponding to absorption bands assigned as singlet to triplet transitions. For these two complexes, therefore, it has been concluded [2,7] that initial excitation is followed by internal conversion/intersystem crossing to a common excited state, nominally the lowest energy triplet LF state (in this case, the LEES), and that this state and those in thermal equilibrium with it are responsible for virtually all of the observed substitution chemistry. Such a conclusion is reinforced by studies of the halopentaamine rhodium(III) complexes for which: (1) Φ_s is

TABLE 1

Quantum yields for hexacoordinate complexes, ML_6, in 298 K aqueous solution

Complex	λ_{irr}	Assignment	Φ_s	Ref.
$Co(NH_3)_6^{3+}$	365	${}^1T_{2g} \leftarrow {}^1A_{1g}$	0.0054	a
	460	${}^1T_{1g} \leftarrow {}^1A_{1g}$	0.00052	
$Co(CN)_6^{3-}$	254	${}^1T_{2g} \leftarrow {}^1A_{1g}$	0.31	10
	313	${}^1T_{1g} \leftarrow {}^1A_{1g}$	0.31	
	365	${}^1T_{1g} \leftarrow {}^1A_{1g}$	0.31	
	405	${}^3T_{1g} \leftarrow {}^1A_{1g}$	0.29	
	436	${}^3T_{1g} \leftarrow {}^1A_{1g}$	0.34	
$Rh(NH_3)_6^{3+}$	254	${}^1T_{2g} \leftarrow {}^1A_{1g}$	0.07	7
	313	${}^1T_{1g} \leftarrow {}^1A_{1g}$	0.075	
$Ir(NH_3)_6^{3+}$	254	${}^1T_{1g} \leftarrow {}^1A_{1g}$	0.083	2
	313	${}^3T_{1g} \leftarrow {}^1A_{1g}$	0.090	

[a] V.F. Manfrin, G. Varani, L. Moggi and V. Balzani, Mol. Photochem., 1 (1969) 387.

virtually independent of λ_{irr} at wavelengths corresponding to LF absorptions [8,9]; (2) sensitization with organic triplets has been demonstrated [7,9] and gives limiting photosubstitution yields equivalent to Φ_s and (3) changes in photosubstitution yields upon perdeuteration of the ammine ligands can be directly correlated with changes in the lifetimes of the LEES as measured from the luminescence spectra in room temperature aqueous solutions [8] (vide infra).

However, while it now appears that the photosubstitution chemistry of the polycyano complexes of cobalt(III), e.g. $Co(CN)_6^{3+}$ parallels that of the Rh(III) and Ir(III) complexes in this respect [10], it is quite obvious that such is not the case for the much studied amine complexes of cobalt(III) [11]. For these, three essential differences have been noted: (1) Φ_s values resulting from LF excitation are much smaller than for the stronger field analogs; (2) these Φ_s are λ_{irr} dependent with higher energy excitation giving markedly higher values (Table 1) and (3) for at least one case, $Co(NH_3)_5Cl^{2+}$, excitation of singlet bands leads to a different mixture of products (NH_3 aquation favored) than does excitation at a wavelength corresponding to the lowest triplet absorption (Cl^- aquation predominates) [12]. As a consequence, one must conclude that much of the photosubstitution observed with the Co(III) amines represents chemical deactivation pathways from electronic configurations higher in energy than the LEES and perhaps even by processes competitive with vibrational deactivation within the excited state formed on initial excitation. The much lower total Φ_s values probably indicate that the major deactivation pathway for the higher energy LF states remains internal conversion/intersystem crossing to the LEES; however, the LEES undergoes deactivation nonradiatively to the ground state much more rapidly than it undergoes substitution. Two explanations for this apparent unreactivity of the LEES of the Co(III) amines have been proposed. One focuses on the ligand substitution pathway, suggesting that this is suppressed from the LEES because the estimated energy of this state is less than that of the transition state of the thermal substitution pathway [13]. The other explanation suggests that the potential surface of the LEES (a quintet) intersects that of the ground state in a manner producing configurational mixing and enhancing radiationless deactivation [4]. Given the absence of any direct measurement of the LEES kinetics for such complexes, the two explanations are neither inconsistent with current data nor are mutually exclusive.

There is a large body of evidence pointing to chemical reactions from the higher energy states of different orbital parentages (e.g. charge transfer or intraligand excited state) being quite competitive with internal conversion to LF states. However, if consideration is restricted to those photolysis wavelengths corresponding to ligand field excitation, this author believes that, for

d^6 "Werner type" complexes of the stronger ligand fields*, (e.g. amine complexes of Rh(III), Ir(III), the Co(III) polycyano complexes, etc.) the photosubstitution chemistry observed largely represents reactions of thermally equilibrated LEES or those states in thermal equilibrium with the LEES. This is not to imply that some of the observed photosubstitutions are not the result of reactions from upper states competitive with vibrational relaxation/internal conversion/intersystem crossing, since this clearly must be the case for the Co(III) ammines. However, when the LEES is itself reactive, the product yields from its chemical pathways swamp out those from the higher excited state. Thus, one can treat the chemical reactions of the thermalized states using the concepts of transition state theory of kinetics with radiative and nonradiative deactivation merely representing additional pathways for decay of this reactive species**.

D. REACTION DYNAMICS OF LIGAND FIELD EXCITED STATES

If the principal photosubstitutions result from chemical deactivation of a thermalized LEES, the quantum yield for photosubstitution Φ_s can be expressed in terms of the rate constants for the various decay pathways from this state as indicated in Fig. 3 ($k_s = k_p$)

$$\Phi_s = \Phi_{isc} k_s \tau \tag{3}$$

where

$$\tau = (k_s + k_n + k_r)^{-1} \tag{4}$$

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* The term "Werner type" complexes is used here to exclude from consideration systems such as the Co(III) methyl complexes described recently [14]. In these cases excitation of low energy absorption bands which nominally might be assigned as LF transitions lead to efficient Co–CH_3 bond homolysis, a reaction which cannot be treated in the same manner as normal ligand substitutions on Co(III) centers. Also excluded from the discussion here are metal carbonyl complexes.

** Applications of transition state kinetic theory to excited state ligand substitution reactions appears to have some problems with the photoreactions of Cr(III) amine complexes. A substantial fraction of the photoaquation occurs via the 'prompt' reaction of the quartet excited state initially formed in the excitation, that is by a pathway which cannot be quenched when the LEES, a doublet state is fully quenched bimolecularly. The observation that doublets are formed within picoseconds of initial excitation into the quartet [1] has led to suggestions that the prompt reaction occurs on a similar time scale, thus not from a thermalized excited state. However, a key experiment is missing, i.e. measurement of the rates of product formation from the prompt reaction using this time resolution. The possibility exists that thermalized quartets and doublets are formed competitively from initial states and that the prompt reaction occurs simply because chemical reaction from the thermalized quartet is simply faster than intersystem crossing in this case where there are large Franck–Condon factors in the quartet to doublet transition and spin-orbit coupling is relatively small.

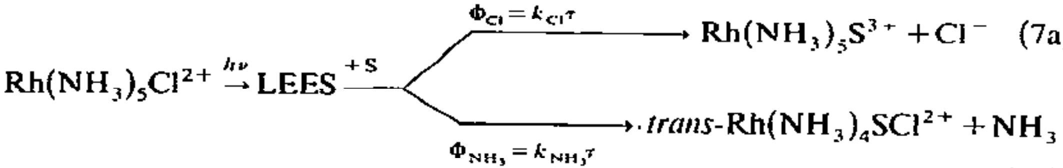
and Φ_{isc} is the efficiency of internal conversion/intersystem crossing which can be taken as unity or near unity according to the results described above. Thus eqn. (3) can be rewritten as

$$\Phi_s = k_s\tau \tag{5}$$

and the emission quantum yield can be expressed similarly

$$\Phi_r = k_r\tau \tag{6}$$

For such a simple case, independent measurement of Φ_s, Φ_r and τ under identical conditions allows calculation of the three rate constants k_s, k_r and k_n, and such analysis can be extended to cases of more than one chemical deactivation pathway, e.g. [8,15,16].



$$\mathrm{Rh(NH_3)_5Cl^{2+}} \xrightarrow{h\nu} \mathrm{LEES} \xrightarrow{+\mathrm{S}} \begin{cases} \xrightarrow{\Phi_{\mathrm{Cl}} = k_{\mathrm{Cl}}\tau} \mathrm{Rh(NH_3)_5S^{3+}} + \mathrm{Cl^-} & \text{(7a)} \\ \xrightarrow[\Phi_{\mathrm{NH_3}} = k_{\mathrm{NH_3}}\tau]{} \textit{trans}\text{-}\mathrm{Rh(NH_3)_4SCl^{2+}} + \mathrm{NH_3} & \text{(7b)} \end{cases}$$

Pulse laser technology now provides the opportunity to study LF excited state reaction dynamics under photochemically relevant conditions. Emission techniques have been used to measure LEES lifetimes for selected complexes of photosubstitution active complexes of Rh(III) [8,15–17], Ir(III) [18], Re(I) [19] and Cr(III) [20], and in several cases absorption techniques have proved valuable in measuring excited state reaction rates [17,20]. However, of published reports through 1980, only for the studies of the d^6 Rh(III) halopentaammines $\mathrm{Rh(NH_3)_5X^{2+}}$ ($\mathrm{X^-} = \mathrm{Cl^-}$ or $\mathrm{Br^-}$) and several d^3 Cr(III) cases can the excited state reaction dynamics be considered those of LF states unperturbed by charge transfer states of comparable or lower energies. The bulk of the subsequent discussion will be concerned with the Rh(III) cases.

A key point implicitly assumed by most theoretical models proposed to rationalize the photosubstitutions resulting from ligand field excitation is the view that it is indeed an excited state of the complex, usually the LEES, which undergoes chemical reaction. However, the continuous photolysis quantum yield results and sensitization experiments are incapable of differentiating between a mechanism where chemical reaction occurs from the thermalized LEES and one where reaction occurs from vibrationally hot, ground electronic state species generated during nonradiative deactivation of the LEES [13]. In both cases, the LEES is the common precursor of the principal chemical, nonradiative and reactive deactivation pathways. Furthermore, even successful correlation of the photoreaction products with bonding changes expected from the electronic redistribution of the excited states may only reflect the population of specific metal ligand vibrational modes in the vibrationally hot ground state resulting from the differences between the excited state and ground state structures. However, for the latter mechanism, there is no implied correlation between the lifetime of the LEES (τ) and the photosubstitution quantum yields (Φ_s), since the branching of nonradiative deactivation to starting material and reaction to products would occur after the rate limiting deactivation from the electronic excited state to vibrational surfaces of the ground electronic state.

In this context, the comparison in Table 2 of the photosubstitution quantum yields (measured by continuous photolysis techniques) and the LEES lifetimes (determined by pulse photolysis) under analogous conditions for the halopentaamminerhodium(III) complexes $Rh(NH_3)_5X^{2+}$ and the perdeuterated derivatives $Rh(ND_3)_5X^{2+}$ is particularly notable. For both the chloro and bromo complexes in aqueous solution, the effects of perdeuteration is to lengthen τ and to increase both Φ_s and Φ_r in a manner sufficiently parallel to indicate that nonradiative deactivation (which is suppressed by perdeuteration), radiative deactivation and ligand substitution are competitive pathways leading from the LEES. In such a case, the quantum yields can be described in terms of the kinetic model as indicated in eqns. (3)–(5).

Analysis of the quantum yield and lifetime data of Table 2 in this manner gives the rate constants in Table 3 for the various deactivation pathways from the LEES of the halopentaamminerhodium(III) complexes. Notably, perdeuteration of either the chloro or bromo complexes has virtually no effect on k_r (within experimental uncertainties) and only a modest slowing effect upon the major ligand substitution rates from the LEES (Cl^- loss from RhA_5Cl^{2+}, ammonia loss from RhA_5Br^{2+}). However, quantum yields for aquation are significantly enhanced owing to the longer lifetimes (Table 2)

TABLE 2

Lifetime and quantum yield data for RhA_5X^{2+} ($A=NH_3$ or ND_3, $X^-=Cl^-$ or Br^-) in 298 K aqueous solution[a]

Complex	τ (nsec)	Φ_r ($\times 10^5$)	Φ_X[b]	Φ_A[b]
$Rh(NH_3)_5Cl^{2+}$[c]	14.2 (14.8)[d]	3.2	0.18	0.02
$Rh(ND_3)_5Cl^{2+}$[e]	27.3	6.6	0.28	≤ 0.05
$Rh(NH_3)_5Br^{2+}$[c]	12.4	1.5	~ 0.02	0.18
$Rh(ND_3)_5Br^{2+}$[e]	24.6	3.6	≤ 0.03	0.26

[a] Data from ref. 8. [b] In moles einstein^{-1}, λ_{irr} 366 nm. [c] In pH 2–4 $HClO_4/H_2O$. [d] Ref. 17. [e] In $DClO_4/D_2O$, closely analogous values were measured in pH 2–4 $HClO_4/H_2O$.

TABLE 3

LEES deactivation rate constants for RhA_5X^{2+} in 298 K aqueous solution [a]

Complex	k_r ($\times 10^{-3}$) (s^{-1})	k_n ($\times 10^{-6}$) (s^{-1})	k_X ($\times 10^{-6}$) (s^{-1})	k_{NH_3} ($\times 10^{-6}$) (s^{-1})
$Rh(NH_3)_5Cl^{2+}$	2.3	56	13	1.5
$Rh(ND_3)_5Cl^{2+}$	1.9	19	10	≤ 2
$Rh(NH_3)_5Br^{2+}$	1.2	65	~1.6	15
$Rh(ND_3)_5Br^{2+}$	1.4	27	≤ 1.2	11

[a] Data from ref. 8.

as the result of nonradiative deactivation rates being significantly decreased by perdeuteration, a feature previously noted to an even greater degree for the spectroscopy of these at low temperatures [3b].

Although it is not unlikely that the two processes occur by markedly different mechanisms, interesting comparisons can be drawn between the rates of the LEES ligand substitution pathways and those of the thermal aquations of the same complexes. Thermal aquation of Cl^- from $Rh(NH_3)_5Cl^{2+}$ in acidic solution displays a first order rate law with an extrapolated 298 K rate constant of 4×10^{-8} s^{-1} and an E_a of 24.4 kcal mol^{-1} [21]. Thermal ammonia labilization was not observed and must be considerably slower than Cl^- labilization. In contrast, Cl^- aquation from the LF state occurs at a rate of 1.3×10^7 s^{-1}, more than 14 orders of magnitude faster, with an E_a of about 6 kcal mol^{-1} [8a]. Furthermore, NH_3 labilization from the LEES is measurable and only about an order of magnitude less than the Cl^- substitution rate. Similar rate enhancements are noted for the LEES of the bromo complex with the additional feature that the major excited state reaction is NH_3 labilization, an antithermal pathway.

An intriguing observation with regard to the LEES of $Rh(NH_3)_5Cl^{2+}$ is that both the room temperature emission and the photoaquation reaction in aqueous solution can be quenched by the Brønsted bases OH^-, CO_3^{2-} and CN^- with quenching rate constants of 2.1×10^{10} and 8.3×10^9 M^{-1} s^{-1}, respectively, for the first two [17]. Since no comparable quenching with OH^- was observed for the LF emission of $Rh(bpy)_2Cl_2^+$ in aqueous solution, it was suggested that the quenching mechanism involved the proton transfer from the metal complex excited state to the Brønsted base during the quenching encounter. A small fraction of the photosubstitution reaction was reported [17] to be unquenchable by hydroxide and it was suggested that some bimolecular anation might be accompanying the quenching or that a portion of the photosubstitution is occurring from state(s) other than the LEES (e.g. from singlet states prior to intersystem crossing). Certainly such quenching phenomena need to be subjected to greater scrutiny.

In Table 4 are summarized the photosubstitution quantum yields for the $Rh(NH_3)_5Cl^{2+}$ ion in a variety of different solvents. The most important aspect of these data is not that quantum yields differ from solvent to solvent (since this might be expected as the result of variations in the nonradiative deactivation rates) but that the nature of the predominant photosubstitution pathway changes. In water, Cl^- photoaquation is predominant over NH_3 photoaquation by a margin of about nine to one, but in several of the organic solvents Φ_{NH_3} is larger than Φ_{Cl} by a similar ratio [15,16]. Given that there are no marked changes in the positions or shapes of the LF bands in the absorption spectrum, it must be concluded that these photoreaction changes result not from solvent induced perturbations in the nature of the electronic excited states but from variations in the kinetic parameters which govern deactivation from the excited states.

The above conclusion is substantiated by the pulse laser studies determining the LEES lifetimes. Although Φ_r could not be determined accurately, the fact that it is very small in each of these cases ($< 10^{-5}$) allows one to calculate the solvent rate constants from eqns. (7a) and (7b) given the approximation

$$\tau = \left(k_{Cl} + k_{NH_3} + k_n\right)^{-1} \tag{8}$$

The rate constants so calculated are summarized in Table 5 and one can see from these that k_{Cl} is the term most dramatically affected by the solvent nature. Comparison with the solvent parameter $\Delta\Delta G_{Cl^-}$ shows that k_{Cl} qualitatively parallels the solvation energy of the chloride ion [15].

The LEES of $Rh(NH_3)Cl^{2+}$ is the ^3E state (formally a $(d_{xy})^2(d_{xz,yz})^3(d_{z^2})^1$

TABLE 4

Quantum yields for photosubstitution of $Rh(NH_3)_5Cl^{2+}$ in various solvents (298 K) [a]

Solvent [b]	Φ_{Cl^-}	Φ_{NH_3}	R [c]
H_2O	0.18	0.02	9
fma	0.057	<0.011	>5
dmso	<0.006	0.029	<0.2
CH_3OH	0.008	0.11	0.07
dmf	0.004	0.070	0.06

[a] Quantum yields in mole einstein^{-1}, 365 nm excitation, ref. 16. [b] fma = formamide; dmso = dimethyl sulfoxide; dmf = *N*,*N*-dimethyl formamide. [c] $R = \Phi_{Cl^-} / \Phi_{NH_3}$.

TABLE 5

Lifetime data and deactivation rate constants in various solvents at 298 K [a]

Solvent [b]	τ [c]	k_n [d]	k_{NH_3} [d]	k_{Cl^-} [d]	$\Delta\Delta G_{Cl^-}$ [e]
$Rh(NH_3)_5Cl^{2+}$					
H_2O	14.2	56	1.4	12.7	-2.7
fma	22.4	45	0.5	2.5	-0.4
CH_3OH	>19.6	>45	<5.6	<0.46	0.0
dmso	35.1	28	0.8	0.17	6.0
dmf	32.4	31	2.2	0.12	7.2
cis-$Ir(bpy)_2Cl_2^+$					
H_2O	~ 1	~ 800		~ 80	-2.7
CH_3OH	36	27		0.5	0.0
CH_3CN	344	2.9		$<10^{-3}$	6.0
dmf	330	3.0		$<10^{-3}$	7.2

[a] Refs. 16 and 18. [b] Abbreviations for solvents in Table 4. [c] In nsec, experimental uncertainty $< \pm 10\%$. [d] Rate constants in s^{-1} ($\times 10^{-6}$). [e] Free energy of solvation for Cl^- in a given solvent relative to methanol in kcal mol^{-1}, V. Mayer, Coord. Chem. Rev., 21 (1976) 129.

configuration although there is significant configuration interaction with the higher ^3E state with the $(d_{xy})^2(d_{xz,yz})^3(d_{x^2-y^2})^1$ configuration) [22] which can be viewed as having the excitation principally localized along the weak field NH_3–Cl^- axis. This view suggests that the NH_3 aquation pathway involves labilization of the ammonia *trans* to the Cl^- although there is no unequivocal evidence to confirm this. However, regardless of which NH_3 is labilized and regardless of whether the actual substitution mechanism involves a dissociative pathway or an associative pathway (see below), the solvent effects on k_{Cl} can be rationalized in terms of a mechanism displaying considerable charge separation along the Rh(III)–Cl^- bond at the transition state, the energy of which is strongly influenced by the solvents' ability to stabilize this charge separation [15,16]. In contrast, ammine labilization should be much less solvent sensitive given the absence of major charge separation accompanying this pathway and the relative insensitivity of NH_3 solvation energies to the nature of the solvent.

A similar study [18] of the solvent effects on the photochemistry of *cis*-$Ir(bpy)_2Cl_2^+$ (eqn. 9) is also summarized in Table 5.

$$cis\text{-}Ir(bpy)_2Cl_2^+ + S \rightarrow cis\text{-}Ir(bpy)_2SCl^{2+} + Cl^- \qquad (9)$$

Interpretation of this system is complicated by the fact that although the LEES is a LF state, a metal-to-ligand charge transfer state is energetically close to the LEES and the energy gap between the two is affected by the sensitivity of the MLCT state to the solvent. Nonetheless, the k_{Cl} values measured by the combined photochemical/photoluminescence technique again parallel qualitatively the chloride solvating ability of the reaction medium.

E. THEORETICAL TREATMENTS OF LIGAND PHOTOLABILIZATION

Over the past decade, there has been considerable discussion regarding the theoretical basis for ligand labilization resulting from LF excitation of d^6 complexes [22–26]. Generally these treatments have attempted to rationalize and predict the pathways of photolabilization (i.e. which ligand is labilized from a particular electronic excited state of a complex) on the basis of ligand field calculations utilizing ligand parameters derived from spectroscopic properties (absorption spectra). In several cases there have also been attempts to rationalize the relative quantum yields observed for series of closely related complexes.

There is no question that these treatments have provided an intellectual framework for visualizing the types of σ and π bonding changes in specific excited states. A particularly interesting treatment, which has appeared in a series of articles by Vanquickenborne and Ceulemans [24], allows the calculation of "indices" $I(ML)$ for metal ligand bonds in the ground and excited states. These indices constitute the contribution made to the M–L bond energy owing to interaction with the d orbitals. These have the advantage that calculation is accomplished relatively easily utilizing solutions to the additive angular overlap model and spectroscopic σ and π parameters for individual ligands. It is argued that such bond indices may provide a comparative measure of the different ligand–metal bond strengths within a given state of a complex and that the ligand with the smallest $I(ML)$ will likely be the one labilized in the dominant reaction mode. The treatment has been quite successful in rationalizing the photosubstitution pathways for a large series of d^3 and d^6 complexes in aqueous solution but has not attempted to predict relative quantum yields for reactions of different complexes [24].

The question of predicting quantum yields has been addressed previously [26]. In this regard, the most serious limitation of the theoretical models based on spectroscopic parameters is the inability of these models to treat the nonradiative deactivation pathway. There are simply no allowances in these treatments to deal with perturbations of the k_n pathway such as those caused by deuterium labelling, changes in the spin orbit coupling as ligands are varied, and temperature and solvent effects on competitive deactivation pathways. Predictions of which ligand will be labilized from an excited state (e.g. the LEES) of an individual complex are inherently more likely to be successful, because the relative yields of competitive ligand substitution pathways from a single state are independent of k_n. The absolute Φ_i values are not. However, it is clear from the data on $Rh(NH_3)_5Cl^{2+}$ delineated in Table 4 that even the identity of the predominant photosubstitution pathway can be a function of the reaction medium independent of the spectroscopic parameters upon which the predictions are formulated.

The $Rh(NH_3)_5Cl^{2+}$ example may simply reflect a case where two competitive pathways are sufficiently balanced that media perturbations can shift the balance from one mode to another. For example, the bond indices for the LEES state (the ^3E) are I^*(Rh–NH_3 eq), 19.9 kK; I^*(Rh–NH_3 ax), 11.4 kK; and I^*(Rh–Cl), 11.0 kK using the recently proposed σ- and π-parameters for NH_3 and Cl^- in the Rh(III) coordination sphere [24b] and ignoring configuration interaction with the upper ^3E state. Thus, according to these, the Rh–Cl bond should be labilized preferentially but the Rh–NH_3ax bond index is sufficiently close that labilization of this site might also be expected. Thus, perturbations of non-spectroscopic parameters such as the solvating ability of the reaction medium might be expected to have major effects on the relative yields of the two pathways. Unfortunately, whether the NH_3 labilized actually originates in the *trans*-position has not been determined. Regardless, the important point is that, while the bond index model may indicate likely trajectories for reactive deactivation of a LF state, the quantitative aspects including the nature of the predominant labilization pathway and the quantum yields will be governed by the intimate mechanisms for reactive and nonradiative deactivation.

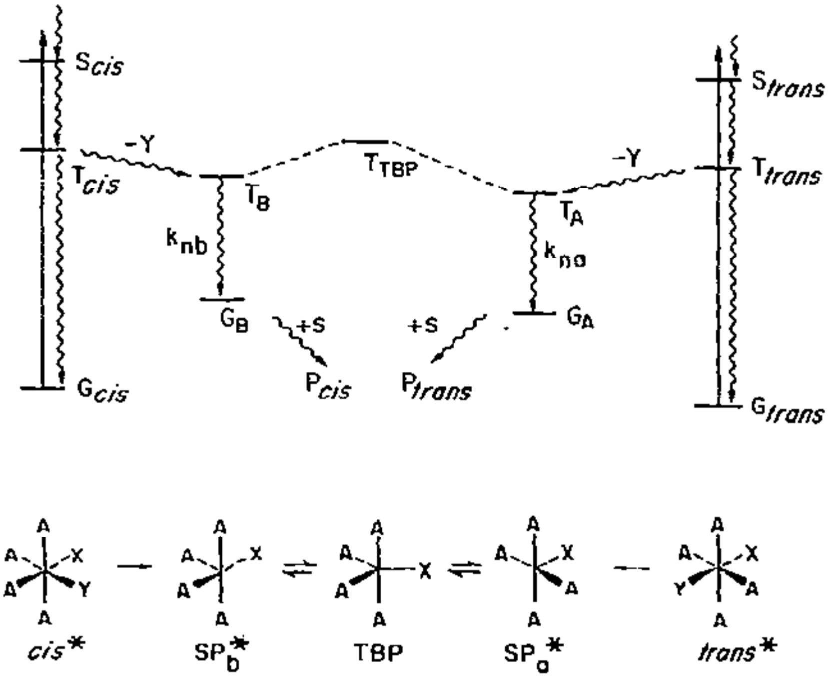
It is well recognized by theorists and experimentalists alike that the theoretical models proposed for ligand photolabilization represent steps in an evolutionary development toward a more thorough understanding of the structures and reactivities of LF excited states. Certainly, it is valuable to have a qualitative understanding of such concepts as the extent of localization of the excitation perturbation along particular metal ligand axes [22] and of the nature of the metal–ligand bonding in the excited state [24]. Furthermore, such models have provided challenges for the design of photochemical and photophysical experiments to provide more sophisticated information for the testing and evaluation of these treatments and to serve as parameters in future, more advanced, models.

F. STEREOCHEMICAL ASPECTS OF LIGAND FIELD PHOTOCHEMISTRY

In 1974 it was demonstrated [27] that the photosubstitution reactions of *cis* and *trans*-$Co(en)_2(H_2O)Cl_2^+$ lead to approximately equivalent mixtures of the *cis* (30%) and *trans* (70%) isomers of $Co(en)_2(H_2O)Cl^{2+}$. There have been several subsequent reports [28,29] of photochemically induced stereomobility of Co(III) complexes. Prior to the above report, there was an indication [30] of similar stereomobility in the photoreactions of *cis*-$Rh(en)_2Cl_2^+$, although there were apparently some problems with the product analysis in this case [31]. A much more clearcut example of the photoisomerization of a heavier metal d^6 complex was the demonstration [32] that upon LF excitation *cis*-$Rh(NH_3)_4Cl_2^+$ undergoes *cis* to *trans* isomerization concomitant with photoaquation (eqn. 10). There have been a number of reports since demonstrating the associated photolabilization and photoisomerization reactions of various Rh(III) amine complexes as well as several Ir(III) complexes. Notably, for the Rh(III) and Ir(III) systems the analogous thermal substitution reactions generally proceed with complete retention of configuration [21]; thus, the thermal and photosubstitution pathways must involve markedly different reaction mechanisms.

$$cis\text{-}Rh(NH_3)_4Cl_2^+ + H_2O \xrightarrow{h\nu} trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} + Cl^- \qquad (10)$$

The report of concomitant photoaquation/photoisomerization reactions of *cis*-$Rh(NH_3)_4Cl_2^+$ was the stimulus of a generalized theoretical model for the photoisomerization of d^6 complexes proposed by Vanquickenborne and Ceulemans [33] and discussed in somewhat modified forms by others [29,34]. The qualitative aspects of the modified model are outlined in Scheme I, the



Scheme I

key feature being that the isomerization step occurs subsequent to the dissociation of a ligand from the LEES of the initial complex. Rearrangement is proposed to occur among the resulting apical and basal substituted square pyramidal intermediates SP_a^* (formed by dissociation of Y from *trans*-ML_4XY^*) and SP_b^* (formed from *cis*-ML_4XY^*). Notably, the model also proposes that SP_a^* and SP^*_b are electronic excited states, the triplet LEES of the pentacoordinate intermediates. Based on these assumed structures and electronic configurations, molecular orbital calculations have been used to evaluate the relative energies for SP_a^* and SP_b^* and of the trigonal bipyramidal configuration (TBP) which serves as the transition state or intermediate along the reaction coordinate between these configurations. The qualitative conclusions from these calculations are that the SP* intermediates of lowest energy will be those species having the weaker σ-donor ligand (X or L) in the apical site and that the energy barrier for isomerization will be a function of the ligand field strength, i.e. the stronger the average ligand field, the higher the barrier for isomerization.

The first of these points rationalizes the observation of *cis* to *trans* isomerization in cases such as eqn. (10) where $L = NH_3$ and $X = Cl^-$, since the favored SP* will have Cl^- in the apical site. Deactivation to the lower energy singlet pentacoordinate species (the ground state of this intermediate), and rapid trapping of this by solvent would give the *trans* product. Also predicted, however, is *trans* to *cis* isomerization in cases where X is a stronger sigma donor than L, e.g. when $X = OH^-$ and $L = NH_3$. This conclusion was substantiated by the results [35] indicated in eqn. (11) and by

$$\textit{cis-}\text{ or }\textit{trans-}\mathrm{Rh(NH_3)_4(OH)Cl^+} \xrightarrow[\text{alkaline solution}]{h\nu} \textit{cis-}\mathrm{Rh(NH_3)_4(OH)_2^+} + \mathrm{Cl^-} \qquad (11)$$

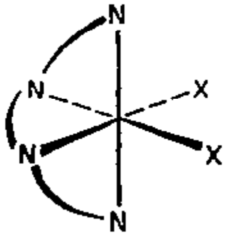
similar *trans* to *cis* photoisomerization reported to accompany the photolabilization of Cl^- from *trans*-$Ir(en)_2(OH)Cl^+$ [36] and *trans*-$Co(en)_2(CN)Cl^{2+}$ [29]. (However, the later observation is somewhat unsettling given the uncertain role of the quintet state for Co(III) amine complexes.)

The second point implicit to the model outlined in Scheme I is that since two different intermediates, SP_a^* and SP_b^*, are produced from the *trans* or *cis* complexes respectively, and since each can decay to the appropriate SP ground state (G_A or G_B) where it is trapped by solvent without further isomerization, photolabilization of X from ML_4XY may not necessarily give identical photoproduct isomer mixtures. This situation would result when the deactivation rates (k_{na} and k_{nb}) are faster than the relaxation of SP_a^* and SP_b^* to a steady state ratio. Such cases might be expected when the ligand field strength of ML_4X is large giving rise to a relatively large barrier for isomerization. In this context, one might explain the stereoretentive photolabilizations of Cl^- from *cis*- and *trans*-$Rh(en)_2(NH_3)Cl^{2+}$ in contrast to the formation of *trans*-$Rh(en)_2(H_2O)Cl^{2+}$, only, from *cis* or *trans*-$Rh(en)_2Cl_2^+$ [31] since the presumed pentacoordinate intermediate of the first case would be $Rh(en)_2NH_3^{3+}$ while that of the other two would be $Rh(en)_2Cl^{2+}$. A similar explanation might be offered for the differential product mixtures from the Ir(III) analogs indicated in eqns. (12) and (13) [36]; however, in this case an alternative would be markedly increased deactivation owing to the larger spin orbit coupling constants for iridium.

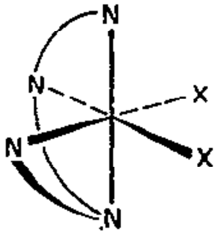
$$\textit{trans}\text{-}Ir(en)_2Cl_2^+ + H_2O \xrightarrow{h\nu} \underset{(>95\%)}{\textit{trans}\text{-}Ir(en)_2(H_2O)Cl^{2+}} \qquad (12)$$

$$\textit{cis}\text{-}Ir(en)_2Cl_2^+\ H_2O \xrightarrow{h\nu} \begin{array}{c} \textit{trans}\text{-}Ir(en)_2(H_2O)Cl^{2+} \\ (\sim 10\%) \\ \text{and } \textit{cis}\text{-}Ir(en)_2(H_2O)Cl^{2+} \\ (\sim 90\%) \end{array} \qquad (13)$$

An alternative mechanism proposed for isomerization accompanying the ligand labilization has been based upon the idea that ligand dissociation from the LEES requires a concerted rearrangement to a TBP intermediate and that it is this intermediate's stereoselective reaction with solvent which determines the product distribution [37]. The stimulus for this proposal derives from the observation that the *cis*-α-$Rh(trien)Cl_2^+$ ion (for which the chelating amine has the configuration shown in **A**)



A



B

is relatively inactive toward photosubstitution while the corresponding β-isomer (**B**) is quite active toward photosubstitution and photoisomerization [37]. If concerted rearrangement to a TBP intermediate were a requirement for ligand labilization, the angle between the two equatorial coordination sites of the TBP may be too large for the middle nitrogens of the tetradentate amine to span without considerable strain, thus making Cl^- dissociation an unfavorable pathway for the α isomer. Alternatively, one might explain the small quantum yield in this case as possibly reflecting an anomalously large rate for the nonradiative deactivation of the LEES of the hexacoordinate complex, a possibility which has not been tested. Nevertheless, given the probability that formation of a square base pyramidal species should also be accompanied by some distortions involving increases in L–M–L bond angles, the result for *cis* α-Rh(trien)Cl_2^+ does not seem inconsistent with the model proposed in Scheme I [34]. Overall, the latter model, while far from being exhaustively tested, appears to be quite self consistent with the experimental data for the photoisomerization of strong field d^6 complexes associated with ligand photolabilization.

G. CONCLUDING REMARKS

The above sections outline just some of the considerable experiments and theoretical introspection which have been directed at understanding the photosubstitution chemistry resulting from the ligand field excitation of d^6 complexes. However, despite the volume of these efforts, one can safely state that the mechanisms for these excited state reactions are far from well understood. For the rhodium(III) haloammine complexes with which measurements of excited state dynamics have been possible under photochemically significant conditions at least some of the questions posed in the introduction appear to be partly answered. Initial excitation of ligand field states is followed by efficient internal conversion to the LEES from which competitive chemical reactions and physical deactivation occur. However, even for these complexes the evidence regarding the chemical deactivation mechanisms is circumstantial at best. Such a situation is certainly not surprising given the difficulties encountered in establishing the mechanisms of the thermal substitution reactions of coordination compounds [38], but it does point to several key areas ripe for future exploration.

One such area is the question of whether the LF excited state substitution pathway is associative (i.e. a pathway where bonding between the incoming ligand and the metal plays a significant role in determining the energy of the transition state of the rate limiting step) or dissociative in nature. For the d^6 complexes discussed in this article, there is a clear bias among many of the theorists and experimentalists concerned with this problem toward a mechanism of a dissociative character. This view is reinforced by the observation of pentacoordinate intermediates in the low temperature matrix isolation photochemical experiments with various hexacoordinate metal carbonyls [39]. Furthermore, the relative success of the bond index model for predicting the identity of the principal ligand labilized from a hexacoordinate complex [24] suggests the importance of a mechanism in which bond breaking is a key factor in determining the energetics of the competitive pathways for ligand labilization from the excited state. However, ligand–metal bond breaking would certainly be important not only in a limiting dissociative pathway but also in dissociative or associative interchange mechanisms and would no doubt have some influence on a limiting associative mechanism.

The solvent effects on the excited state reaction rates of $Rh(NH_3)_5Cl^{2+}$ point to the importance of solvating the Cl^- labilized (or the charge separation generated as the Rh–Cl bond dissociates) on the rate of Cl^- labilization. Again such data suggest a limiting dissociative or interchange mechanism for the LEES of this complex. This perception is also reinforced by the observations that neither the NH_3 nor Cl^- labilization rates for $Rh(NH_3)_5Cl^{2+}$ can be correlated with the donor properties of the different solvents [15,16]. In a similar context, recent measurements [40] of the rates of Br^- labilization from the LF state of several bromoammine complexes show that k_{Br^-} values follow the order

cis-$Rh(NH_3)_4Br_2^+$ > *trans*-$Rh(NH_3)_4Br_2^+$ >> $Rh(NH_3)_5Br^{2+}$

and the k_{NH_3} values the order

cis-$Rh(NH_3)_4Br_2^+$ > $Rh(NH_3)_5Br^{2+}$ >> *trans*-$Rh(NH_3)_4Br_2^+$

Comparisons of these rates suffer from the complications of changes in the nature and extent of excited state distortions as functions of the symmetry changes. However, the larger k_{Br^-} values with the dibromo complexes are certainly consistent with a pathway where Rh^{3+}–Br^- dissociation is important at the transition state. Furthermore, the larger k_{NH_3} value for *cis*-$Rh(NH_3)_4Br_2^+$ over that for $Rh(NH_3)_5Br^{2+}$ (despite a smaller quantum yield for the former complex) suggests that Rh–H_2O bond making, which should be more favorable with the more highly charged 2+ complex, is not the dominant energetic factor in determining the relative NH_3 labilization rates. (The low value of k_{NH_3} for *trans*-$Rh(NH_3)_4Br_2^+$ is consistent with the requirement that the NH_3 released is from a position *trans* to the bromide.)

Among thermal substitution studies, good insight with regard to the dissociative or associative nature of the rate determining transition state has been drawn from rate studies under various applied pressures [41]. Although somewhat ambiguous corrections need to be applied for solvation changes especially for the labilization of ionic ligands, the volumes of activation values so determined, if negative, suggest a mechanism associative in character but, if positive, suggest one dissociative in character. Several such studies of pressure effects on quantum yields and LEES lifetimes now in progress [42–44] show promise of improving our understanding of excited state substitution mechanisms.

A less ambiguous demonstration of mechanism would be the direct observation of intermediates either 5 or 7 coordinate expected for the limiting dissociative or associative pathways respectively. Of course, such a discrete intermediate is not a feature of an interchange pathway, but the failure so far to observe such intermediates is not surprising given the short lifetimes expected for these. With the exception of the low temperature matrix isolation studies on metal carbonyls carried out in the absence of coordinating solvent, perhaps the best evidence for dissociated intermediates is drawn from the stereochemical studies. For the d^6 Werner complexes, the stereochemical observations accompanying ligand labilization are quite self consistent with the theoretical models illustrated by Scheme I requiring rearrangement among five coordinate intermediates. Notably, these models require formation not only of dissociated intermediates but also of ones in electronic excited states and that these be sufficiently long lived to undergo isomerization. Such an intermediate should be observable by spectroscopic methods (absorption or emission spectra) subsequent to excitation from a picosecond laser source.

In conclusion, this article has attempted to outline some experimental and theoretical studies which the author considers to provide key information with regard to the photosubstitution mechanisms of d^6 complexes. It should be clear from these that while our understanding of such mechanisms is growing increasingly more sophisticated, exciting possibilities exist, especially by the application of new instrumental techniques, for equally significant further increases in our understanding.

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