

has been observed also in the complexes of the trien ligand methylated at the secondary nitrogen atoms, α -[Co(4,7-Me₂-trien)Cl₂]⁺ \rightarrow β -[Co(4,7-Me₂-trien)CO₃]⁺,¹¹ but on the basis of the above mechanistic proposals the active β compounds

(11) G. H. Searle and F. R. Keene, to be submitted for publication.

of this methylated ligand should be extremely inert to racemization and this aspect is currently being examined.

Registry No. (+)₅₄₆- α -[Co(trien)(H₂O)₂](ClO₄)₃, 14267-03-9; (-)₅₄₆- β -[Co(trien)(H₂O)₂](ClO₄)₃, 15154-95-7; (\pm)- β -[Co(trien)CO₃](ClO₄)·H₂O, 38531-78-1.

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A Model for Predicting the Photoreactions and Relative Quantum Yields of Transition Metal and Organometallic Complexes. II. Cobalt(III) and Rhodium(III)

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The photoreactions of low-spin complexes of the d⁶ metals cobalt(III) and rhodium(III) are shown to depend on the spectrochemical splitting parameter Dq and on the energies of the donor orbitals of the ligands and the metal d orbitals in a simple and predictable way. The molecular axis which is photolabilized is predicted by considering bonding changes which occur when the lowest triplet and singlet excited states of the complex are populated. The relative quantum yields of solvation of the two ligands on the labilized axis are interpreted from a simple analysis of the energies of their donor orbitals. It is shown that the "radical pair" model proposed by Adamson may be incorporated into the analysis in order to predict the wavelength dependence of the quantum yield ratio of the two ligands. The total solvation quantum yield of ligands on the labilized axis is shown to depend on the crystal field parameter Dt .

Introduction

The photochemistry of transition metal complexes has been described as the chemistry of excited electronic states.¹ Although the nature of these excited states may be deduced from ligand field theory,² no connection between a complex's excited states and its photoreactions had heretofore been made. We recently developed a model of transition metal photochemistry based on the known antibonding properties of the excited states in the exact symmetry caused by the donor atoms of the complex and applied it to the photochemistry of the extensively studied chromium(III) complexes.³ The model successfully predicted the photoreactions and relative quantum yields for chromium(III) complexes and led to an understanding of Adamson's important empirical rules.⁴

It was of interest to extend the successful model to other metal systems where no empirical trends have been elucidated. Cobalt and rhodium were chosen for this study for two reasons. First, the extent of the photochemically studied complexes is second only to that of chromium.⁵⁻⁷ Second, there seemed to be no rational order or reason to the photoreactions. The latter reason provided the primary impetus for this study since a major result of our previous work on chromium(III) was a simple, logical, and general model for organizing existing data and for predicting photoreactions in terms of spectroscopic properties.

The empirical rules of Adamson summarized most of the photoreactions of chromium(III). The rules are⁴ (1) the axis having the weakest average crystal field will be the one

labilized and (2) if the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates. The photoreactions of the d⁶ complexes considered in this paper may exhibit reduction of the metal in addition to ligand replacement. When ligand replacement occurs, rule 1 is usually obeyed but rule 2 is often violated.

In this paper we interpret in detail the photoreactions of cobalt and rhodium. It is shown that the general model may be used to explain and predict the redox and ligand replacement reactions. The validity of rule 1 is explained in terms of our ligand field model. The identity of the ligand on the labilized axis which is replaced is shown to depend in a predictable fashion on the orbital energies of the metal and the ligands. The explanation of the redox behavior is contained in the above arguments. Finally, the relative quantum yields in a series of complexes are predicted by considering π -bonding changes resulting from excitation.

d-Orbital Orderings

The correlation diagram for low-spin d⁶ complexes is given in Figure 1. The ordering of the excited electronic states under C_{4v} or D_{4h} geometry depends upon the nature of the ligands. Figure 1 illustrates the splitting for weak axial ligands ($Ds, Dt > 0$). The actual ordering of the excited states of a particular complex may be determined from analysis of polarized single-crystal spectra⁸ or by fitting a theoretically calculated spectrum to one experimentally determined. The latter method has been the most widely used following the pioneering work of Wentworth and Piper.⁹

The ground state of the low-spin complexes, ¹A_{1g}, corresponds to the strong-field (t_{2g})⁶ configuration. The singlet and the triplet excited states shown in Figure 1 all arise from a (t_{2g})⁵(e_g)¹ configuration. The electrostatic crystal field

(1) A. W. Adamson, *Coord. Chem. Rev.*, **3**, 169 (1968).

(2) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.

(3) J. I. Zink, *J. Amer. Chem. Soc.*, **94**, 8039 (1972).

(4) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

(5) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

(6) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

(7) A. W. Adamson, *Pure Appl. Chem.*, **20**, 25 (1969).

(8) W. Moffitt and C. J. Ballhausen, *J. Inorg. Nucl. Chem.*, **3**, 178 (1956).

(9) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

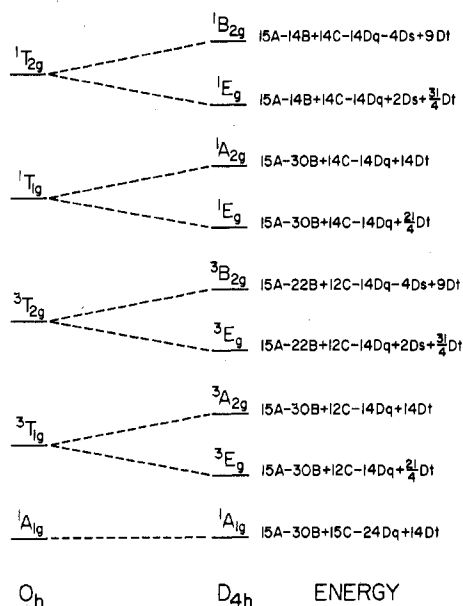


Figure 1. Correlation diagram for the singlet and triplet states of a d^6 configuration. The energies of the levels are shown on the right.

thus splits the singlet and the triplet states in an analogous manner. The difference in energy between a singlet and the corresponding triplet arises from the interelectronic repulsions represented by the Racah parameters B and C . Although the triplet and singlets must split identically, we will show that some triplet states may cross with important photochemical consequences.

The energies of the electronic states under D_{4h} or C_{4v} symmetry may be correlated with ligand properties using the crystal field parameters D_s and D_t or the McClure parameters $\delta\sigma$ and $\delta\pi$.¹⁰ The latter are easily interpreted using the definitions¹⁰

$$\delta\sigma = \sigma_z - \sigma_{xy} \quad (1)$$

$$\delta\pi = \pi_z - \pi_{xy} \quad (2)$$

where σ_i and π_i are respectively the σ - and π -antibonding propensities of the ligands along the i th axis. The parameters D_s and D_t are functions of radial integrals (similar to Dq) and are not as readily interpreted. Assuming that the radial parameters are constant for a given ligand, the approximate relationship shown by eq 3 holds (where n is the num-

$$D_t = \frac{2n}{7} (Dq_{xy} - Dq_z) \quad (3)$$

ber of axial ligands different from the equatorial ones and Dq_{xy} and Dq_z are the values of Dq in the xy and z directions, respectively). The two sets of parameters are interrelated

$$D_s = -\frac{8}{21}\delta\sigma - \frac{2}{7}\delta\pi \quad (4)$$

$$D_t = -\frac{8}{35}\delta\sigma + \frac{8}{35}\delta\pi \quad (5)$$

The energies of the states in terms of the crystal field parameters are given in Figure 1.

The complexes may now be classified according to the ordering of the excited states as shown in Figure 2. In the

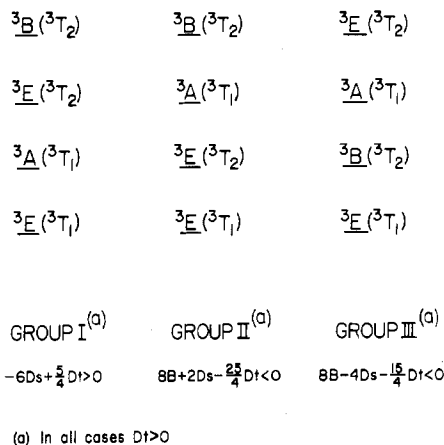


Figure 2. Classification of complexes according to the triplet-state energy orderings. In all cases $D_t > 0$.

original applications of the photochemical model,³ complexes were classified according to the one-electron d-orbital orderings which in turn are based on the relative σ - and π -interaction strengths of the ligands. It is more convenient to classify the complexes according to the relative order of their excited electronic states since it changes in the order of the states which govern the photoreactions and the relative quantum yields. The lowest singlet and lowest triplet excited states¹¹ will always be 1E and 3E , respectively, when D_t is positive. Positive values of D_t occur when the axial field is weaker than the in-plane field. Most tetragonal complexes with weak axial ligands will belong to group 1. If $8B + 2D_s - 25/4 D_t < 0$, the complex will belong to group 2. For many of the complexes considered here, this requires that D_s be negative. (Specific conditions for individual complexes will be discussed in detail later.) The ordering of levels shown for group 3 complexes will occur when $8B - 4D_s + 15/4 D_t < 0$. As we show later, for complexes of interest here D_s must be an unreasonably large positive number in order that this ordering occur. The singlet states do not show the variation in ordering which can occur for the triplet states primarily because those originating from 1T_2 and those from 1T_1 are separated by a factor $16B$ (compared to $8B$ for the triplet). The value of D_s required in order for crossover of the singlets to occur is very large and outside the realm of values found for most ligands.

The change from one group to another may be correlated with the σ - and π -bonding properties of the ligands using eq 4 and 5. Complexes with weaker axial ligands than equatorial ligands may belong to any of the three listed groups. As the π -donating ability of the axial ligand increases, D_s decreases (becomes more negative) and the complex is more likely to be in group 2. As the π -acceptor strength of the axial ligand increases, D_s increases. It is unlikely that D_s ever becomes large enough to allow ordering 3 to occur.

Bonding Changes in Excited States

When an electronic transition occurs, the electronic population of the ground state decreases and that of excited states increases. Since the two states in a ligand field transition involve metal d orbitals which participate in the metal-ligand bonding, shifts of electron density will change the metal-

(10) D. S. McClure, "Advances in the Chemistry of Coordination Compounds," S. S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 498.

(11) The symmetry state should have a "g" subscript under D_{4h} . Thus the lowest excited state is 1E_g under D_{4h} and 1E under C_{4v} symmetry. For convenience, the g subscript will be dropped.

ligand bond strength. We may conceptually divide the changes in bonding into two parts: (a) the change arising from loss of electron population from the ground state and (b) the change arising from populating a previously unpopulated excited state. In this section we will examine in detail the bonding implications of both of these effects for the spin-allowed and spin-forbidden transitions.

The ground state of low-spin d^6 complexes in octahedral or tetragonal symmetries, 1A_1 , consists of two electrons in each of the d_{xy} , d_{xz} , and d_{yz} orbitals. These three metal orbitals all have the proper symmetry to participate in π bonding. If the ligands cannot form π bonds (e.g., NH_3), these three metal orbitals are nonbonding. If the ligands have accessible orbitals of π symmetry, the three highest filled molecular orbitals (which in the crystal field picture are pure metal d_{xy} , d_{xz} , and d_{yz} atomic orbitals) are π bonding or π antibonding depending on whether the ligand π orbitals are empty or filled, respectively. Thus, all electronic transitions arising from orbitals containing metal d_{xy} , d_{xz} , or d_{yz} character will result in changes in the π system of the complex. Under octahedral symmetry all ligands will be equally affected since the d_{xy} , d_{xz} , and d_{yz} orbitals are degenerate. Under tetragonal symmetry the z axis or xy plane will be specifically affected depending on whether the electron is promoted from the degenerate pair of d_{xz} and d_{yz} orbitals or from the d_{xy} orbital, respectively.

The excited state to which an electron is promoted in the low-energy ligand field transitions always involves the unoccupied $d_{x^2-y^2}$ and/or d_{z^2} orbitals which in the molecular orbital picture are σ -antibonding molecular orbitals. If the excited state is primarily $d_{x^2-y^2}$ (or d_{z^2}) in character, σ bonding in the xy plane (or z axis) will be weakened. Thus, photochemical reactions will be governed by the ever present σ -bond weakening together with a possible π -bond change which depends on the particular excitation.

As an example of the analysis of the total bonding changes caused by a particular excitation, consider the $^1A_1 \rightarrow ^1E(T_1)$ transition. From the wave functions¹² for $^1E(T_1)$ (Table I), we find that the transition results from promotion of an electron from the degenerate d_{xz} , d_{yz} set to primarily the d_{z^2} orbital. In this case, the Slater determinant representing the $^1E(T_1)$ eigenstate does not contain the pure one-electron d_{z^2} orbital but instead contains a linear combination of d_{z^2} and $d_{x^2-y^2}$. However, in this and all other eigenfunctions considered in this paper, one of the linear coefficients is larger than the other and the function corresponding to the largest coefficient dominates. In this case the relative probability of finding the electron in the d_{z^2} orbital compared to that of finding it in the $d_{x^2-y^2}$ orbital is $3/4:1/4 = 3:1$. Thus, the $^1A_1 \rightarrow ^1E(T_1)$ transition will be considered to arise mainly from a d_{xz} , $d_{yz} \rightarrow d_{z^2}$ one-electron transition. If the axial ligand has filled π orbitals, the loss of electron density from the (π antibonding) d_{xz} , d_{yz} pair will result in a strengthening of the π bonding in the z direction. Increase of electron density in the σ -antibonding d_{z^2} orbital weakens the σ bonding in the z direction. The net effect on the bonding will depend on the relative strengths of the σ and π interactions of the ligand since the σ weakening and π strengthening oppose each other in this case. It is expected that for most ligands the σ effect will dominate. The results of the analysis for all of the low-lying ligand field transitions are given in Table II. In the above analysis only the z axis was considered when discussing changes in π bonding arising from the metal d_{xz} and d_{yz} orbitals. In

Table I. Wave Functions for a d^6 Configuration^{a,b}

A_1	$(d^2_{xy})(d^2_{xz})(d^2_{yz})$
$E(T_{1g})$	$\frac{\sqrt{3}}{2}(d^2_{xy}d^2_{xz}d^1_{yz}d^1_{z^2}) + \frac{1}{2}(d^2_{xy}d^2_{xz}d^1_{yz}d^1_{x^2-y^2})$ $\frac{\sqrt{3}}{2}(d^2_{xy}d^1_{xz}d^2_{yz}d^1_{z^2}) + \frac{1}{2}(d^2_{xy}d^1_{xz}d^1_{yz}d^1_{x^2-y^2})$
$A_1(T_{1g})$	$(d^1_{xy}d^2_{xz}d^2_{yz}d^1_{x^2-y^2})$
$E(T_{2g})$	$-\frac{1}{2}(d^2_{xy}d^2_{xz}d^1_{yz}d^1_{z^2}) + \frac{\sqrt{3}}{2}(d^2_{xy}d^2_{xz}d^1_{yz}d^1_{x^2-y^2})$ $-\frac{1}{2}(d^2_{xy}d^1_{xz}d^2_{yz}d^1_{z^2}) + \frac{\sqrt{3}}{2}(d^2_{xy}d^1_{xz}d^2_{yz}d^1_{x^2-y^2})$
$B_2(T_{2g})$	$(d^1_{xy}d^2_{xz}d^2_{yz}d^1_{z^2})$

^a From ref 12. ^b The spatial orbitals occurring in the wavefunctions representing singlet and triplet states are the same.

Table II. Changes in Bonding Resulting from Spin-Allowed and Spin-Forbidden Transitions

State	Change in electron density ^a	Axis strengthened or weakened
$^1E(^1T_1)$ and $^3E(^3T_1)$	$+\sigma^*_z$ $-\pi^*_{xz,yz}$	Weaker z Stronger z
$^1A_2(^1T_1)$ and $^3A_2(^3T_1)$	$+\sigma^*_{x^2-y^2}$ $-\pi^*_{xy}$	Weaker xy Stronger xy
$^1B_2(^1T_2)$ and $^3B_2(^3T_2)$	$+\sigma^*_z$ $-\pi^*_{xy}$	Weaker z Stronger xy
$^1E(^1T_2)$ and $^3E(^3T_2)$	$+\sigma^*_{x^2-y^2}$ $-\pi^*_{xz,yz}$	Weaker xy Stronger xy

^a Compared to ground state. A plus sign means gain of electron density; a minus means loss. σ and π refer to the type of bonding affected. The subscript refers to the d orbital involved.

general, the other axes should be considered as well. However, in most of the photochemical studies of d^6 metal complexes the equatorial ligands have been those which form only σ bonds allowing π bonding to be neglected along all axes but the z axis. Furthermore, when the weak-field axis is the z axis, the photochemical action takes place along that axis and subtle π changes along the other axes are photochemically unimportant.

In the limit of octahedral geometry the T states are not split. Examination of the wavefunctions reveals that all axes in the molecule are affected equally when the T states of an octahedral complex are populated. The bonding changes caused by irradiating the excited states of an octahedral complex are nondirectional as expected.

Predictions of the Photoreactions

The photoreactions of a complex can be predicted using the considerations of the previous two sections if the photoactive excited state can be identified. In this section we apply the fundamental postulate of our model—the *lowest excited energy level of a given multiplicity will be the dominant photoactive level of that multiplicity*³—in order to predict which axis of the complex will be labilized. Molecular orbital theory will then be applied to predict the relative amounts of labilization for ligands on the labilized axis. Trends in quantum yields for ligand replacement in a series of complexes may be inferred from the model by considering trends in the amount of ligand labilization. Other processes which are known to affect the quantum yields (such as medium effects, ligand charge and geometry, and photophysical processes) are not explicitly included. The relationship of the model to the overall measured photoreaction has been discussed.¹³ The model's simple but direct correlation of bonding properties with photoreac-

tions is surprisingly successful, implying that perhaps the effects of the competing processes mentioned above are relatively constant in a series of similar complexes and that the bonding changes are dominant.

The lowest singlet excited state of a d^6 configuration will be $^1T_{1g}$ under O_h symmetry and 1E under D_{4h} or C_{4v} symmetry when the unique axis is the weak-field axis (*i.e.*, $Dt > 0$).¹¹ The lowest triplet state will be $^3T_{1g}$ under O_h symmetry and 3E under D_{4h} or C_{4v} with $Dt > 0$. Using Table II we predict that the weak Z axis should always be the labilized axis for d^6 complexes with $Dt > 0$. This prediction is in complete accord with experiment (*vide infra*). It is of interest that the model predicts a concomitant π -bond strengthening along the Z axis for ligands with filled π orbitals. Thus, in the case of C_{4v} symmetry where the Z axis contains one strong π -donor ligand and a second one which does not have π -bonding capability (*e.g.*, NH_3), the π strengthening resulting from excitation might stabilize the π -donor ligand relative to the non- π -bonding ligand. Since σ bonding is in general stronger than π bonding, the π effects discussed here are subordinate to labilizations caused by populating the σ -antibonding orbitals. Although the π effects do not determine the photoreactions, they prove to be important in determining the relative quantum yields in a series of complexes.

When two different ligands comprise the labilized axis, the identity of the one which will be lost during the photoreaction can be predicted using simple molecular orbital theory. The MO diagram for atoms along the labilized axis is shown in Figure 3. The energy of the lowest unoccupied MO, $E(\psi_3)$, is always greater than the energy of the most stable ligand donor orbital, $E(\psi_G)$.¹⁴ The degree to which one ligand is preferentially labilized over the other depends upon two related factors: the difference in energy between the two ligand donor orbitals and the difference in energy between $E(\psi_3)$ and the ligand energies $E(\psi_G)$ and $E(\psi_L)$. The importance of the first factor is most easily shown when $E(\psi_G) = E(\psi_L)$. In this case both ligands will be labilized identically. The greater the energy difference between $E(\psi_G)$ and $E(\psi_L)$, the greater the degree to which the bond between the metal and the lowest is preferentially labilized compared to that between the metal and the highest. The second case is illustrated by the following examples. When $E(\psi_G) < E_3 < E(\psi_L)$, the bond between the metal and the least stable ligand is strengthened while the other bond is weakened. When $E(\psi_3) \gg E(\psi_L) > E(\psi_G)$, both bonds are labilized. The greater the energy of ψ_3 compared to G and L , the smaller the difference between the amount of labilization of the two bonds. The latter case is most likely to occur when the metal orbitals are low in energy and the mixing of ligand and metal orbitals is very great such that the bonding orbitals are very stable and the antibonding orbitals greatly destabilized (*vide infra*). Trends in the relative values of $E(\psi_G)$, $E(\psi_L)$, and $E(\psi_3)$ are easily ascertained using published VSIP's^{15,16} and the spectrochemical series.

Application of the Model to Cobalt(III)

The photochemical behavior of cobalt(III) complexes consists primarily of photoinduced reduction to cobalt(II).⁵

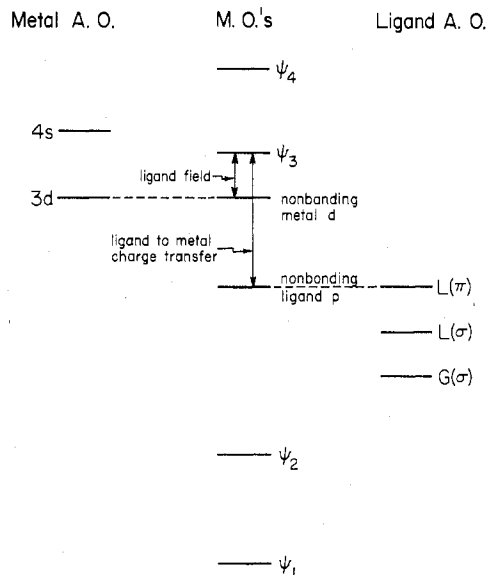


Figure 3. Approximate MO diagram for σ interactions along the unique axis. $G(\sigma)$ and $L(\sigma)$ are ligand σ -donor orbitals of appropriate symmetry. $L(\pi)$ represents a nonbonding ligand p orbital of π symmetry. See text for details.

Because complexes of the reduced metal are kinetically labile and rapidly exchange ligands in solution,¹⁷ characterization of the primary photoproduct by conventional means is difficult. Photoredox reactions have been shown to occur with high quantum yields when charge-transfer bands are irradiated although reduction may also occur when ligand field absorptions are irradiated. The qualitative features of the photoreactions arising from irradiating charge-transfer bands are easily understood in terms of our model. The lowest energy ligand to metal charge-transfer (LTMCT) transition involves promotion of an electron from the highest filled molecular orbital which is mainly ligand in character to the lowest unfilled antibonding orbital primarily metal in character.^{18,19} In the case of C_{4v} and D_{4h} complexes when the unique axis is the weak axis, the lowest energy empty metal orbital is ψ_3 which is primarily d_{z^2} in character. Assuming as before that the lowest energy charge-transfer excited state is the dominant photoactive charge-transfer state, we predict that one of the consequences of excitation to charge-transfer states will be a general weakening of the bonds along the z axis. The molecular orbital theory of ligand labilization presented in this paper may be applied in the usual manner. However, the overall reaction cannot be treated as simply because the transfer of charge may drastically change the properties of both the metal and the ligand (*vide infra*).

In the specific case of the monoacidopentaammine complexes of cobalt(III), the lowest energy LTMCT transition involves excitation of an electron from a p orbital of π symmetry localized primarily on the acido group to the antibonding ψ_3 MO.¹⁹ Thus the model predicts that the predominant primary photoreaction of the above complexes should be either oxidation of the acido group, solvation of one of the ligands on the z axis, or both.

Photoinduced ligand replacement occurs with low quantum yield when ligand field and/or charge-transfer absorp-

(14) This result was proven in ref 3 using the Hylleraas-Undheim theorem: E. Hylleraas and B. Undheim, *Z. Phys.*, **65**, 759 (1930).

(15) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

(16) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1964, pp 120-122.

(17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967.

(18) (a) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, Chapter 8; (b) *Prog. Inorg. Chem.*, **12**, 101 (1970).

(19) H. Yamatera, *J. Inorg. Nucl. Chem.*, **15**, 50 (1960).

tion bands are irradiated. The origin of the bond labilization leading to ligand replacement reactions is clouded in cobalt(III) complexes since the competing redox processes discussed above may occur in addition to the labilization caused by populating antibonding orbitals. Even when net ligand replacement is observed with no net reduction of the metal, an instantaneous charge-transfer species may have been formed which reacts *via* heterolytic bond breaking to give products indistinguishable from those formed in nonredox ligand replacement reactions. The ligand which is photolabilized by a mechanism of instantaneous LTMCT followed by heterolytic bond breaking would be expected to be the ligand from which the charge originates. In the molecular orbital model, the orbitals of the ligand which loses charge are lowered in energy and the d orbitals of the metal are raised in energy. The bond between the reduced metal and the oxidized ligand is thus strongly weakened since ψ_3 represents stronger destabilization of the bond as the ligand's energy drops lower. In some cases the energy of the oxidized ligand may drop lower than that of the other ligand on the same axis although the reverse ordering was found in the ground state. For example, if the oxidized ligand is chloride and the other ligand on the axis is ammonia, charge transfer from the chloride to the metal may cause the energy of the chlorine donor orbital to drop below that of the ammine. Using the molecular orbital arguments discussed previously, the chlorine is predicted to be preferentially aquated in the new, charge-transferred configuration. In general, *the charge-transfer mechanism will lead to increased labilization of the ligand which primarily provides the charge*. Labilization of the oxidized ligand is also expected because (a) the excitation energy is concentrated between the metal and the oxidized ligand rather than in the MO involving the metal d_{z^2} orbital and the two ligands on the z axis and (b) the Lewis basicity of a ligand is decreased as the formal positive charge on the ligand is increased. We show below that the axis which is labilized when ligand field bands are irradiated may be predicted using the antibonding approach. However, the possibility of charge transfer must always be considered, especially when quantum yields are analyzed.

The mono- and trans-disubstituted complexes of cobalt(III) which have been photochemically studied and which undergo ligand replacement reactions are tabulated in Table III. In all of the examples in Table III the 3E and 1E states are respectively the lowest excited triplet and singlet states (*vide supra*). The labilized axis is thus predicted to be the z axis (Table II) in accord with experiment. The labilized ligand on the z axis is not in general the one whose donor orbital lies lowest but instead appears to be in general the one with the weakest metal-ligand bond. As discussed previously, the preferential weakening of one of the metal-ligand bonds compared to that of the other on the same axis is decreased the higher the energy of the ψ_3 antibonding orbital. Thus, in the case of cobalt(III) where the metal d orbitals are low in energy (compared to chromium, for example) and there is strong metal ligand interaction, $E(\psi_3) > E(\psi_G)$ and the difference between the M-G and M-L bond weakening is smaller than that for chromium(III). The metal-weak ligand bond remains the weakest resulting in aquation of the weak ligand. This process may be considered to be a photocatalyzed thermal reaction since no reversals of relative bond strength in the excited state compared to the ground state occur. If the ligand replacement reaction proceeds *via* a mechanism involving electron transfer followed by heterolytic bond breaking, the excitation

energy will be concentrated in the bond between the metal and the most easily oxidized ligand and the most easily oxidized ligand on the labilized axis will be the most reactive. Support for this explanation is found in monohalo-pentaammine complexes where the quantum yield of aquation increases in the order $F < Cl < Br$ (in opposition to the order predicted without considering charge transfer, *vide infra*) and iodide exhibits only redox. From the above discussion it is clear that the lowest energy triplet and singlet states govern the reaction axis but that factors in addition to the nature of the MO along the z axis may influence the ligand labilization.

The qualitative predictions of this section are most clearly illustrated by the behavior of *trans*-chlorothiocyanato-bis(ethylenediamine)cobalt(III) studied in detail by Adamson in 1970.²⁰ In this system the weak-field z axis is the one containing the anions. The energy of the σ -donor orbital of NCS^- lies lower than that of Cl^- . The result of ligand field irradiation predicted by the above arguments should be solvation with a larger quantum yield for loss of NCS^- than for Cl^- although discrimination between the two should not be large. The observed ratio of thiocyanate to chloride aquation was 1.6. Irradiating the lowest charge-transfer transition should lead to a mixture of redox and aquation (observed: 66% reduction to Co^{2+} and 34% aquation). The ratio of quantum yields should be 1.6 if only the MO mechanism is involved but should increase if the oxidizing abilities of the ligands are important since the π orbitals of thiocyanide are higher in energy than the 3p orbital of chloride (IP of nitrogen 2p is $106 \times 10^3 \text{ cm}^{-1}$; IP of chlorine 3p is $111 \times 10^3 \text{ cm}^{-1}$). The observed ratio of 6.3 implies that the latter mechanism is reinforcing the former.

Prediction of the relative quantum yields of a series of complexes is complicated by the possibility of redox reactions and the experimental uncertainties in measuring such small reactivity. The predictions will not be discussed in detail here but will be deferred until the next section where they are compared with photoreactions of rhodium(III).

Application of the Model to Rhodium(III)

Irradiation of rhodium(III) complexes in the d-d bands leads to high quantum yields of ligand replacement reactions. In contrast, irradiation of the charge-transfer bands leads to lower product yields but does not lead to net oxidation or reduction reactions.²¹ The striking differences between cobalt and rhodium photochemistry have been recently discussed²¹ in terms of inefficient internal conversion from charge transfer to d-d excited state manifolds in rhodium compared to cobalt. In terms of MO theory, the trend toward increased photoreduction should increase as the metal d orbital energies decrease and the ligand orbital energies increase. Using ionization potentials as a zeroth-order approximation to the metal d orbital energies, cobalt (IP = 7.9 eV) would be expected to undergo photoredox reactions more readily than rhodium (IP = 7.7 eV). Both the MO and internal conversion explanations are undoubtedly important. Because of the decreased importance of redox processes in the photochemical behavior of rhodium compared to cobalt, our model is more directly applicable to rhodium than it is to cobalt.

The predictions of the photoreactions may be simply made. The axis which is labilized is easily predicted using Table I. In all of the complexes having D_{4h} or C_{4v} symmetry

(20) A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **74**, 67 (1970).

(21) T. L. Kelley and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 1797 (1972).

Table III. Experimental Quantum Yields of Ligand Aquation for Cobalt Complexes having C_{4v} or D_{4h} Site Symmetry

Complex	Wavelength irradiated, Å	Ligand aquated ^a	Quantum yield	Ref
Co(NH ₃) ₅ F ²⁺	4880	NH ₃	7.82 × 10 ⁻⁴	b
		F ⁻	1.31 × 10 ⁻⁴	b
Co(NH ₃) ₅ Cl ²⁺	3700	Cl ⁻	1.1 × 10 ⁻²	c
		Cl ⁻	1.5 × 10 ⁻³	c
Co(NH ₃) ₅ Br ²⁺	4100	Br ⁻	6.9 × 10 ⁻²	c
		Br ⁻	2.0 × 10 ⁻³	c
		Br ⁻	1.0 × 10 ⁻³	c
Co(NH ₃) ₅ I ²⁺		Redox only		c
Co(NH ₃) ₅ (NCS) ²⁺	3700	NCS ⁻	1.5 × 10 ⁻²	c
		NCS ⁻	5.4 × 10 ⁻⁴	c
Co(NH ₃) ₅ N ₃ ²⁺	2537	NH ₃	2.5 × 10 ⁻¹	d
<i>trans</i> -Co(NH ₃) ₄ (N ₃) ₂ ⁺	2537		3.6 × 10 ⁻¹	d
Co(NH ₃) ₄ (H ₂ O)(N ₃) ²⁺	2537		2.5 × 10 ⁻¹	d
<i>trans</i> -Co(en) ₂ Cl ₂ ⁺	2540		10 ⁻²	5
		Cl ⁻	10 ⁻²	5
<i>trans</i> -Co(en) ₂ Br ₂ ⁺	3700	Br ⁻	6.3 × 10 ⁻²	6
		Br ⁻	6 × 10 ⁻⁴	6
<i>trans</i> -Co(en) ₂ (H ₂ O)(Cl) ²⁺	2540	Cl ⁻	10 ⁻²	5
		Cl ⁻	10 ⁻²	5
<i>trans</i> -Co(en) ₂ (NCS)Cl ⁺	3300-3900	Cl ⁻	9.4 × 10 ⁻¹	19
		NCS ⁻	1.01	19
Co(CN) ₅ Cl ³⁻	3700	Cl ⁻	2.5 × 10 ⁻¹	e, 5
Co(CN) ₅ Br ³⁻	3700	Br ⁻	6.9 × 10 ⁻¹	e, 5
Co(CN) ₅ I ³⁻	3800	I ⁻	1.7 × 10 ⁻¹	5
		I ⁻	1.7 × 10 ⁻¹	5
		I ⁻	6.7 × 10 ⁻¹	5

^a The possibility of ammonia aquation was not considered in many of the studies. In many cases no attempt was apparently made to look for released ammonia. It is possible that ammine aquation was not detected due to the extremely low overall quantum yield. ^b A. W. Adamson, Abstracts, 14th International Conference on Coordination Chemistry, Toronto, 1972. ^c A. W. Adamson, *Discuss. Faraday Soc.*, **29**, 163 (1960). ^d J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, **74**, 1021 (1970). ^e A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, **80**, 3865 (1958); *J. Inorg. Nucl. Chem.*, **8**, 209 (1958).

whose photochemical behavior has been studied, the weak-field axis is labilized as predicted. The known photoreactions of rhodium are tabulated in Table IV.

The prediction of the identity of the ligand on the labilized axis which is replaced during the photoreaction is dependent on the relative energies of the ligand AO's and the antibonding ψ_3 MO. When the energies of the two ligand AO's are close (e.g., NH₃ and Cl⁻), the difference between the amount of labilization in the Rh-N and Rh-Cl bonds is expected to be small. Evidently the weakest of the two metal-ligand bonds (Rh-Cl) remains weakest and is preferentially aquated. When the energy difference is greater (e.g., NH₃ and I⁻) the ligand with the lowest AO energy (NH₃) is labilized to a much greater extent and is preferentially aquated. Such behavior intermediate between that of cobalt where the weak ligand is usually labilized and chromium where the strong ligand is usually labilized is expected since the metal d-orbital energy of rhodium (IP = 7.7 eV) lies between that of cobalt (IP = 7.9 eV) and chromium (IP = 6.8 eV). A test of the theory would be provided by the bromo complex. The predicted behavior is preferential aquation of the ammonia but with increased halide aquation compared to chloride.

The relative quantum yields of photoaquation in a series of complexes may be predicted by considering the relative populations of the excited states and by assuming that the lifetimes of the active states are similar in the series.³ Only the lowest excited states govern the reaction because they are the most highly populated. However, other excited states may also be populated (although their effects will be much smaller since internal conversion rapidly transfers their energy to the lowest state). The relative populations of the states will then determine the relative quantum yields if all else remains constant. The model cannot yet be used to predict absolute quantum yields but it can predict an order of quantum yields for a series of complexes of a metal

Table IV. Experimental Quantum Yields of Ligand Aquation for Rhodium Complexes having C_{4v} or D_{4h} Site Symmetry

Complex	Wavelength irradiated, Å	Ligand aquated	Quantum yield	Ref
Rh(NH ₃) ₅ Cl ²⁺	2540	Cl ⁻	1.1 × 10 ⁻¹	5
	3500	Cl ⁻	1.6 × 10 ⁻¹	b
	3500	NH ₃	< 10 ⁻³	b
	3650	Cl ⁻	1.4 × 10 ⁻¹	5
Rh(NH ₃) ₅ Br ²⁺	3600	Br ⁻	1.9 × 10 ⁻²	5
	3600	NH ₃	1.8 × 10 ⁻¹	5
Rh(NH ₃) ₅ I ²⁺	3850	I ⁻	10 ⁻²	b
	3850	NH ₃	8.2 × 10 ⁻¹	b, 21
	4200	NH ₃	8.7 × 10 ⁻¹	21
	4700	NH ₃	8.5 × 10 ⁻¹	21
<i>trans</i> -Rh(NH ₃) ₄ I ₂ ⁺	4700	I ⁻	4.8 × 10 ⁻¹	21
<i>trans</i> -Rh(en) ₂ Cl ₂ ⁺	a	Cl ⁻		c
<i>trans</i> -Rh(en) ₂ Br ₂ ⁺	a	Br ⁻		c
<i>trans</i> -Rh(en) ₂ I ₂ ⁺	a	I ⁻		c

^a A Vycor-filtered GEU A11 1200-W lamp was used. ^b T. L. Kelly and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 278 (1972). ^c R. A. Bauer and F. Basolo, *J. Amer. Chem. Soc.*, **90**, 2437 (1968).

when one ligand is varied under similar experimental conditions.

The lowest energy excited state is always ³E(³T₁) when $Dt > 0$. The next lowest state of the same multiplicity is ³A(³T₁) in group 1 or ³E(³T₂) in group 2. The crossover of the latter two states occurs when $8B + 2Ds - 2s^2/4Dt = 0$. If we consider the second lowest state to be the second most important in governing the photoreactions, the quantum yield for aquation along the labilized axis will be largest when the effect of the second lowest state reinforces the first and smallest when the states oppose each other. From Table I the ³A(³T₁) state opposes ³E(³T₁) through both the σ and π bonding while ³E(³T₂) opposes ³E(³T₁) through σ and reinforces it through π . When Ds is constant, weakening the axial ligand increases Dt causing the energy difference

between ${}^3E(T_1)$ and all other levels to increase. When Dt is constant, decreasing Ds causes ${}^3E({}^3T_2)$ to move closer to ${}^3E({}^3T_1)$ but leaves the separation between the latter and 3A unchanged. On the basis of the above theoretical analysis, the dominant parameter affecting the quantum yield in a series of complexes will be Dt except when strongly π -interacting ligands are present. In the latter case, changes in Ds must also be considered. When changes in Dt are dominant, the larger Dt the greater the quantum yield for aquation along the z axis.

The analysis for the singlet states is simplified by the fact that no levels can cross with the common ligands. Hence the only important parameter affecting the quantum yield is Dt . The larger Dt the greater the quantum yield.

The parameter Dt is expected to be positive for weak axial ligands. The parameter Ds may be either positive or negative. When $Dt > 0$, Ds will always be negative when the axial ligand is a stronger π donor than the in-plane ligands. The general trend for Ds is that it becomes a larger negative number as the π -donor ability of the axial ligands increases over that of the in-plane ligands. Reasonable median values of the parameters for monoacidoammine complexes of rhodium(III) are $B \cong +350 \text{ cm}^{-1}$, $Ds \cong \pm 200 \text{ cm}^{-1}$, $Dt \cong +300 \text{ cm}^{-1}$.

Only a few studies have been made on which our predictions may be checked. For complexes of the form $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$, our model predicts that (a) the total labilization (represented by the sum of the quantum yields of aquation for ligands on the z axis) will decrease as the ligand field strength of the unique axis approaches that of the other axes (*i.e.*, as Dt decreases) and (b) the quantum yield of aquation of the amine will decrease and that of X^- will increase as the energy of the donor orbital of X^- decreases and approaches that of the amine. Prediction (a) can only be tested against the experimental results shown in Table IV if it is assumed that the photolabilization of ligands not mentioned is negligible. Using the above assumption, it is seen that the total quantum yield decreases in the order $\text{Rh}(\text{NH}_3)_5\text{I}^{2+} > \text{Rh}(\text{NH}_3)_5\text{Br}^{2+} > \text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ as predicted on the basis of the decreasing value of Dt . Prediction (b) is also fulfilled (Table IV) since the energies of the halide donor orbitals approach that of the amine in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$. However, charge and π -bonding effects may also be involved since we are comparing aquation of the charged, π -bonded chloride with the uncharged σ -bonded ammonia.

Of equal interest is the trend in pairs of the type $\text{RhL}_5\text{X}^{2+}$ to $\text{trans RhL}_4\text{X}_2^+$. Here the effects of π bonding and Ds may become dominant, particularly if a crossover of levels occurs. Using $B = 400 \text{ cm}^{-1}$ (the value found in $\text{Rh}(\text{NH}_3)_6^{3+}$) and $Dt = 300 \text{ cm}^{-1}$ (calculated from the spectrum of $\text{Rh}(\text{NH}_3)_4\text{I}_2^{2+}$), ${}^3E({}^3T_2)$ lies lower than ${}^3A({}^3T_1)$

when $Ds < -50 \text{ cm}^{-1}$. This value is very reasonable since I^- is a good π donor. The increasing population of the ${}^3E({}^3T_2)$ state increases the π stabilization along the z axis and stabilizes ligands along that axis which have π metal-ligand interactions. The π effect (through Ds) opposes the effect of increasing Dt . Since the quantum yield of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ is greater than that of $\text{Rh}(\text{NH}_3)_4\text{I}_2^+$ and since the aquated ligand is respectively NH_3 and I^- (σ and π , respectively), the π effect apparently dominates. Again the difference in charge may also affect the quantum yields and account for part of the difference. Experiments involving axial ligands with the same charge are in progress to test the importance of π bonding *vs.* charge.

The previously puzzling observation that the quantum yield for Cl^- aquation of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ increased with increasing wavelength²² is easily explained by our model. The long-wavelength irradiation populates the ${}^3E({}^3T_1)$ and ${}^1E({}^1T_1)$ states directly while shorter wavelength irradiation populates other states as well. Since the states immediately above the ${}^3E({}^3T_{1g})$ and ${}^1E({}^1T_{1g})$ states oppose the labilization, the quantum yield is lower for the higher energy irradiations.

From the above discussion it is clear that the photochemistry of d^6 complexes is complicated by effects not present in chromium(III) complexes. In the latter metal the labilizations were completely predictable from an analysis of the antibonding properties of the excited states. In the d^6 complexes, particularly cobalt(III), the low energy of the metal d orbitals lessens the preferential labilization of one ligand over another on the labilized axis and causes metal photoreduction reactions readily to occur. By incorporating metal and ligand orbital energies into the model, the photoreactions and relative quantum yields may be understood and predicted in a systematic and simple fashion.²³

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(23) Note Added in Proof. In this paper we have deduced the relative quantum yields in a series of complexes on the basis of the relative populations of the lowest excited states. Subsequent to acceptance of this work, we have shown that the fractional composition of the lowest excited state varies in a regular manner when configuration interaction is included (J. I. Zink, manuscript submitted). In the case of the d^6 complexes, the relative d_{z^2} character of the lowest excited state increases as Dt increases. Thus the correlation between the relative quantum yields and the magnitude of Dt may be better interpreted in terms of the fractional d_{z^2} character in the lowest excited state rather than in terms of the relative populations of the states.