A Model for Predicting the Photoreactions and Relative Quantum Yields of Transition Metal and Organometallic Complexes. I. Chromium(III)

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Abstract: A model based on the antibonding properties of excited electronic states has been developed which correctly predicts the types of photoreactions and relative quantum yields of transition metal compounds. The model is specifically applied to the photochemistry of the extensively studied chromium(III) complexes. Adamson's rules are explained in terms of the bonding changes which occur when the lowest energy doublet and quartet excited states are irradiated. The axis which is labilized is determined solely by the ordering of the excited electronic states. It is proven that the strongest ligand on the labilized axis should always undergo photoreaction. The relative quantum yields for aquation and the results of selectively irradiating the absorption bands are correctly predicted by considering π bonding changes resulting from excitation.

The photochemistry of chromium(III) complexes has been one of the most studied aspects of modern inorganic photochemistry and continues to be one of the areas most actively investigated.[1–5] The photoreaction of octahedral chromium(III) complexes is almost always ligand substitution or racemization.[1] The behavior of mixed ligand complexes upon irradiation is, by comparison, much more complicated. The governing paradigm of photoreaction for complexes possessing lower than octahedral symmetry is embodied in "Adamson's Empirical Rules" first reported in 1967.[6] The rules were stated by Adamson in his classic paper as follows. (Rule 1) Consider the six ligands to lie in pairs at the ends of three mutually perpendicular axes. That axis having the weakest average crystal field will be the one labilized, and the total quantum yield will be about that for an O_h complex of the same average field. (Rule 2) If the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates. These rules have proven valid for almost all complexes studied to date. No serious attempt has been made to systematically justify the rules in terms of excited states, orbitals, or bonding.

Our interest in the photochemical behavior of transition metal complexes arose from our experience in assessing the importance of individual orbitals in the interpretation of covalency in some complexes of nickel[7] and copper.[8] A detailed study of the characteristics of the individual metal orbitals proved invaluable in interpreting nmr and esr parameters. In this paper, a model based on fundamental crystal field and molecular orbital theory is presented which explains the validity of the empirical rules and provides a means of predicting relative quantum yields.

The foundation of the model presented here is the strengthening or weakening of metal–ligand bonds which occurs when an electron is excited from a ground state orbital to an excited state which is bonding or antibonding, respectively. The relationship between the various photoexcitations and the resulting photochemical reactions is governed by (a) the orderings of the energy levels in the complex, (b) the bonding or antibonding properties of the orbitals, and (c) the relative population of the various excited states. In a d^3 complex, both doublet and quartet excited states occur. The role of quartet[6,9,10] and doublet[11,12] states in the photochemistry of chromium(III) complexes has been examined, and in general both types of states have been demonstrated to be photoactive. The splitting of the states caused by the ligand field of octahedral or lower symmetry is an important consideration in the applications of the model. In the following sections of this paper, the splittings, bonding properties, and populations of the states are analyzed in terms of their photochemical implications.

d-Orbital Orderings

The correlation diagram for d^3 complexes is given in Figure 1.[13] The orderings of the levels split under D_{4h} or C_{4v} symmetry depend on the nature of the ligands (*vide infra*). The right side of the diagram represents the splittings for positive values of Dt. Most of the complexes which have been photochemically studied have positive values of Dt. The "g" subscripts which appear with the states on the right side of Figure 1 are valid only under D_{4h} symmetry. Under C_{4v} symmetry the g subscript is dropped. Thus $^4B_{1g}$ and $^4B_1$ are the ground states under D_{4h} and C_{4v} symmetry respectively.

The actual ordering in any particular complex must be determined from polarized single crystal spectra

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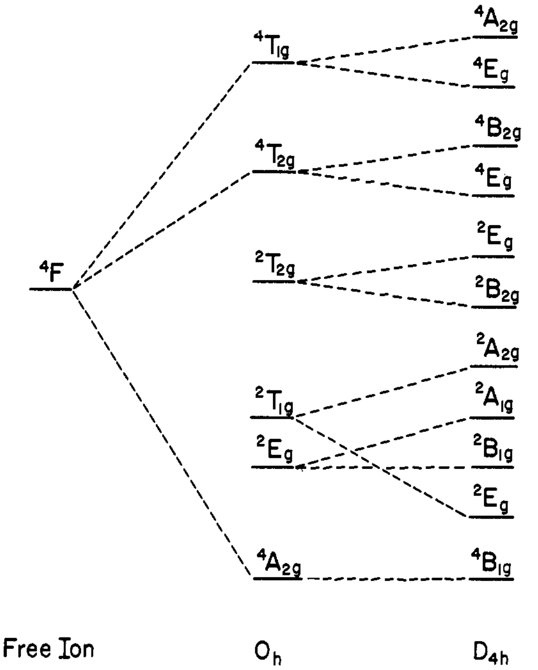

Figure 1. Correlation diagram for the lowest quartet and lowest doublet states of a d^3 configuration.

or by fitting a spectrum calculated from theory to that observed. Both methods have been applied to tetragonal chromium(III) complexes.[14–16] The experimental orderings of the quartet states and the corresponding one-electron energy level orderings are shown in Figure 2. Ordering I arises for complexes with axial ligands weaker than the in-plane ligands but with stronger axial π bonding. Order II is the same as I except that axial π bonding is weak. Order III is that expected when the axial ligand is stronger than the in-plane ligands. The anomalously strong behavior of the fluoride ion in the two complexes in class III has been discussed by Rowley.[16]

In order to discuss the chemical consequences of excitation to the upper quartet energy states, we also need to know the quartet state wave functions. They have been calculated by Ballhausen[17] and are given here for convenience.

$$^4B_{1g}(^4A_{2g}) \quad \theta = |(xz)(yz)(xy)|$$

$$^4B_{2g}(^4T_{2g}) \quad \psi_1 = |(xz)(yz)(x^2 - y^2)|$$

$$^4E_g(^4T_{2g}) \begin{cases} \psi_2 = -(1/2)|(yz)(xy)(x^2 - y^2)| + (\sqrt{3}/2)|(yz)(xy)(z^2)| \\ \psi_3 = -(1/2)|(xy)(xz)(x^2 - y^2)| - (\sqrt{3}/2)|(xy)(xz)(z^2)| \end{cases}$$

$$^4A_{2g}(^4T_{1g}) \quad \phi_1 = |(xz)(yz)(z^2)|$$

$$^4E_g(^4T_{1g}) \begin{cases} \phi_2 = -(1/2)|(yz)(xy)(z^2)| - (\sqrt{3}/2)|(yz)(xy)(x^2 - y^2)| \\ \phi_3 = -(1/2)|(xy)(xz)(z^2)| + (\sqrt{3}/2)|(xy)(xz)(x^2 - y^2)| \end{cases}$$

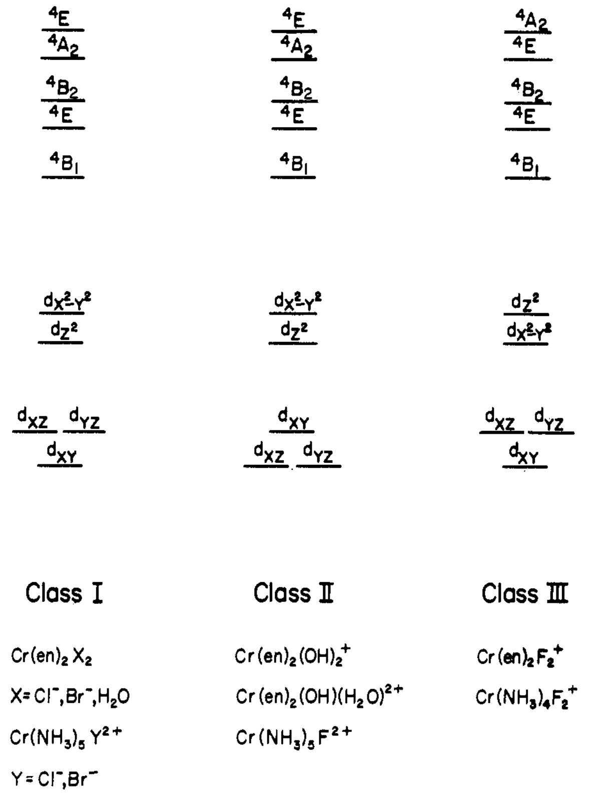

Figure 2. Experimental energy level orderings of the states (top) and the one-electron d orbitals (middle) of some chromium(III) complexes.

The ordering of the lowest doublet states may be derived from the occupancies of the d_{xy}, d_{xz}, and d_{yz} orbitals. In the strong field model, the nine possible configurations may be grouped into five groups of nondegenerate states. They will be referred to by greek letters as follows.

$$\alpha = (d_{xz})^2(d_{yz})^1 \text{ and } (d_{xz})^1(d_{yz})^2$$

$$\beta = (d_{xz})^2(d_{xy})^1 \text{ and } (d_{yz})^2(d_{xy})^1$$

$$\gamma = (d_{xy})^2(d_{xz})^1 \text{ and } (d_{xy})^2(d_{yz})^1$$

$$\delta = (d_{xz})^{\uparrow}(d_{yz})^{\downarrow}(d_{xy})^{\uparrow} \text{ and } (d_{xz})^{\downarrow}(d_{yz})^{\uparrow}(d_{xy})^{\uparrow}$$

$$\epsilon = (d_{xz})^{\uparrow}(d_{yz})^{\uparrow}(d_{xy})^{\downarrow}$$

Linear combinations of the pairs of configurations represented by the Greek letters transform as the following irreducible representations under D_{4h} symmetry: ^2E_g, α; $^2A_{2g}$ and $^2B_{2g}$, β; ^2E_g, γ; $^2A_{1g}$ and $^2B_{1g}$, δ. The ϵ state transforms as $^2B_{1g}$. One of the two B_{1g} states listed above forms part of the $^4B_{1g}$ ground state. The relative energies of the states are $\epsilon < \delta < \gamma < \beta < \alpha$ for cases I and III (where $d_{xy} < d_{yz}$) and $\epsilon < \delta < \alpha < \beta < \gamma$ for case II (where $d_{xz} = d_{yz} < d_{xy}$). The orderings calculated here assume that the pairing energy is greater than the energy difference between d_{xy} and d_{xz}, d_{yz}. This will always be true for chromium(III) since the pairing energy for electrons in Cr(III) d orbitals is 2.7×10^4 cm^{-1} while the maximum splitting is about 4×10^3 cm^{-1}.[18]

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Changes in Bonding When Excited States Are Populated

In an electronic transition, electron density is lost from the ground state and acquired by the excited state. Thus, we may conceptually consider two important changes in the bonding to occur as a result of the transition: (a) the change arising from loss of electron density from the ground state molecular orbital and (b) the change arising from populating an excited state molecular orbital. We will examine in detail the bonding implications of both of the effects for all of the low-lying transitions in chromium(III) complexes.

The ground state of all of the mixed ligand tetragonal complexes considered here ($^4B_1$) consists of one electron in each of the d_{xy}, d_{xz}, and d_{yz} metal orbitals. These three metal orbitals are all of π symmetry. In the molecular orbital (MO) theory, they are part of π bonding and antibonding MO's if the ligand has orbitals of π symmetry which may interact with them. When the π orbitals of the ligands are respectively empty or full, the singly occupied d_{xy}, d_{xz}, and d_{yz} orbitals are part of π bonding or π antibonding MO's, respectively. If no ligand π orbitals are available, the d_{xy}, d_{xz}, and d_{yz} orbitals are nonbonding. In this paper the only π interacting ligands to be discussed will be those with filled π orbitals (π donors). Thus, loss of electron density from the d_{xy}, d_{xz}, and d_{yz} orbitals results in a strengthening of the π bonding in the complex. All spin-allowed transitions result in stronger π bonds. The direction or axis along which the bond is strengthened will be determined by the nature of the excited state (*vide infra*). Transitions to some excited states deplete the d_{xy} orbital, resulting in stronger π bonds in the xy plane, while others deplete the d_{xz} and d_{yz} orbitals, resulting in stronger π bonding in the z direction.

The excited state to which an electron is promoted in the spin-allowed transitions involves the unoccupied $d_{x^2-y^2}$ and d_{z^2} orbitals. In the MO theory, they are part of σ antibonding MO's. If the excited state wave function 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. All spin-allowed transitions will thus result in a weakening of the σ bond between metal and ligand in addition to the π strengthening discussed above.

As an illustration of the analysis of the bonding changes caused by a particular transition, consider $^4B_1 \rightarrow {}^4B_2(^4T_{2g})$. Here the transition clearly involves a promotion of an electron from the d_{xy} to the $d_{x^2-y^2}$ orbital as may be verified from the wave functions θ and ψ_1. The loss of electron density from the d_{xy} orbital increases the π bonding in the xy plane at the same time that the increase in electron density in the $d_{x^2-y^2}$ orbital weakens the σ bonding in the xy plane. In this case, the net overall effect on the bonding will depend on the relative σ and π bonding ability of the in plane ligand since the σ and π effects oppose each other in the xy plane. If the in-plane ligands are ethylenediamine or ammonia, for example, the π bonding in the xy plane is nonexistent to begin with and cannot be strengthened. (In this case the d_{xy} orbital is formally nonbonding.) The net result would be a weakened metal in-plane ligand bond arising from populating the σ antibonding molecular orbital in the xy plane. The analysis for the other spin-allowed transitions is summarized in Table I.

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

State	Change in electron density[a]	Axis strengthened or weakened
$^4E_g(^4T_{1g})$	$+\sigma_{xy}^*$	Weaker xy
	$-\pi_{xz,yz}^*$	Stronger z
$^4A_{2g}$	$+\sigma_z^*$	Weaker z
	$-\pi_{xy}^*$	Stronger xy
$^4B_{2g}$	$+\sigma_{xy}^*$	Weaker xy
	$-\pi_{xy}^*$	Stronger xy
$^4E_g(^4T_{2g})$	$+\sigma_z^*$	Weaker z
	$-\pi_{xz,yz}^*$	Stronger z
$^2\alpha$	$-\pi_{xy}^*$	Stronger xy
	$+\pi_{xz,yz}^*$	Weaker z
$^2\beta$	0	0
$^2\gamma$	$-\pi_{xz,yz}^*$	Stronger z
	$+\pi_{xy}$	Weaker xy
$^2\delta$	0	0
$^2\epsilon$	0	0

[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.

The analysis for spin-forbidden transitions to the lowest doublet states is more complicated because the transitions involve pairing of an electron in one of the d_{xy}, d_{xz}, or d_{yz} orbitals. Such transitions can at most only change the π bonding because no σ orbitals are involved. Three of the transitions, $^4B_1 \rightarrow {}^2\epsilon$, $^4B_1 \rightarrow {}^2\beta$, and $^4B_1 \rightarrow {}^2\delta$ do not change the π bonding at all. The latter statement is most easily illustrated by the $^4B_1 \rightarrow {}^2\delta$ transition which involves only a "spin flip" in one of the orbitals leaving the electron density unchanged. As an example of the former statement that only the π bonding can change, consider the $^4B_1 \rightarrow {}^2\alpha$ transition. Here an electron is transferred from the d_{xy} to the d_{xz} orbital in addition to the change in spin multiplicity. As a result, the π interaction in the xy plane is strengthened and the π interaction in the z direction weakened. The analysis for the other spin-forbidden transitions is summarized in Table I.

Two cautions must be observed when applying the results of this section to photochemical problems. First, in the Slater determinants representing some eigenstates, one-electron functions appear which are not pure d orbitals in the sense that they involve linear combinations of several different d functions. In all cases discussed here, one of the linear coefficients is larger than the other, and the corresponding function may be considered to dominate. Changes in bonding are based on the dominant orbital but will be of less influence in determining the course of a photochemical reaction than those involving "pure" functions. In the limit of octahedral symmetry where, for example, the $d_{x^2-y^2}$ and d_{z^2} orbitals have equal coefficients, no one function dominates and all axes are labilized to the same extent. Ramifications of these considerations are considered later. Second, we have assumed that the d_{xz} and d_{yz} orbitals affect π bonding in the z direction only. This assumption need not be true in general. However, in most of the chromium complexes studied to date, the in-plane ligands can only form σ bonds. Thus, the d_{xz} and d_{yz} orbitals can only affect π bonding on the z axis. In the limit where all of the ligands are equally π bonding, the d_{xz} and d_{yz} orbitals may affect all of the π bonds in the complex and their effect may become nondirectional. However, the d_{xy} orbitals will always involve only the xy plane.

Predictions of the Photoreactions

On the basis of the previous discussion, it is only necessary to know which excited state or states are populated (and retain their population for a time sufficiently long for reaction to occur) in order to predict which ligand axis of the complex will be labilized. Experiment has shown that both the lowest doublet[11,12] and the lowest quartet[6,9,10] states are photoactive when the ligand field bands are irradiated. Nonradiative photophysical processes may allow a state to become populated indirectly by energy transfer even if it was not populated directly by absorption of electromagnetic energy. Such photophysical processes are known to be efficient in complexes of chromium(III). The model takes into account all of the states which may become populated during irradiation of the ligand field bands.

In order to apply the previous considerations, we must make one reasonable assumption: the lowest energy level of a doublet or quartet manifold will be the dominant photoactive level of the manifold.[19,20] For example, consider the ^4E and $^4B_2$ levels arising from the $^4T_{2g}$ level when the symmetry is lowered from O_h to C_{4v}. Since $^4E(^4T_{2g})$ is lower in energy than $^4B_2(^4T_{2g})$ in all three classes of Figure 2, the $^4E(^4T_{2g})$ level will be the most important of the two in determining the photochemical reaction. If all of the complexes had identical orderings of their energy levels, all of the photochemical reactions would be identical. It is the relative orderings of the low-lying excited states which determine the populations which in turn determine the axis labilized (*vide infra*). The magnitude of their separations determines the quantum yields as we will show in the following section.

In complexes of chromium(III), the splitting of the ^4T states may range from 4000 cm^{-1} in a D_{4h} symmetry to 0 cm^{-1} in octahedral symmetry. In the tetragonal complexes considered here with in-plane nitrogen donors and weaker axial ligands, the smallest separation is 1670 cm^{-1}. Since $kT \sim 200$ cm^{-1} at temperatures commonly encountered in solution photochemistry, thermal equilibration among the states would result in almost complete population of the lowest state. The complex is not at thermal equilibrium in an excited state and the above arguments do not rigorously apply. However, the lowest state would be expected to be more highly populated, especially since rapid relaxation can occur between the two *via* spin-orbit coupling.

The results of considering the lowest level of each manifold to be the dominant photoactive level are summarized in Table II. The z axis will always be the axis labilized when energy level orderings I or II occur in the complex and the complex is irradiated with white light. (The results of selectively irradiating specific absorption bands will be considered later.) In class II complexes all three photoactive states result in z axis labilization. In class I complexes, however, two of the three photoactive states result in z axis labilization while the photoactive doublet state labilizes π bonding in the xy plane. Since the σ antibonding orbitals are higher in energy than the π antibonding orbitals, populating the former will have the greatest labilizing effect. Furthermore, as discussed previously, the complexes considered here have no π bonding in the xy plane. Thus z axis labilization is also predicted for class I complexes (but with a smaller quantum yield than for class II; *vide infra*). Orderings I and II encompass all of the complexes studied photochemically except those containing trans difluoro ligands. The prediction of z axis labilization is the same as the prediction of Adamson's first rule. When ordering III occurs the σ effects would weaken all axes equally while the π bonding changes combine to labilize the xy plane and strengthen the z axis. Assuming as before that the π interaction in the xy plane is weak, the strengthening in the z direction is the only significant effect of the π bonding changes. The net result of both σ and π is thus a general weakening of all axes (from σ) and a strengthening of the z axis (from π). Under ordering III, the xy plane will be labilized. A recent photochemical study of *trans*-$Cr(en)_2F_2^{2+}$ supports the prediction.[21] In this complex, the ethylenediamine is labilized rather than the fluorine. The authors claimed that this violated Adamson's rules. However, if "strong field ligand" is redefined in terms of a ligand's effect on the ordering of the orbitals rather than in terms of Dq alone, fluorine is the strong field ligand and Adamson's rules are obeyed. (Ordering III is expected with the strongest ligands on the z axis.) The model presented here correctly predicts which ligand will be aquated solely on the basis of the experimental orbital orderings. One need not be concerned with definitions of ligand strength.

Table II. Predicted Bond Labilizations and Strengthenings during Irradiation of the Three Classes of Chromium(III) Complexes

Class	Level populated	Direction labilized and bonding affected	Direction strengthened (from loss of π^*)
I	$^2\gamma$ (lowest active doublet)	xy (π)	z
	^4E (lowest quartet from $^4T_{2g}$)	z (σ)	z
	$^4A_2$ (lowest quartet from $^4T_{1g}$)	z (σ)	xy
II	$^2\alpha$ (lowest active doublet)	z (π)	xy
	^4E (lowest quartet from $^4T_{2g}$)	z (σ)	z
	$^4A_2$ (lowest quartet from $^4T_{1g}$)	z (σ)	xy
III	$^2\gamma$ (lowest active doublet)	xy (π)	z
	^4E (lowest quartet from $^4T_{2g}$)	z (σ)	z
	^4E (lowest quartet from $^4T_{1g}$)	xy (σ)	z

Adamson's second rule defines which of the two ligands on the labilized axis is lost. The model presented here explains the second rule by focusing attention on the antibonding molecular orbital along the labilized axis.

Consider only the axis labilized. It may be represented as W–Cr–S, where W and S are two ligands with S being the stronger and W the weaker of the two. We define ψ_W, ψ_S, and ψ_{Cr} as the wave functions of appropriate symmetry for bonding for the weak ligand, strong ligand, and chromium, respectively. ψ_W and

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(19) This assumption is very similar to Kasha's rule: M. Kasha, *Discuss. Faraday Soc.*, 9, 14 (1950).

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ψ_s could be ligand atomic orbitals or hybrid orbitals. ψ_{Cr} is the metal d_{z^2} orbital. The three possible molecular orbitals are

$$\phi_b = \alpha\psi_w + \beta\psi_{Cr} + \gamma\psi_s \quad (1)$$

$$\phi_n = a\psi_w + b\psi_{Cr} + c\psi_s \quad (2)$$

$$\phi_a = \alpha'\psi_w + \beta'\psi_{Cr} + \gamma'\psi_s \quad (3)$$

The nodeless ϕ_b molecular orbital is bonding[22] and is filled. ϕ_n has one node. If ligands W and S are identical, $a = c$ and $b = 0$. The orbital is then nonbonding. The secular determinant neglecting ligand–ligand interactions is

$$\det \begin{array}{|ccc|} \psi_w & \psi_{Cr} & \psi_s \\ H_{11} - E & H_{12} & 0 \\ H_{21} & H_{22} - E & H_{23} \\ 0 & H_{32} & H_{33} - E \end{array} = 0 \quad (4)$$

The symbols have their usual meanings. The second root of the determinant, E_2, corresponds to the wave function ϕ_n. If both a and b have the same sign and c has the opposite sign, the wave function ϕ_n represents stabilization between the weak ligand and the metal and destabilization between the strong ligand and the metal. The coefficients of eq 2 may be found from eq 5 and 6.

$$a(H_{11} - E_2) + bH_{12} + 0 = 0 \quad (5)$$

$$0 + bH_{32} + c(H_{33} - E_2) = 0 \quad (6)$$

From (5)

$$a/b = -H_{12}/(H_{11} - E) \quad (7)$$

From (6)

$$b/c = -(H_{33} - E)/H_{32} \quad (8)$$

Since $H_{23} < 0$, we find from (7) and (8) that if $H_{11} > E_2$ and $H_{33} < E_2$, then $a/b > 0$ and $b/c < 0$. This result is satisfying since the energy of the MO should be less than that of the orbital of the weak ligand (corresponding to stabilization of bonding) while it should be higher than that of the orbital of the strong ligand (corresponding to destabilization). According to the Hylleraas–Undheim theorem,[23,24] the second root of a determinant of the general form of (4) will always lie between H_{11} and H_{33}. Thus, within the limitations of neglecting ligand–ligand interactions, ϕ_n always represents metal–weak ligand stabilization and metal–strong ligand destabilization, regardless of the magnitudes of the off-diagonal elements. Strong is defined in this context as the ligand whose Coulomb intergral lies lowest in energy.

The metal 4s orbital has the proper symmetry to mix with the $3d_{z^2}$ orbital. The molecular orbital treatment of the bonding along the z axis including metal 4s character requires a 4 × 4 determinant leading to four MO's. According to the Hylleraas–Undheim theorem, the third root of the 4 × 4 problem, E_3', will always lie between the second and third roots of the 3 × 3 case, E_2 and E_3. Thus $E_3' > H_{33}$ and the wave function corresponding to E_3', ψ_3', will always represent destabilization of the metal–strong ligand bond. In the 4 × 4 problem, E_3' may be higher or lower in energy than H_{11}. If $E_3' < H_{11}$, the metal–weak ligand bond is stabilized, while if $E_3' > H_{11}$, it is destabilized. In both cases the strong ligand is destabilized to a greater extent than the weak ligand. Thus, populating ψ_3' will result in labilization of the strong ligand to the greatest extent. Since ψ_3' is primarily metal d_{z^2} in character, transitions to a crystal field state mainly d_{z^2} in character (*e.g.*, $^4E(^4T_{2g})$) correspond to populating ψ_3' in the MO picture. Hence for class I and II complexes the strongest ligand on the z axis will be preferentially labilized.

In the above discussion, the strong ligand has been assumed to be the one whose Coulomb integral is greatest (*i.e.*, the one having the largest valence state ionization energy). A more quantitative definition of "strong ligand" which may be applied with almost as much intuitive ease as the above definition is given by Mulliken's "magic formula"[25] (eq 9), where D is

$$D = AIS/(1 + S) \quad (9)$$

the bond dissociation energy, A is an empirical factor, I is the average of the valence state ionization energies (VSIE's) of the two atoms forming the bond, and S is their overlap integral. The previously used definition of ligand strength is thus proportional to the more rigorous one when overlap is neglected. In cases where the VSIE's of the two ligands on the labilized axis are similar in magnitude to each other but the overlap integrals are quite different, the signs and magnitudes of the ligand coefficients in the antibonding ψ_3' MO may be strongly dependent on the relative magnitudes of the overlap integrals. In such cases it is more accurate to use the definition of strong ligand provided by eq 9 when the molecular orbital principles discussed above are used to predict which ligand on the z axis will be preferentially labilized.

Adamson's second rule may be explained in a more intuitive fashion by noting that in most cases the weakest ligand on the labilized axis has the greatest π bonding character. Transitions to states which strengthen π bonding in the z direction will thus stabilize the weak ligand. From Table II it is seen that z axis π bonding will be strengthened by some transitions in all three classes. The π stabilizing effect along the labilized axis should be most important in class I complexes since both the lowest active doublet and the lowest quartet strengthen π bonding in the z direction.

Relative Quantum Yields

The relative quantum yields of photoaquation in a series of complexes will depend upon three factors. One of the most important of these is the total effect of all of the intrinsic labilizations arising from all of the photoactive excited states. Under some splitting patterns the intrinsic labilizations arising from different excited states oppose each other while in others the same axis is labilized by all of the excited states. The second and more subtle factor influencing the relative quantum yields is the magnitude of the separations between the levels. The further apart the levels the greater the population of the lowest level resulting in a greater labilizing effect from the one which is lowest.

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(22) The coefficients in eq 1 are all positive and the wave functions are all in phase.

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The two factors are not completely separable since variation of the ligands may change the splitting pattern from one class to another. For example, increasing the π interaction along the z axis changes the splitting pattern from case II to case I. Because the complexes for which data are available fall into the three distinct classes defined earlier, it is convenient to consider the two factors independently. A third and important influence on the quantum yields is the rate of intramolecular energy transfer. Radiationless deactivation and luminescence can compete with the bond labilizations and drastically affect the quantum yields of chemical reaction. In the discussion which follows the predictions of the model will be examined assuming that the rates of energy transfer processes are similar in series of similar complexes. If the rates were known they could be incorporated directly into the model leading to a quantitative theory. In the absence of rate data for photophysical processes, accurate qualitative predictions of relative quantum yields may be made (*vide infra*) as long as the above assumption is kept in mind. In this section we will examine the effects of (a) class, (b) π bonding variations in a class, and (c) selective irradiation on the relative quantum yields.

The total intrinsic labilization arising from all photoactive excited states clearly requires that class II complexes have a larger quantum yield than those of class I when π interacting ligands are involved in the photoreaction and all bands are irradiated. Comparison of class I and II in Table II illustrates this result. All three of the active levels of class II complexes cause labilization of the z axis with only one of them strengthening the π bonding in the z direction. Class I complexes, on the other hand, will have the z axis labilized by two out of the three levels but also will have two transitions which strengthen the π bonds in the z direction in opposition to the net result. The difference in quantum yields predicted above should be greatest when the aquated ligand has π bonding ability. All complexes for which both the experimental energy level orderings and quantum yields of aquation have been measured support the above predictions. The quantum yields of class II complexes $Cr(en)_2(OH)_2^+$ (ϕ = 0.10) and $Cr(en)_2(OH)(H_2O)^{2+}$ (ϕ = 0.30–0.40) are both much greater than that of class I complex $Cr(en)_2(H_2O)_2^{3+}$ (ϕ = 0.04).[6] It would be of great interest to compare the quantum yields of class I molecules $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5Br^{2+}$ with that of class II molecule $Cr(NH_3)_5F^{2+}$ if the latter were available. We have not attempted to compare class III molecules with the other two classes. Class III is a unique case since two axes are labilized *via* a molecular orbital involving the metal $d_{x^2-y^2}$ atomic orbital.

The relative separations of the energy levels will influence the quantum yields of a series of complexes *within the same class.* The differences between classes I and II arise because the doublet energy levels cross each other to give different orderings. For example, as we go from class II (weak axial π bonding) to class I (strong axial π bonding), the d_{xy} orbital drops from a position higher in energy than the d_{xz} and d_{yz} orbitals to a position lower in energy. The crossover point marks the formal distinction between classes. The quantum yield of complexes in class II is greater than that of those in class I because the labilizing effect of the active doublet reinforces that of the quartet in the former class. We thus expect that an increase in the π donor ability of the axial ligand would cause a decrease in the quantum yield. Examination of all of the series of complexes studied in which only the axial ligand is varied reveals that experiment supports our prediction. Table III summarizes the experimental results.

Table III. Experimental Quantum Yields[a,b]

Complex	Ligand aquated	Band irradiated[c]	Quantum yield	ϕ_σ/ϕ_π[d]
$Cr(NH_3)_5H_2O^{3+}$	NH_3	Q_1, Q_2	0.20	
		Q_1	0.15	
$Cr(NH_3)_5Br^{2+}$	NH_3	Q_1	0.35	40
		Q_2	0.35	32
	Br^-	Q_1	0.0087	
		Q_2	0.011	
$Cr(NH_3)_5Cl^{2+}$	NH_3	Q_1	0.36	9
		Q_2	0.38, 0.35	7
	Cl^-	Q_1	0.04	
		Q_2	0.007, 0.05	
$Cr(NH_3)_5NCS^{2+}$	NH_3	Q_1	0.48	23
		Q_2	0.46	15
		D	0.15	8
	NCS^-	Q_1	0.021	
		Q_2	0.030	
		D	0.018	
$Cr(en)_2(OH)_2^+$	I[f]	Q_1[e]	0.003	
$Cr(en)_2(H_2O)(OH)^{2+}$	I[f]	Q_1[e]	0.3	
		Q_2[e]	0.4	
		D[e]	0.05	
$Cr(en)_2(H_2O)_2^{3+}$	I[f]	Q_1, Q_2[e]	0.04	
$Cr(en)_2Cl_2^+$	Cl^-[g]	Q_1	0.32	
	Cl^-[g]	Q_2	0.32, 0.35	

[a] Taken from ref 1, pp 96–99. All disubstituted complexes are trans. [b] The first four complexes are arranged in order of decreasing π donor strength along the unique axis. [c] Q_1 = lowest energy spin-allowed absorption ($^4T_{2g}$), Q_2 = second lowest energy spin-allowed absorption band ($^4T_{1g}$), and D = lowest energy doublet band. [d] See text for details. [e] Reference 6. [f] I = isomerization. [g] Reference 26.

The physical reason for the observed trends in quantum yields lies in the relative populations of the states. As an illustration, consider the class I molecules in Table III. As the π bonding ability of the ligands decreases, the separation between the d_{xy} orbital and the degenerate d_{xz} and d_{yz} orbitals decreases. When the doublet states are populated (directly or indirectly), the decrease in energy between the $^2\gamma$ and $^2\alpha$ states results in a decrease in the population difference between them with the $^2\gamma$ state losing electron density as the $^2\alpha$ state gains. From Table I, populating the $^2\alpha$ state results in labilization of the z axis. Thus, as the energy separation decreases, the z axis labilization from the doublet state increasingly reinforces the labilizations from the quartet states resulting in an increased quantum yield. The variations in quantum yield within a class are dominated by changes in the π bonding if the equatorial ligands are held constant. This result was to be expected since π bonding changes cause the different energy level orderings between classes I and II.

If an absorption band is selectively irradiated, only that band and those lower in energy which may be indirectly populated from the directly irradiated band will be photoactive. Thus the direction which is labilized and the ratio of quantum yields for ligands on the labilized axis may be different from the result observed if all bands are irradiated. From Table II, class III molecules should show the greatest differences since the two spin-allowed bands each labilize a different axis. No experimental data are available for these complexes. Class I and II molecules differ from each other only in the direction labilized by the doublet state and direction strengthened from loss of π antibonding character during the excitation. Thus, selective irradiation should primarily affect π bonding ligands along the labilized z axis.

The predicted results of selective irradiation may be quickly summarized using Table II. For class I complexes, the ratio of quantum yields of aquation for the strongest σ and strongest π bonding ligand on the labilized axis, ϕ_σ/ϕ_π, should decrease as the ^4E, $^4A_2$, and $^2\gamma$ states are irradiated. For class II complexes, the ratio should follow the same order (*i.e.*, $^4E > {}^4A_2 > {}^2\alpha$) but the value of the ϕ_π for doublet irradiation should be much greater than that for class I. Note that our model must treat the ligands according to their bonding nature (σ or π) and cannot predict the ratio based only on total bond strength or $10Dq$. Quantitative selective irradiation experiments have been performed on three complexes. The relative magnitudes of the ratios are correctly predicted as shown in Table III.

Mechanism of the Photoreaction

One of the unsolved problems in the field of chromium(III) photochemistry is the mechanism of the photoreaction. The model discussed in this paper implicitly assumes that the primary photoreaction is dissociative, *i.e.*, that the primary process is loss of the ligand whose bond to the metal is labilized. The model does not directly treat the subsequent fate of the complex. The incoming ligand which replaces the labilized ligand may do so in a reaction concerted with the loss of the labilized one. Alternatively, loss of the labilized ligand may result in a five-coordinate metal complex which in turn may undergo stereochemical rearrangement (*e.g.*, square pyramidal, SP, to trigonal bipyramidal, TBP) prior to attack by the incoming ligand. In either case, the *stereochemistry of the product need not necessarily be the same as that of the reactant.*

Several recent experimental results illustrate the stereochemical ambiguities. Photolysis of trans-disubstituted complexes leads to production of some cis-photoproduct, *e.g.*[26]

$$trans\text{-}[Cr(en)_2Cl_2]^+ \xrightarrow[H_2O]{h\nu} >70\%\ cis[Cr(en)_2H_2OCl]^+$$

It is clear in the above example that the labilized ligand was originally on the z axis but that the incoming ligand is bonded in the xy plane in the product. The recent report of the photoinertness of the *trans*-dichloro(cyclam)-chromium(III) ion[27] may be interpreted in terms of both the impossibility of an attack of the entering ligand concerted with loss of the labilized one and a geometry change (to TBP) concerted with loss of the labilized ligand. The rigidity of cyclam would prevent either of the above from occurring and thus prevent the photoreaction from occurring. Whether or not the results of the above experiments imply that the entering ligand cannot occupy the coordination site vacated by the labilized ligand is at present unclear. It is certain, however, that photoproducts need not have the same stereochemical configuration as the reactant.

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