Correspondence

Some Comments on the "Ligand Field Model" for the Prediction of Photochemical Reactivities for d^6 Metal Complexes

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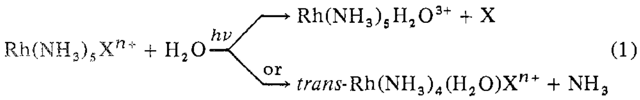
Sir:

Recently, Zink[1-3] proposed the "ligand field model" (LFM) to rationalize the accumulated quantum yield data for photosolvation reactions of d^6 transition metal complexes. In these articles it was claimed[2] "that the ligand field bonding model is self-contained and, in principle, is capable of explaining all the experimental observables". The purpose of this correspondence is to offer some critical remarks regarding this model and to draw attention to some experimental data inconsistent with the LFM in its present stage of development. These remarks hopefully will provide a more balanced view of the LFM and the context in which it may prove useful.

Discussion here will be limited to hexacoordinate rhodium(III)–ammine complexes which undergo photoaquation along the unique axis as the result of d–d excitation (eq 1).



$$Rh(NH_3)_5X^{n+} + H_2O \xrightarrow{h\nu} \begin{cases} Rh(NH_3)_5H_2O^{3+} + X \\ \text{or} \\ trans\text{-}Rh(NH_3)_4(H_2O)X^{n+} + NH_3 \end{cases} \qquad (1)$$

The fundamental postulate of the LFM approach is that the more the excitation energy is "concentrated" along the unique axis the greater will be the quantum yield for loss of ligands on that axis.[2] The distribution of excitation energy is based upon the fractional d-orbital composition, and the unique-axis σ^* orbital (d_{z^2} in crystal field theory) population is pinpointed as the key feature determining photolabilization in the absence of strongly π-interacting ligands. With one qualification (vide infra) it is an implicit assumption in the LFM as currently applied that the relationship of $d_{z^2} \propto$ the z-axis photolabilization quantum yield Φ_s is due primarily to an increased rate of solvolysis (k_s, Figure 1) as the d_{z^2} population of the reactive excited state increases. It is proposed that the lowest excited state of a given multiplicity is the dominant photoactive state of that multiplicity.

Given these assumptions, the ligand field model puts into a more theoretical framework the qualitative thinking of previous workers regarding the reactivities of the excited states of d^6 complexes.[4] However in quantitative application the LFM has some serious deficiency. By placing the responsibility for changes in the quantum yields for a homologous series ML_5X principally on the substitution reactivity changes in the excited states, the LFM automatically assumes that other pathways for depletion of the excited state differ little over the series considered. These processes are illustrated in Figure 1. The quantum yield for formation of substitution products is defined as

$$\Phi_s = \Phi_i \frac{k_s}{k_s + k_r + k_n} \qquad (2)$$

where k_r and k_n are the rate constants for radiative and nonradiative deactivation of the excited state and Φ_i represents the interconversion efficiency from initially populated excited states to the reactive state. It has been pointed out previously[5,6] that there is a dearth of information available on rates k_s, k_r, and k_n for d^6 complexes under photochemically relevant conditions. Such data in principle can be obtained by measuring the photochemical quantum yields and photoluminescence quantum yields and lifetimes under identical conditions. However, complexes such as the cobalt(III) and rhodium(III) amines do not detectably luminesce (i.e., $k_r << k_n + k_s$) in the ambient-temperature, fluid solutions used in most photochemical studies. Although this allows the reduction of eq 2 to

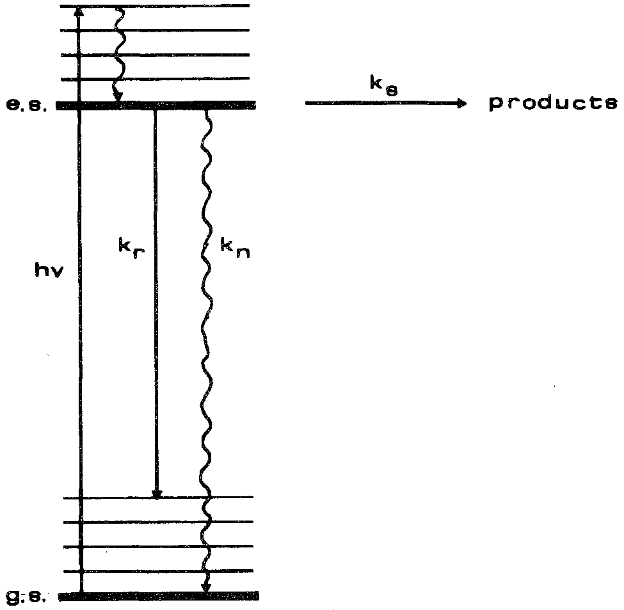


Figure 1. Model for the reactivity of a single excited state of a metal complex. $h\nu$ is the energy of vertical excitation to a Franck-Condon state, and k_s, k_r, and k_n are the rate constants for the thermally equilibrated excited state to undergo reaction to products or radiative or nonradiative deactivation to the ground state, respectively.

$$\Phi_s = \Phi_i \frac{k_s}{k_s + k_n} \qquad (3)$$

the available quantum yield information at best allows evaluation only of the k_s/k_n ratio for any particular complex.

For the purpose of evaluating the LFM generality, we will first consider the hexaamminerhodium(III) complexes $Rh(NH_3)_6^{3+}$ and $Rh(ND_3)_6^{3+}$. Absorption spectrum differences between these ions in aqueous solution are not detectable, and therefore the LFM is incapable of predicting any differences in the photoaquation quantum yields. Yet at 25° in aqueous solution, the Φ_s values differ by a factor of nearly 2 (0.075 and 0.14 mol/einstein, respectively).[7] In addition the apparent activation energies for the photoaquation differ. Although any of the three terms comprising Φ_s (eq 3) may be responsible for the differences, several arguments[7] point to variations in the nonradiative deactivation term as responsible for the differences in Φ_s. Significant but somewhat smaller increases in Φ_s are the result[8,9] of perdeuterating the ammonias of $Rh(NH_3)_5Cl^{2+}$ and of $Rh(NH_3)_5py^{3+}$. Clearly, over a homologous series such as $ML_4L'X$, where either X or L' is being varied, it is a dangerous assumption to conclude that nonradiative deactivation will remain uniformly constant. Significant differences in k_n have been measured at 77°K for the Rh(III) series $Rh(NH_3)_5X^{n+}$ (Table I) and it is certainly

Table I. Excited-State Properties of the Rhodium(III) Ammines, $Rh(NH_3)_5X^{n+}$

Complex	λ_{max}, nm ($A_1 \rightarrow E(T_1)$)	$\Phi_s(298°)$,[a] mol/einstein	$E_{emission}$,[b] kK	$10^3 k_n(77°)$,[c] sec^{-1}	Dt,[d] cm^{-1}
$Rh(NH_3)_5I^{2+}$	416	0.83[e]	13.28[f]	128[g]	1000 (789)
$Rh(NH_3)_5Br^{2+}$	359	0.20[e]	14.30[f]	96.1[g]	564 (560)
$Rh(NH_3)_5Cl^{2+}$	349	0.13-0.16[e]	14.78[f]	81.9[g]	472 (450)
$Rh(NH_3)_5OH^{2+}$	321	$<10^{-2}$ [h]			
$Rh(NH_3)_5H_2O^{3+}$	316	0.43[h]	15.00[i]	290[i]	131
$Rh(NH_3)_6^{3+}$	305	0.075[j]	16.45[f]	50.5[g]	0
$Rh(ND_3)_6^{3+}$	305	0.14[j]		0.84[g]	0

[a] Total quantum yield for photosubstitution of unique-axis ligands. [b] Energy for λ_{max} of emission band for the solid salt $[Rh(NH_3)_5X](ClO_4)_n$. [c] Rate constant for nonradiative deactivation as determined in luminescence experiments. [d] Calculated according to A. B. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968, p 312. Values in parentheses are those quoted in ref 2. [e] Reference 8. [f] T. Thomas and G. Crosby, *J. Mol. Spectrosc.*, 38, 118 (1971). [g] T. Thomas, R. J. Watts and G. Crosby, *J. Chem. Phys.*, 59, 2123 (1973). [h] P. Ford and J. D. Petersen, *Inorg. Chem.*, 14, 1404 (1975). [i] J. Petersen, unpublished observations. [j] Reference 7.

not inconceivable that comparable or greater differences will carry over to the photochemical conditions.

Incorvia and Zink[2] very briefly considered the question of k_n variation and suggested that as the relative population in the d_{z^2} orbital increases, the corresponding decreases in $d_{x^2-y^2}$ population may lead to decreased rates of nonradiative deactivation. There appears to be no experimental support for this suggestion; in fact, an opposite trend is observed for the k_n values measured at 77°K. Nonetheless these rate differences may not be entirely incompatible with their suggestion since under conditions where photoreaction cannot occur, excitation along the z axis may result in a dominant nonradiative deactivation pathway via a strong coupling mechanism.[10]

It was recently implied[2] that the LFM and the rate description of the quantum yield are independent models for photoreactivity. This is misleading since in fact the various processes occurring as a result of photolytic excitation can each be described by rate terms (perhaps unknown), and the ultimate test of any theoretical approach must eventually be the successful prediction of these rates (or relative rates).

Another criticism, voiced previously,[11] is that the LFM employs absorption spectral data (therefore Franck–Condon states) in the calculations used to predict relative quantum yields. For a series such as $Rh(NH_3)_5X^{n+}$ where X or X^- is the leaving group, predictions of photochemical labilities are based on the ground-state configurations (not those of the thermally equilibrated excited states) and ignore possible mechanistic differences in the steps leading to substitution. For example, the LFM "predicts" that Φ_s should be smaller for $Rh(NH_3)_6^{3+}$ than for the $Rh(NH_3)_5Cl^{2+}$, and this indeed is observed[7,8] for photolyses at 298°K. However, a larger apparent activation energy was observed for $Rh(NH_3)_6^{3+}$ photoaquation, and *extrapolations of the Φ_s values to higher temperature indicate that the Φ_s values will have a reverse order at $T > 350°K$.*

Even at 298°K, use of the Franck–Condon state energies does not correctly predict the relative photolabilizations for the $Rh(NH_3)_5X^{n+}$ series. The LFM uses Dt (a measure of ligand field strength differences between the axial and equatorial ligands) as a convenient approximation of percent d_{z^2} population in the excited state to predict the relative order of z-axis labilization quantum yields.[2] Examination of Table I shows that two of the six entries for the $Rh(NH_3)_5X^{n+}$ series do not fall in the appropriate order, the hydroxo which is too photoinert and the aquo which is too photolabile. One could argue that the hydroxo ligand can participate readily in excited-state π bonding thus negating the destabilization in the σ bonding or that it couples with solvent in an unusually strong fashion thus accelerating the nonradiative deactivation paths. The same, however, cannot be argued for the aquo complex. Luminescence data for $Rh(NH_3)_5H_2O^{3+}$ indicate a relatively low-energy emission band comparable to that of $Rh(NH_3)_5Cl^{2+}$ and substantially lower energy than the emission of $Rh(NH_3)_6^{3+}$ (Table I). Given the similarity in emission bandwidths, this would suggest that the thermally relaxed excited state responsible for emission of the aquo complex may be considerably more distorted from the ground-state configuration than indicated by the absorption spectra data (i.e., the Franck–Condon states). Admittedly for the $Rh(NH_3)_5X^{n+}$ series, the unique ligand does not in each case have the same ionic charge, but the breakdown of the predicted order illustrates that such a perturbation may indeed be significant to the quantitative photochemistry of otherwise analogous complexes.

In conclusion, although the ligand field bonding model has had some success in rationalizing photosubstitution quantum yields, it does include some basic assumptions which are unlikely to be correct. The model has made a serious contribution in putting the qualitatively expressed ideas regarding reactivities of ligand field excited states, e.g., "Adamson's empirical rules", into a more theoretical framework and in drawing renewed attention to the contributions of both σ- and π-bonding changes on excitation. However, at least for the rhodium(III)–ammine complexes, the LFM in its current state of development cannot successfully account for the observed photoreactivities.

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