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Assigning Reactive Excited States in Inorganic Photochemistry

The matter of assigning reactive excited states in inorganic photochemistry turns out to have complexities as more detailed and more varied information is obtained. Three cases are considered. For Cr(III) amines there is still much controversy in the assignment of chemical reactivity to doublet and quartet states. In the case of $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$ complexes, it may be necessary to invoke three different reactive or emitting ligand-field excited states, while for $\text{W}(\text{CO})_5\text{L}$ species, at least two, including a charge transfer state, are needed.

Introduction

We are seeing currently the development of an extended research field for that special breed of physical inorganic chemist, the excited-state kineticist. Studies of excited-state rate processes are an increasingly important adjunct to conventional quantum yield and product characterizations. Increasingly complex and intimate excited-state reaction schemes are being constructed. The identification of the reactant species, ordinarily obvious in thermal reactions, turns out not to be so obvious in excited-state chemistry. We limit ourselves here to three examples involving transition metal complexes in solution.

The general picture, and some vocabulary, should be presented first. In the case of mononuclear complexes having monodentate or simple bidentate ligands, to which this discussion will be confined, the visible UV absorption spectra show two principal types of transitions, ligand field (LF) and charge transfer (CT). There may be several LF absorptions, and we designate these as L_1 , L_2 , etc., with a left superscript to indicate the spin multiplicity of the terminal state. Thus the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition for a $d^3 O_h$ complex is labelled 4L_1 . Already there is a difficulty; spin and orbital angular momentum increasingly mix on going to the heavier transition metals, and the use of spin-only designations, while convenient, is suspect.

LF bands are usually broad, and it is now generally accepted that the optical

transitions are Franck–Condon in type, so that absorption of light gives a distribution of vibrationally excited molecules, which rapidly relax or thermally equilibrate to the temperature of the medium. The broad absorption band is essentially the Franck–Condon envelope for the transition. The *thexi* state, as we will call the thermally equilibrated excited state, may have not only different metal–ligand bond lengths, but also different bond *angles*.¹ The classic indication of such distortion is the presence of a very large Stokes' shift in those Cr(III) complexes that show fluorescence.^{2,3} Similar broad emission bands and large Stokes' shifts are observed for spin forbidden transitions as well, although the d^3 case is an exception. In the 2L_1 transition, there has merely been rearrangement of electrons in the t_{2g} set of orbitals; these are non-bonding, and little excited-state distortion occurs so that the phosphorescence spectrum is narrow and vibronically structured, and not much displaced from the 2L_1 band.

Because of the distortion problem, we will avoid the use of orbital symmetry symbols in labelling LF *thexi* states. Rather, we designate them by their nominal spin multiplicity: S (singlet), D (doublet), T (triplet), and Q (quartet or quintet), with a right subscript to give the energy ordering, and a right superscript zero to denote thermal equilibration. The $^4T_{2g}$ ligand-field state is labelled Q_{FC} (as a Franck–Condon state), and becomes Q_1^0 after thermal equilibration. States related by descent of symmetry from O_h may be designated by primes.

Again as noted earlier,¹ *thexi* states are good *thermodynamic* species. An ensemble of such a species has entropy, free energy, and a standard redox potential, as well as energy. It is a topological isomer of the ground state, just as square planar and tetrahedral ML_4 complexes are isomers. The *thexi* state is a good *kinetic* species. Its reactions can be activated, stereospecific, subject to ionic strength effects, etc. Its intimate reaction mechanism should be treatable by conventional theories for rate processes. The identification of the reactive *thexi* state in inorganic photochemistry is thus a matter of serious chemistry.

The typical excited-state processes with which we deal are illustrated in Figure 1, for the d^3 system. Q_{FC} may thermally equilibrate to Q_1^0 , or may undergo prompt intersystem crossing (*pisc*), to D_1^0 . The *thexi* states may exit by emission, of rate constant k_r , by non-radiative return to the ground state, k_{nr} and k'_{nr} , or by chemical reaction, k_{cr} and k'_{cr} . They may interconvert by intersystem crossing (*isc*) and back intersystem crossing (*bisc*). A non-classical chemical reaction is that which occurs during non-radiative relaxation — the so-called *hot ground-state reaction*. These have been very difficult to establish, and will not be considered here.

We turn now to specific systems to examine what progress has been made in identifying reactive states and in obtaining actual rate constant values.

Cr(III) Amines

The photochemistry, essentially substitutional, has been studied extensively.⁴⁻⁶ The interesting situation is that after some 20 years of activity in the field, there are still questions as to the roles of D_1^0 , Q_1^0 , and, in the case of non- O_h complexes, any Q_1^0 . An early supposition was that *all* reaction was from D_1^0 ;^{7,8} it was known as relatively long-lived state, typically with millisecond phosphorescence lifetimes at 77 K, and the spin pairing could free an orbital to facilitate a concerted substitution process. In seeking to test the doublet hypothesis, we came to the conclusion that the Q_1^0 state could not be ignored, and produced the photolysis rules:⁹

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.

2) If the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates.

The rules are approximately obeyed, although there are exceptions,^{4,5,10} and make theoretical sense if Q_1^0 is the reactive state. From the ligand-field point of view, an electron has been promoted to an e_g antibonding orbital and, in a non- O_h complex, the antibonding axis could be expected to be the one for which the average ligand strength was the weaker. In Figure 1, provided that distortion has not significantly disturbed the octahedral framework, Q_1^0 would usually be the axially labilized t_{2g} state in a C_{4v} complex, and $Q_1^{0'}$, the equatorially labilized one. More quantitative and more elaborate ligand-field explanations have been made which adequately predict both the rules and the exceptions to them.¹⁰⁻¹² At one point, it became widely thought that *all* reaction occurred from Q_1^0 , but now the pendulum is swinging back a little.

Complexes of the type $Cr(NH_3)_5X^{2+}$ show two photoreaction modes, ammonia aquation and aquation of the X^- group. The absorption spectrum for $X^- = NCS^-$ is shown in Figure 2; this case provided an early indication that both D_1^0 and Q_1^0 are reactive,^{13,14} both in that the ratio of reaction modes changed with wavelength, and from sensitization results. A point of relevance later is that the ammonia photoaquation, the rules-predicted mode, is *antithermal*, i.e., the labilized ligand is not the thermally reactive one. In the case of *trans*- $Cr(en)_2(NH_3)(NCS)^{2+}$, *three* reaction modes have been reported,¹⁵ aquation of one end of an ethylenediamine ligand, ammonia aquation, and (presumably) thiocyanate aquation. Are the excited states just being sloppy or are three different ones now involved?

A new leverage became available when it was found that D_1^0 emission could be observed in *room temperature* solutions with lifetimes now in the micro- or

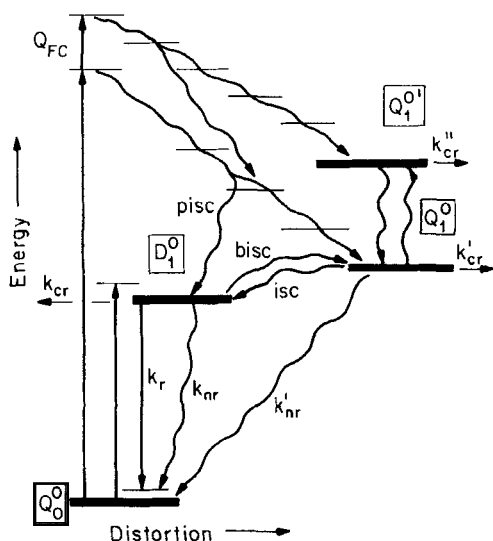


FIGURE 1 Energy vs. distortion diagram for a d^3 system. Bars locate the electronic states, indicated in square frames. Vertical lines denote radiative and wavy lines, non-radiative processes. The light horizontal lines indicate successive vibrational wells as the solvent cage adjust to geometry changes (for clarity, shown only for the thermal equilibration of Q_{FC}).¹

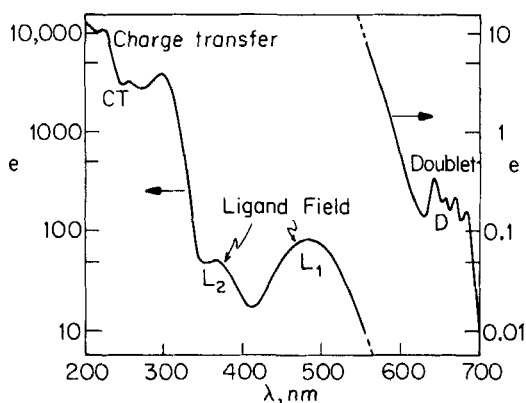


FIGURE 2 Absorption spectrum for $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$.⁵

nano-second range (indicating that k_r was no longer important).^{16–19} The emission could be quenched,⁶ and an important observation was that, on quenching the emission, much of the photochemistry is also quenched in the cases of *trans*- $\text{Cr}(\text{NH}_3)_2(\text{NCS})_4$ ²⁰ and $\text{Cr}(\text{en})_3^{3+}$,^{17,21,22} but not for $\text{Cr}(\text{CN})_6^{3-}$.²³ D_1^0 is clearly implicated in the first two cases, and the simplest

explanation of D_1^0 involvement is that it is chemically reactive and furnishes part of the overall quantum yield. Alternatively, however, promptly formed D_1^0 could be returning to Q_1^0 by bise, so that all reaction is still from Q_1^0 .

In an effort to probe these alternatives, we monitored the rate of appearance of primary photoproduct, in the case of $Cr(en)_3^{3+}$, and found that indeed 30% of photoproduct, $Cr(en)_2(enH)(H_2O)^{4+}$, appeared in less than a few nanoseconds, with the remainder growing in with the D_1^0 emission lifetime.²⁴ Because of ground-state bleaching, it was also possible to determine the efficiency of D_1^0 formation and thence ϕ'_D , the efficiency of the 'slow' product formation. This was significantly greater than the overall quantum yield, indicating that chemical reaction was indeed occurring from D_1^0 as well as from Q_1^0 , see further below.

Further support for D_1^0 as a reactive state has come from emission rules for room temperature solutions,¹⁹ of which the second is:

Rule 2: If two different kinds of ligands are coordinated, the emission lifetime will be relatively short if that ligand which is preferentially substituted in the thermal reaction lies on the weak-field axis of the complex.

Implied in the rule is that the emission lifetime, τ , is determined mainly by k_{cr} , rather than by k_{nr} or k_{bisc} . A rationale for the rule is that the reactivity of D_1^0 tends to parallel that of the ground state; that the paralleling is in reaction rate, as well as in reaction mode, is indicated by some more recent observations.²⁵

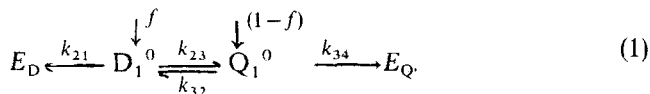
Our hypothesis at this point is that where the photolysis rules predict the thermal reaction mode [as for any O_h complex and for *trans*- $Cr(NH_3)_2(NCS)_4^-$], the photoreaction may partly be from Q_1^0 and partly from D_1^0 , the latter being the quenchable portion. Where the photolysis rules predict an antithermal reaction, this is from Q_1^0 , while any thermal reaction mode present is from D_1^0 .

At present there is no consensus, and some specific contentions on the matter of D_1^0 reactivity.^{17,21,22,26-30} In addition, an alternative attempt to account for two reaction modes has been to invoke a $Q_1^{0'}$, with ligand-field analysis as to how axial and equatorial labilization should behave.³¹

The Case of $Cr(en)_3^{3+}$

We turn now to the specific case of aqueous $Cr(en)_3^{3+}$ to see how emission life time measurements can be helpful in assessing D_1^0 reactivity (see also Gutierrez and Adamson³² for the case of *trans*- $Cr(NH_3)_2(NCS)_4^-$ ³²). If our interpretation is correct $1/\tau$ gives k_{cr} ; on the alternative hypothesis, $1/\tau$ is related to k_{bisc} .

We are dealing with a coupled reaction scheme, Eq. (1):



Following an excitation pulse producing unit concentration of Q_{FC} , *pisc* occurs with efficiency f , so that at small times (on the nanosecond time scale), we have $(D_1^0)^0 = f$ and $(Q_1^0)^0 = (1-f)$. The exiting rate constants are $k_{21} = k_r + k_{nr} + k_{cr} \simeq k_{nr} + k_{cr}$, and $k_{34} = k_r' + k_{nr}' + k_{cr}' \simeq k_{nr}' + k_{cr}'$, and the efficiency of chemical reaction from D_1^0 is $\phi_D' = k_{cr}/k_{21}$, while that from Q_1^0 is $\phi_Q' = k_{cr}'/k_{34}$. The intersystem crossing rate constants are denoted by k_{23} (*bisc*) and k_{32} (*isc*). In the case of quenching of D_1^0 emission, the exiting rate constant k_{21} is augmented by the term $k_q(A)$, where A is the acceptor or quenching species.

The solution of Eq. (1) has been published,^{33,34} and we proceed to the aspect of interest here. The rate at which exiting occurs from D_1^0 is $k_{21}(D_1^0)$, and the total exiting up to time t is

$$E_D = k_{21} \int_0^t (D_1^0) dt.$$

Analysis gives

$$E_D = \frac{k_{21}}{\lambda_2 - \lambda_1} \left[\frac{f(\lambda_2 - \alpha) + (1-f)k_{32}}{\lambda_1} (1 - e^{-\lambda_1 t}) - \frac{f(\lambda_1 - \alpha) + (1-f)k_{32}}{\lambda_2} (1 - e^{-\lambda_2 t}) \right], \quad (2)$$

where

$$\alpha = k_{21} + k_{23}$$

$$2\lambda_{1,2} = (\alpha + \beta) \pm [(\alpha - \beta)^2 + 4k_{23}k_{32}]^{1/2} \quad (3)$$

$$\beta = k_{32} + k_{34},$$

and λ_1 and λ_2 are the two observable decay constants which maybe measured.³⁴ Similarly, the total exiting from Q_1^0 is given by

$$E_Q = \frac{k_{34}}{\lambda_2 - \lambda_1} \left[\frac{f k_{23} + (1-f)(\lambda_2 - \beta)}{\lambda_1} (1 - e^{-\lambda_1 t}) - \frac{f k_{23} + (1-f)(\lambda_1 - \beta)}{\lambda_2} (1 - e^{-\lambda_2 t}) \right]. \quad (4)$$

TABLE I
Excited state kinetics for Cr(en)_3^{3+}

Case	$\frac{k_{21}}{k_{23}}$	$\frac{k_{32}}{k_{34}}$	f	$\frac{\lambda_1}{\lambda_2}$	B^a	C	D	$\frac{\varphi'_D}{\varphi'_Q}$	$\frac{\varphi_{\text{slow}}}{\varphi_{\text{fast}}}$	$(D_1^0)^0$
1.	1 0.01	0.01 1000	0.3	1000 1.01	0.297	0.700	0.003	0.87 0.16	0.26 0.11	0.30
2.	1 0.01	0.01 1000	0.89	1000 1.01	0.881	0.110	0.009	0.29 1.00	0.26 0.11	0.88
3.	1 0.01	429 1000	0.0	1429 1.01	0.298	0.700	0.002	0.87 0.16	0.26 0.11	0.30
4.	0.01 1	0.01 1000	0.7	1000 1.01	0.007	0.300	0.694	0 0.37	0.26 0.11	0.70

^a The quantity A, Eq. (5), is always a small number in these regimes.

If λ_1 and λ_2 correspond to the positive and negative roots, respectively, of Eq. (3), then it follows from Eq. (3) that $\lambda_2 \leq \beta \leq \lambda_1$. Eq. (2) and (4) may be abbreviated thus

$$E_D = A(1 - e^{-\lambda_1 t}) + B(1 - e^{-\lambda_2 t}) \quad (5)$$

$$E_Q = C(1 - e^{-\lambda_1 t}) + D(1 - e^{-\lambda_2 t}) \quad (6)$$

and the total yield of photoproduct, φ , is just $E_D + E_Q$.

In the present case, λ_1 is a large number and λ_2 is unity, if time is measured in units of $1.8 \mu\text{sec}$ (since the experimental emission lifetime given by $1/\lambda_2$ is $1.8 \mu\text{sec}$). At a time small compared to $1/\lambda_2$, but large compared to $1/\lambda_1$, we have

$$\varphi_{\text{fast}} = \varphi'_D A + \varphi'_Q C \quad (7)$$

Further product formation then grows in, the eventual additional yield being

$$\varphi_{\text{slow}} = \varphi'_D B + \varphi'_Q D. \quad (8)$$

The quenchable fraction of the total yield is $\varphi_{\text{slow}}/\varphi$. Experimentally, $\varphi = 0.37$,⁵ $\varphi_{\text{fast}} = 0.11$, and $\varphi_{\text{slow}} = 0.26$. In addition, our monitoring results gave $f = 0.30$ [assuming that $(D_1^0)^0$ is formed by *pisc*].²⁴

Suppose, as regime Ia, that $k_{\text{bisc}} = 0$. A possible set of k values is given in case 1 Table I. Case 2 is for the maximum possible f value, if φ_{fast} is not to drop below 0.11 and φ'_D is at its minimum allowable value of 0.29, which means that $k_{\text{cr}}/k_{\text{cr}}$

+ k_{nr}) = 0.29 or $k_{nr} = 2.4 k_{cr}$. The emission lifetime is given essentially by $1/k_{21} = 1/(k_{nr} + k_{cr})$, and we note that experimentally τ showed linear Arrhenius plots with an apparent activation energy of 10 kcal mol⁻¹.¹⁹ Good Arrhenius behavior seems unlikely if two quite different kinds of rate constants are making comparable contributions. Case 1, with $\phi'_D = 0.87$ or, were f slightly smaller, with $\phi'_D = 1$, is more acceptable in this respect. Analysis of this regime thus suggests that τ is indeed controlled mainly by k_{cr} .

Regime Ib is one of which $(D_1^0)^0$ appears via *isc*, f being zero. Case 3 in Table I gives an acceptable calculation in terms of the observables, but a numerical difficulty arises. If D_1^0 is to appear within a few picoseconds, as it apparently does,^{35,36} k_{32} must be about 10¹¹ sec⁻¹ and k_{34} must also be of this magnitude if ϕ_{fast} is to be as large as 0.11. The energy difference between Q_1^0 and D_1^0 has been estimated to be about 13 kcal mol⁻¹.³⁷ Neglecting entropy contributions, $k_{23}/k_{32} = 3 \times 10^{-10}$ so that $k_{23} = 30$ sec⁻¹, an uncomfortably small value. Regime Ia is to be preferred over Ib, but the latter cannot be ruled out.

In regime IIa, we suppose that $k_{cr} = 0$ ($k_{21} = k_{nr}$), so that all chemical reaction is via *bisc* and Q_1^0 ; this is the alternative hypothesis. The emission lifetime is now related to k_{23} , which is therefore taken to be about unity in case 4 of Table I. This case is acceptable as to ϕ_{fast} and ϕ_{slow} but requires the yield of $(D_1^0)^0$ to be 0.7 contrary to our observation of 0.3; no lower value for this yield can be found in this regime. There are again numerical difficulties. The regime requires that k_{nr} not be much greater than k_{23} since k_{nr} is a wasting process. This is unlikely since both reactions are non-radiative transitions, but with less geometry change for k_{nr} than for k_{23} . In addition, little activation energy is expected for k_{nr} , while k_{23} must now be assigned the 10 kcal mol⁻¹ barrier obtained from the temperature dependence of τ . Also, since $k_{23} \approx 1/\tau \approx 0.5 \times 10^6$ sec⁻¹, we find $k_{32} \approx 0.5 \times 10^6 / 3 \times 10^{-10} \approx 2 \times 10^{15}$ sec⁻¹. This is much too fast. Even if the energy gap between Q_1^0 and D_1^0 is reduced to the minimum value of 10 kcal mol⁻¹ (set by the temperature dependence of τ), k_{32} is still about 1×10^{13} sec⁻¹, which in turn implies an equally uncomfortably large value of k_{34} . Regime IIb, in which $(D_1^0)^0$ is produced by *isc* rather than by *pisc*, runs into similar difficulties.

Although the above presentation has been sketchy, it illustrates the point that quantitative considerations can limit the type of kinetic scheme that is acceptable. In the case of $Cr(en)_3^{3+}$, the result is a distinct favoring of regime Ia, namely chemical reaction from D_1^0 formed by *pisc*.

Rh(NH₃)₅X²⁺ Complexes

We take up briefly two more types of complexes. The aqueous photochemistry of Rh(III) amines is mostly substitutional.³⁸⁻⁴¹ $Rh(NH_3)_5Cl^{2+}$ photo-

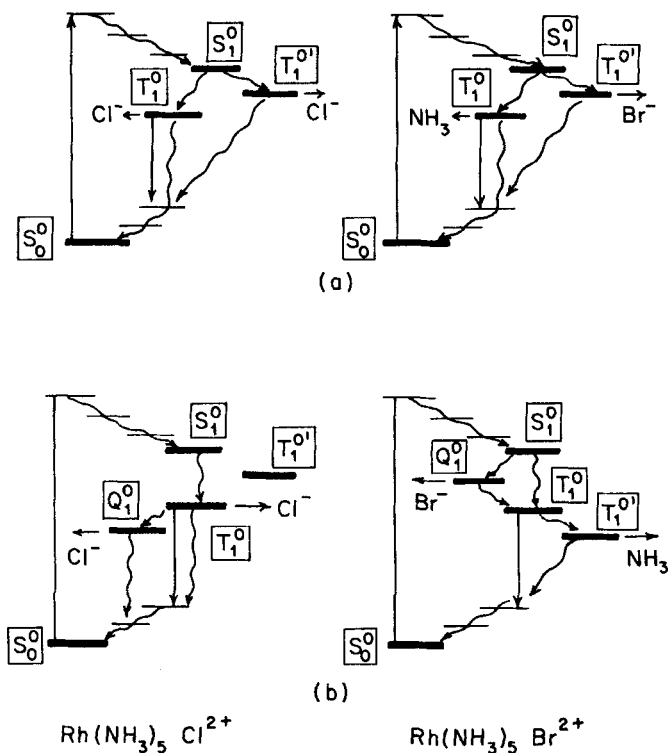


FIGURE 3 Energy vs. distortion diagram for $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$. (a) Two reactive or emitting states. (b) Three reactive or emitting states.

aquates Cl^- with $\phi = 0.16$ at 350 nm, while $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ shows both ammonia photoaquation, ($\phi_{\text{NH}_3} = 0.18$) and bromide aquation ($\phi_{\text{Br}} = 0.019$).⁴² Emission from aqueous solutions has recently been observed^{43,44} and may be quenched by OH^- ion.^{45,46} On quenching the emission, we found that ϕ_{Cl} was 85% quenched, in the case of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$,⁴⁵ and that ϕ_{NH_3} was fully quenched, but ϕ_{Br} not at all in the case of $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$.⁴⁶

An interesting and important problem is now posed. Conventional wisdom assigns the emitting state as a triplet and since the emission spectra and lifetimes are very similar for the two complexes, it would seem that it is the same triplet state in both cases, which we call T_1^0 . A simple explanation of the quenching results is that T_1^0 is chemically reactive, but if this is so, then Rh–Cl bond-breaking occurs in the one case and Rh– NH_3 bond-breaking in the other. The bromide mode of reaction can then be assigned to some other state, say $\text{T}_1^{0'}$, as illustrated in Figure 3a. Although ligand-field rationalizations can be made, it seems awkward to ask that the chemical reaction mode makes so complete a change between $\text{X} = \text{Cl}^-$ and $\text{X} = \text{Br}^-$.

An alternative scheme, shown in Figure 3b, invokes *three* excited states. The bromide yield is assigned to a quintet state, Q_1^0 , and the quenchable photochemistry to T_1^0 or to $T_1^{0'}$, whichever is the lower lying, but with the emission from T_1^0 in both cases. [The quintet state is not necessarily high in energy in C_{4v} ligand-field theory.⁴⁷] Q_1^0 is placed with less distortion than T_1^0 because of its more symmetric arrangement of antibonding electrons and might be similar to D_1^0 in d^3 systems in having ground state-like reactivity.

At present, no decision seems possible between the two and the three reactive state schemes. The former has been suggested,⁴⁸ but from data that do not rule out the alternative.

$W(CO)_5L$ Complexes

Another d^6 situation is that of group VI carbonyl compounds. $W(CO)_5L$ complexes, where L is a n -electron donor, undergo photodissociation of the L ligand and, in the presence of a second ligand, L' , the intermediate $W(CO)_5$ is scavenged to yield $W(CO)_5L'$.^{49,50} The quantum yield for such reactions is ordinarily several tenths, but as L becomes more electron-withdrawing, a CT band moves to the long wavelength side of the first LF band and the yield drops to around 0.02.⁵¹

For the case of $L=4$ -cyanopyridine, we observed emission at room temperature in methylcyclohexane solution with 0.1 M ethanol present as L' (as well as without the ethanol).⁵² The emission was quenchable by anthracene, for example, and on quenching the emission, the photoproduction of $W(CO)_5$ (ethanol) was also quenched. Clearly the emitting state, possibly a triplet charge transfer state, 3CT , is implicated in the photochemistry. We can write $\phi = k_{cr}/(k_r + k_{nr} + k_{cr})$ for this state and, since ϕ is small, $\phi \simeq k_{cr}/k_{nr}$; k_r is taken to be negligible. The temperature dependence of ϕ gives an apparent activation energy of 7.6 kcal mol⁻¹, so if 3CT is both the reactive and the emitting state, $7.6 = E_{cr}^* - E_{nr}^*$. In the one-reactive state scheme, Figure 4a, $1/\tau = (k_r + k_{nr} + k_{cr}) \simeq k_{nr}$, and from the temperature dependence of τ , $E_{nr}^* \simeq 1.5$ kcal mol⁻¹, whence $E_{cr}^* = 9.1$ kcal mol⁻¹. This may be high for what is thought to be a simple bond dissociation reaction.

An attractive alternative is a two-state scheme in which chemical reaction occurs from a LF state lying above the emitting CT one, and in steady-state equilibrium with it, as shown in Figure 4b. The observed E_ϕ^* is now attributed primarily to the energy difference, ΔE , between the two states. In this scheme, excitation leads through intersystem crossings to 3CT . This state is emitting but not highly chemically reactive. The higher LF state, presumably T_1^0 , does react efficiently, but the overall quantum yield is low because of the competition with non-radiative relaxation of 3CT . If L is such that T_1^0 is the

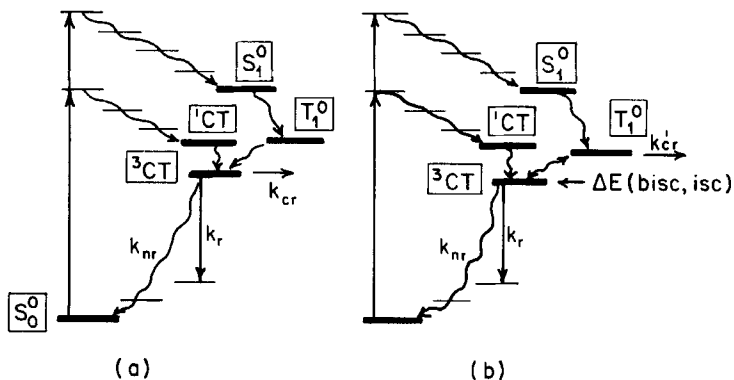


FIGURE 4 Energy vs. distortion diagram for $W(CO)_5L$. (a) Reactive and emitting state the same. (b) Emission from 3CT and reaction from back-populated T_1^0 .

lower lying state, then the quantum yield should be large, as observed.

The two-state scheme has been favored;^{49,53,54} also a similar one has been proposed for $Ru(NH_3)_5L^{2+}$ complexes.⁵⁵ Quantitative considerations indicate at least some caution, however. In the two-state scheme, k_{bisc} must compete with k_{nr} , and the emission lifetime of 360 nsec at 25°C gives $k_{nr} \approx 2.8 \times 10^6 \text{ sec}^{-1}$. We have $\Delta E = E_\phi^* + E_{nr}^* - E_{cr}^* = 9.1 - E_{cr}^*$, where E_{cr}^* is the activation energy for reaction from T_1^0 , which is probably small. If we take ΔE to be the full 9 kcal mol⁻¹, and suppose that $k_{bisc} \approx 0.1 k_{nr}$, then $2.8 \times 10^6 \times 0.1 = A_{bisc} e^{-9000/RT}$, whence $A_{bisc} = 1 \times 10^{12} \text{ sec}^{-1}$. No allowance has been made for entropy change, and this A_{bisc} value, while marginally acceptable, is a bit large. Further study of the $W(CO)_5L$ complexes is needed.

Summary and Conclusion

The three cases described here illustrate one of the problems for the excited-state kineticist. His colleagues who deal with ground-state reactions usually know what the reactant species is. The photochemist spends much effort in trying to find out what *his* reactants actually are, and in few cases so far has this effort been unambiguously successful. That is, while reasonable guesses provide good working hypotheses, it has been a difficult matter to be sure whether one is dealing with a one reactive state scheme, or a two or three reactive state one. Determining the thexi-state spin multiplicity and its actual structure is yet more difficult. Fast magnetic susceptibility methods may help on the former question, and also photochemistry in high magnetic fields. The structure problem may yield to excited-state resonance Raman spectroscopy.⁵⁶

An important reason for establishing at least the *number* of reactive thexi states in a given system is that ligand-field theoreticians have been interested in explaining thexi-state reactivity in terms of specific metal–ligand bond labilization leading to dissociation and a five-coordinate intermediate.^{10–12} In such analyses, it makes a difference in d^3 if the state is D_1^0 or Q_1^0 , and, in d^6 , whether it is S_1^0 , T_1^0 , Q_1^0 , or 3CT . It can be embarrassing to provide a theoretical explanation for the wrong scheme! The *mechanism* of thexi-state reactions has not been a focus of this paper. My personal opinion, however, is that the solvation reactions are more likely to be concerted with solvent rather than being limitingly dissociative in type.

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