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STRUCTURE AND REACTIVITY OF THE METAL-CENTERED TRANSITION METAL EXCITED STATES

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CONTENTS

ABBREVIATIONS

acac	2,4-pentanedione
AOM	angular overlap model
ax	axial
bpy	2,2′-dipyridyl
chda	*trans*-1,2-diaminocyclohexane
CTTM	charge transfer to metal
diamsar	1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane
dien	diethylenetriamine
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DTNE	1,2-bis(1,4,7-triaza-1-cyclononyl)ethane
E_a	activation energy (theoretical)
E_A	Arrhenius activation energy (experimental)
E_{exit}	energy of excitation
E_{th}	threshold energy
el	electronic
en	ethylenediamine
eq	equatorial
f_L, f_U	the fraction of product formed from lower and upper state, respectively
FMA	formamide
FC	Franck–Condon
GS	ground state
LFSE	ligand field stabilization energy
k_{bisc}	back intersystem crossing rate constant
k_{ic}	internal conversion rate constant
k_{isc}	intersystem crossing rate constant
k_{nr}, k'_{nr}	non-radiative decay rate constants of vibrationally equilibriated lower and higher energy electronic excited states, respectively
k_p, k'_p	rate constants for product formation from the vibrationally equilibrated lower and higher energy electronic excited states, respectively
k_v, k'_v	vibrational relaxation rate constants of vibrationally equilibrated lower and higher energy electronic excited states, respectively
$k_{Y,D}$	rate constant for product formation from the vibrationally equilibrated lowest energy doublet state of Cr(III)
$k_{Y,Q}$	rate constant for product formation from the quartet state of Cr(III)

MLCT	metal to ligand charge transfer
N_4	a tetraaza macrocyclic ligand
nu	nuclear
ox	oxalate
P	pressure
$p_{Y,i}$	probability of forming product Y when the ith excited state enters the product forming decay channel
phen	1,10-phenanthroline
Q_{FC}	Franck–Condon excited state
Q_0	zeroth vibrational level of a quartet electronic excited state
sar	3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane
sen	4,4′,4″-ethylidynetris(3-azabutan-1-amine)
sep	1,3,6,8,10,13,16,19-octaazabicyclo(6.6.6)icosane; sepulchrate
spy	square pyramid
tbpy	trigonal bipyramid
TCTA	1,4,7-tris(acetato)-1,4,7-triazacyclononane
tn	1,3-diaminopropane
$\Delta V^{\ddagger}_{i,j}$	volume of activation for the ith process (or observable quantity) of the jth excited state
$\Delta V^{\ddagger}_{i}$, $\Delta V^{\ddagger}_{\phi(i)}$	volume of activation for the photoinduced process or the quantum yield respectively, for loss of a ligand $i = X^-$, NH_3, etc.
$\Delta V^{\ddagger}_{p(Y,L)}$, $\Delta V^{\ddagger}_{p(Y,U)}$	pressure coefficient of the probability of loss of ligand Y from the lower or upper excited state, respectively, when two states are photoactive
$\Delta V^{\ddagger}_{\tau(j)}$	pressure coefficient of the lifetime of the jth state
$\eta_{i,j}$	efficiency of the ith process of the jth excited state
$\phi(Y)$	total substitutional quantum yield
$\phi(i)$	quantum yield for process i (e.g. $i = X^-$, NH_3, etc.) for photoinduced substitutions of these ligands
τ_S	mean lifetime of the Sth excited state
$[14]aneN_4$	1,4,8,11-tetraazacyclotetradecane; cyclam
$[9]aneN_3$	1,4,7-triazacyclononane
ms-$Me_6[14]aneN_4$	$(5,12)$-$Me_6[14]aneN_4$ = 5,12-*meso*-5,7,7,12,14,14-hexamethyl-1,4,-8,11-tetraazacyclotetradecane; tet*a*
rac-$Me_6[14]aneN_4$	$(5,12)$-$Me_6[14]aneN_4$ = 5,12-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; tet*b*

A. INTRODUCTION

We undertook this review in order to explore the possibility of correlating patterns of photochemical and photophysical behavior with information pertinent to molecular structure for photoactive transition metal excited states. Satisfactory realization of such a goal is difficult even for ground state reactions, where precise structural variations have been extensively documented. The task is made far more difficult when excited state reactivity is also considered, not only because (excited state) structural information is harder to obtain, but also because the excited state is initially prepared (by means of absorption of radiation by the ground state) with an energy content exceeding the activitation energy requirements of many simple ground state processes. Given that a "reactant" so prepared generally meets the energy requirements of a variety of reaction channels, any selectivity of excited state reactions seems surprising. Yet, in spite of this, there is a general consensus that there are distinct, structure dependent patterns of photochemical reactivity. The apparent systematic features of photochemical reactions and the implication that excited state reactivity can be selective, have stimulated a great deal of experimental and theoretical study.

In this article we review the spectroscopic information which reflects on the structure of the metal centered, or ligand field, excited states of transition metal complexes. For each class of transition metal complexes we have attempted to relate the inferred structural information to the reported photochemical and photophysical behavior. Wherever possible, these relationships are illustrated using simple, primitive models for excited state reactivity. Treatment of the literature has been selective rather than comprehensive: we have attempted to restrict our coverage to those studies which bear upon the relationships, if any, between excited electronic and molecular structure and excited state chemical behavior.

(i) Structure of electronically excited transition metal complexes

The classification and rationalization of excited state reactivity patterns is rendered especially difficult by the paucity of structural information about the reactive species. Absorption of monochromatic radiation can generate the excited systems with reasonably well defined electronic configurations. Early work on transition metal complex substrates indicated that for a single compound, irradiation of absorption bands of markedly different type (e.g. *d–d*, charge transfer, etc.) could lead to characteristically different reaction products [1–3] and contributed to a tendency to classify reactivity patterns in terms of these initial states. Unfortunately, the excited states which are initially generated by the absorption of radiation, the Franck–Condon

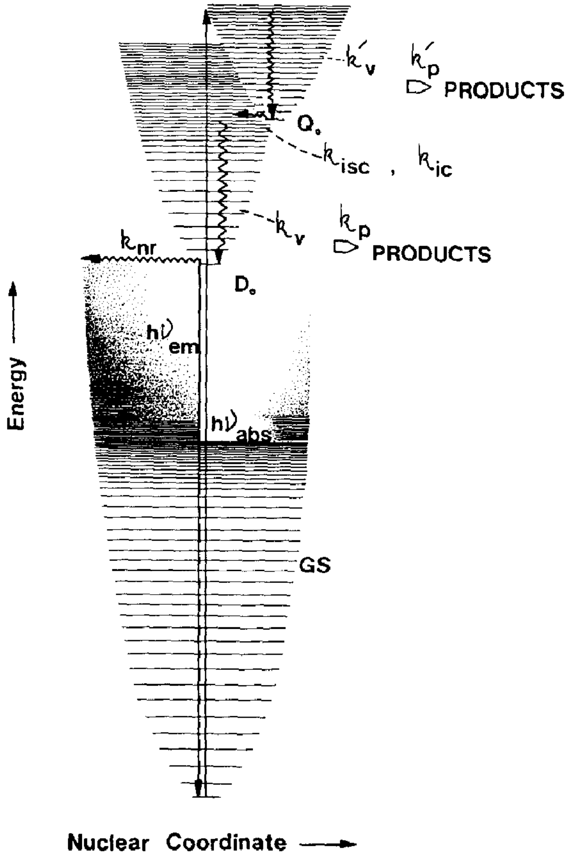

Fig. 1. Definitions of kinetic parameters for excited and ground state electronic configurations of an octahedral coordination complex. Energies and displacements are based on $Cr(NH_3)_6^{3+}$. First order rate parameters are indicated for the characteristic dynamic processes: (a) vibrational relaxation within an electronic potential energy surface, k_v, k'_v; (b) intersystem crossing, k_{isc}, and internal conversion, k_{ic}, for crossing between excited state surfaces; (c) formation of chemical products, k_p, k'_p; (d) non-radiative crossing to the ground state potential energy surface k_{nr}. The doublet electronic excited state D is drawn so as to be nested with the ground state, GS. Absorption of radiation populates a vibronic state, Q_{FC}, which has the molecular geometry of the ground state. Vibrational relaxation within Q results in a change of molecular geometry at the vibrationally equilibrated level Q_0 this is represented by a displacement along the nuclear coordinate.

excited states, have the ground state molecular structure. Consequently, their molecular structure most often corresponds to a significant distortion of the vibrationally equilibrated structure of the electronically excited state. This situation is illustrated schematically for the electronically excited state Q in Fig. 1: the potential energy minimum of this state is horizontally displaced with respect to the potential energy minimum of the ground state. Since vibrational lifetimes are very short in condensed phases ($< 10^{-10}$ s), any chemical reactions of these Franck–Condon states must occur very rapidly indeed! In fact more extensive studies of wider classes of compounds have demonstrated that vibrational equilibration of electronic excited states does occur in many (but probably not in all) transition metal complexes and that distinct correlations of photoreaction patterns with the electronic configurations of Franck–Condon states are not generally observed; these issues are developed in some detail in the sections which follow.

(ii) Comparisons with organic compounds

Many aspects of the photochemistry of transition metal complexes have parallels or precedents in the photochemistry of organic molecules [4,5]. Conversely, there are also, in principle, striking differences and, indeed, many of these differences are observed in practice. For example, both vibrational and electronic quanta are smaller in the heavy metal complex than in most hydrocarbon compounds. The more densely packed states, together with generally greater spin–orbit coupling, give rise to much greater mixing of states, and thus to more rapid internal conversion (between states of the same spin multiplicity) and intersystem crossing (between states differing in spin multiplicity) processes in transition metal complexes than one finds in "typical" organic systems. Partially filled, essentially non-bonding, metal-centered orbitals (d or f) can function in either a donor or acceptor capacity and have no simple organic analogs. Indeed, the material summarized in this article deals with the chemistry which takes place following excitation of electrons within the metal-centered non-bonding orbitals themselves (i.e., within the t_{2g} subshell of octahedral transition metal complexes) or that following promotion to metal-centered anti-bonding orbitals (e_g^* in O_h complexes).

(iii) Time evolution of electronically excited systems

It is convenient to express the evolution of an electronically excited molecule in terms of the time dependent transition probabilities, or, more simply, by assigning rate constants to the various possible processes. The approach is illustrated in Fig. 1 for a simple three state system based on $Cr(NH_3)_6^{3+}$. Light absorption by the ground state (GS) usually results in a Franck–Condon excited state (Q_{FC}) having the same spin multiplicity as the ground state. In general the photonic energy absorbed ($h\nu_{abs}$) will result in vibrational as well as electronic excitation of the molecule; i.e., $E(Q_{FC}) > E(Q_0)$ where $E(Q_0)$ is the energy of the lowest vibrational level of electronic state Q. Relaxation of the initial, or Franck–Condon, state to Q_0 may be the fastest of the excited state processes (e.g., $k'_v \gg k'_p$, k_{isc}, etc.) or it could alternatively occur in competition with other processes of the state Q (e.g.;, $k'_v \sim k'_p$, k_{isc}, k'_{nr}, etc.).

In principle, photoproducts may be generated from any of the excited states populated along the relaxation trajectory. However, such reactions can only occur from the lower energy states if the rate of the chemical process is faster than anything else (e.g., $k'_\mathrm{p} \gg k_\mathrm{isc}$, k_ic). It is therefore convenient to distinguish as *Type I* systems those for which relaxation of the upper state populates, to at least some extent, most of the excited states of lower energy (as when k_ic, $k_\mathrm{isc} \gg k'_\mathrm{nr}$, k_p); in *Type II* systems, upper state excitation is not followed by the predominant population of excited states of lower energy (i.e., k_ic, $k_\mathrm{isc} \ll k'_\mathrm{nr}$, k'_p). The frequent observation of emission or excited state absorption spectra characteristic of the lowest energy excited state (e.g., D_0) regardless of the absorption band irradiated, is an indication that many systems are of *Type I*. For example, most transition metal complexes excited in their ligand field absorption bands seem to exhibit *Type I* behavior. Two classes of photochemical behavior have been discussed in *Type I* systems: (*A*) fast reaction behavior ($k_\mathrm{p} \geq k_\mathrm{v}$ or $k'_\mathrm{p} \geq k'_\mathrm{v}$); and (*B*) slow reaction behavior ($k_\mathrm{p} < k_\mathrm{v}$ or $k'_\mathrm{p} < k'_\upsilon$) [6]. In *Type IB* systems the excited states come rapidly to vibrational equilibrium with the medium, and the chemical behavior of the equilibrated states (Q_0, D_0, etc.) may be treated using conventional kinetic approaches; examples are to be found in the chemical behavior of the lowest energy doublet state of Cr(III) complexes. In *Type IA* systems the reaction must occur in competition with vibrational relaxation, and this dictates such a short time scale (for reaction) that Franck–Condon-like factors, which result from differences in "reactant" and "product" nuclear positions, have been postulated to be less important than symmetry related selection rules [6]; the visible photolysis of $Co(NH_3)_5Cl^{2+}$ seems to result in this kind of behavior.

Type II systems are less well documented, but this behavior may be exhibited in some photoredox systems, and also in a few systems which have an upper state chromophore possessing a unique distortion mode, as seems to be the case in certain polyketonate–uranyl complexes [7].

A conceptually useful approach to the dynamics of the excited system is to formulate the rate parameters as functions of fundamental frequencies (corresponding to the unretarded rates for the relaxation channels under consideration) ν_i^0, and a series of retardation factors, f_i^j,

$$k_\mathrm{obs} = \sum_i \nu_i^0 f_i^\mathrm{el} f_i^\mathrm{nu} f_i^\mathrm{s} \tag{1}$$

where the superscripts el, nu, and s, denote retardation originating from purely electronic orbital effects, changes in nuclear configurations, and changes in spin multiplicity respectively; the summation is over all relevant relaxation channels for the process considered [5,6]; and the ν_i^0 weighted so that $\Sigma_i \nu_i^0 = \nu^0$ when the $f_i^j = 1$ ($\nu^0 =$ the fully allowed rate of a strongly coupled surface crossing process, and j = el, nu, s). This approach has been rationalized in terms of Fermi's Golden Rule, assuming a Born–Oppenheimer separability of electronic and nuclear motion [5]; it relates the retardation factors to the electronic matrix element and to vibrational overlap (or Franck–Condon factors). Equation 1 is thus a useful conceptual basis for discussion of the dominant, or most rapid, processes characteristic of the excited system. These dominant processes will be strongly allowed (i.e. for the dominant channel, a, $f_a^j \geq f_i^j$, $i \neq a$). The appropriate selection rules may sometimes be inferred from common orbital concepts and Franck–Condon analysis using eqn. (1).

(iv) Descriptions of excited state relaxation coordinates

There has been some effort expended in attempts to define critical points along the photoreaction coordinate in transition metal systems. Thus Zink [8–13] has used ligand field models and Vanquickenborne and Ceulemans [14–19] have used angular overlap models and orbital correlation approaches to develop "photochemical selection rules" for d^3 and d^6 complexes; these "rules" are largely extensions or generalizations of "empirical rules" that were proposed some time ago by Adamson [20]. Both of these theoretical approaches [8–19] treat the orbital populations and infer the predominant distortion coordinate for the excited system using ground state nuclear coordinates. An e_g distortion coordinate can be inferred from the theoretical considerations [8–19], and an e_g-Jahn–Teller distortion is reported in the thermally equilibrated ${}^4T_{2g}$ state of $Cr(NH_3)_6^{3+}$ [21] and in the ${}^3T_{1g}$ state of $Co(NH_3)_6^{3+}$ [22], but the ligand field absorptions must be coupled with, and therefore populate, ungerade vibrations. Nevertheless, excitations well into the absorption manifold are expected to excite at least some of the vibrational combination bands with progressions in the e_g components [21–25]; for excitations of sufficiently high energy, a statistical distribution of normal modes is expected.

In principle, two points in each excited state potential energy surface are reasonably well defined: (1) the initial point of entry induced by photon absorption, this has the ground state geometry and the process activates the excited state vibrational mode(s) dictated by the vibronic selection rules; (2) the geometry and energy of the potential energy minimum can be estimated from a careful analysis of the absorption (or emission) band shape (e.g., refs. 21, 22, 25). In addition, absorption and emission band shape analysis for systems in solution under photochemical conditions might provide useful information about the *shape* of the excited state potential energy surface.

(v) *Estimates of the magnitudes of the critical rate parameters*

Detailed numerical values of the rate parameters are expected to vary from complex to complex. However, it is possible to map out some general features.

While vibrational relaxation rates can be slow in isolated molecules or at cryogenic temperatures [26,27], they tend to be in the ps time regime in condensed phases at room temperature [27]. Molecules with heavier atoms tend to have shorter relaxation times. Vibrational relaxation times of transition metal complex excited states in aqueous solutions are highly likely to be less than 10^{-10} s. Experimental measurements of the rates of conversion between states (k_{ic} or k_{isc}) have only been reported for $^4E \rightarrow {}^2E$ conversions in a few closely related thiocyanato–amine complexes of chromium(III) and for $Cr(acac)_3$ [28–30]. The relaxation times observed for excited state absorbancies in these compounds are on the order of 10^{-11} s. This is a plausible magnitude for the vibrationally controlled $^4E \rightarrow {}^2E$ spin relaxation rate ([31] and also an analysis based on the theoretical treatment of Buhks et al. for thermal spin relaxation processes [32]; see Section B(i) (c) and (d) below). It is noteworthy that thermal spin relaxation rates are largely controlled by vibrational (or nuclear) factors [32,33] in transition metal complexes.

Thus, based on extrapolations of the available information, we would generally expect to find $k_{isc} \leq k_{ic} \leq k_v$, k'_v, as the electronically excited system comes into thermal equilibrium with the environment. However, it is likely that there are some systems for which the rate of transfer of vibrational energy to the solvent medium will limit the rate of thermal equilibration of the excited system. The magnitude of this limit is not yet clear.

In most molecules, one expects appreciable vibronic coupling between the states. The strength of the coupling is expected to be a critical factor in the selection rules for population of possible states following excitation. The vibrational modes that are activated upon entry into each electronic potential energy surface are likely to be a contributing factor in determining the relaxation trajectory across that surface; these modes must be considered with care when one considers the possibility of transitions between surfaces for non-thermalized systems (i.e., for "prompt" intersystem crossings, "prompt" photoreactions, etc.). The nuclear motions that are characteristic of these vibrational modes are highly likely to dictate which of the reaction channels couple with the relaxing systems [6]. However, entry into the excited state potential energy surface at energies well above the minimum must involve excitaton of most vibrational modes via the population of high order vibrational progressions. As a consequence, single mode models are not likely to be useful for treating "fast" processes. Statistical models provide a reasonable basis for discussion of the behavior of vibrationally equilibrated states.

(vi) Effects of pressure on photochemical and photophysical properties

Processes which are accompanied by a change in nuclear coordinates, such as a change in metal–ligand bond lengths when an excited state relaxes or the interchange of coordinated ligands with solvent species in an excited state reaction, will generally be accompanied by a change in molecular volume. Depending on the mechanism, there may be a correlated change in partial molar volume along the reaction coordinate for these processes, and such changes in the molar volumes will result in the chemical or physical process becoming pressure dependent [34–38]. The resulting volumes of activation must be consistent with any proposed mechanism, and several laboratories have been exploring the use of pressure dependencies of quantum yields $\phi(\mathrm{Y})$, giving $\Delta V^{\ddagger}_{\phi(\mathrm{Y})}$, and excited state lifetimes (τ), giving $\Delta V_{\tau}^{\ddagger}$, as mechanistic tools in the study of excited state processes. In principle, there are many competing processes in each excited state (Fig. 1), and there may in practice be more than one excited state involved in the observed photochemical and photophysical behavior. This leads to very complex situations, but some useful limiting conditions can be defined: (1) competitive kinetic behavior for a single photoactive excited state; (2) competitive kinetic behavior for two or more photoactive excited states; and (3) two photoactive excited states, the higher energy state following competitive kinetics while the lower energy state has only a single channel for relaxation. The first limit has been used in discussions of Rh(III), and the last two can be used in discussions of Cr(III) excited state behavior. Competitive kinetic behavior can, in principle, be generalized to take account of an arbitrary number of photoactive excited states. However, the generalized photochemical situation must also take into account the possibility of fast processes leading to non-competitive kinetic behavior; behavior of this kind has not yet been treated in the discussion of pressure effects on excited state reactions. The limiting situations are qualitatively contrasted in Fig. 2.

(a) Competitive kinetic behavior of a single photoactive excited state

In all of the competitive kinetic limits it is assumed that each observable quantity results from a distinct excited state relaxation channel; i.e., a relaxation channel which can be characterized by a rate constant that is independent of the rate constants of all the other relaxation channels. This limit has often been used in the discussion of Rh(III) photochemistry [35–39]. For a product Y

$$\phi(\mathrm{Y}) = \eta_{\mathrm{isc}} k_{\mathrm{Y}} \tau p_{\mathrm{Y}} \text{ and } \Delta V_i^{\ddagger} = -RT\left[\frac{\partial \ln k_i}{\partial P}\right]_T \qquad (2)$$

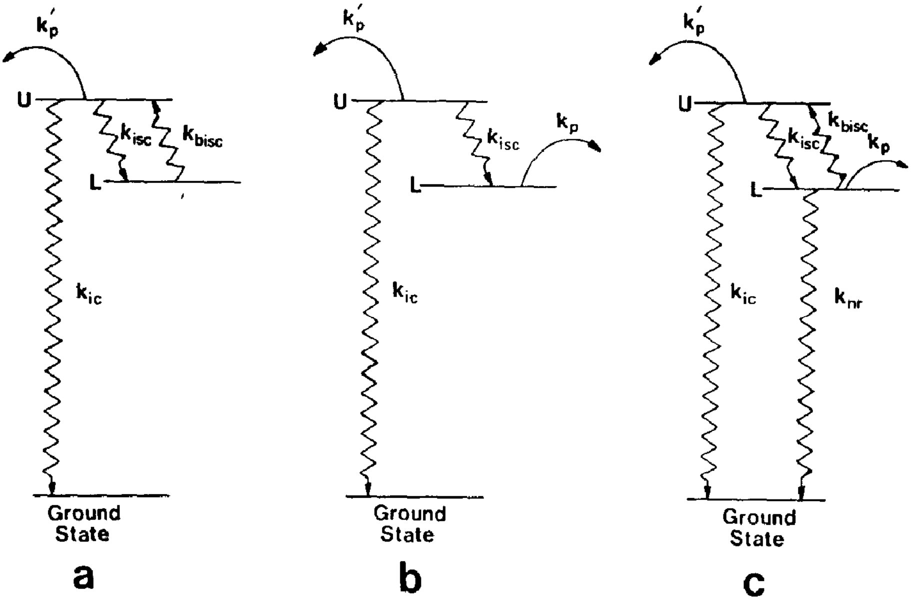

Fig. 2. Qualitative illustrations of some of the different kinds of behavior postulated for a molecule with two photoactive excited states: (a) the lower energy excited state can only decay by means of back intersystem crossing; (b) the lower state can only decay by means of chemical reaction; and (c) non-radiative relaxation, back intersystem crossing and product formation are kinetically competitive pathways for decay of the lower excited state. In each instance three kinetically competitive processes contribute to the decay of the upper state: product formation, intersystem crossing and internal conversion to the ground state (non-radiative relaxation).

so that

$$\Delta V^{\ddagger}_{\phi(Y)} = \Delta V^{\ddagger}_{Y} + \Delta V^{\ddagger}_{\tau} + \Delta V^{\ddagger}_{p(Y)} + \Delta V^{\ddagger}_{\eta(\mathrm{isc})} \tag{3}$$

and

$$\Delta V^{\ddagger}_{\tau} = -\sum_{i} \eta_i \, \Delta V^{\ddagger}_{i} \tag{4}$$

where p_Y is the probability that any photochemical intermediate formed goes on to form product Y, $\Delta V_i^{\ddagger}$ is the volume of activation for the ith process ($i = Y$ is used for entry into a relaxation channel which can lead to a chemical product; notation for other processes is as in Fig. 1) and η_i is the efficiency of the ith process ($\eta_i = k_i\tau$).

The factor p_Y in eqn. (2) and the $\Delta V^{\ddagger}_{p(Y)}$ term in eqn. (3) are often neglected in literature discussions, but these terms should be considered, if only for the sake of completeness. Their role is to take account of the possibility that some kinds of transient intermediate may regenerate the original ground state in competition with chemically distinct products, or that a single relaxation channel may give rise to a distribution of relaxation trajectories, a fraction of which (p_{Y}) lead to products.

(b) Competitive kinetic behavior of two or more photoactive excited states

In the usual two state situation, the upper state (denoted with a subscript U below) is populated by direct light absorption, while the lower energy state (denoted with a subscript L below) differs in spin multiplicity from the ground state, and is significantly populated only by intersystem crossing (k_{isc}) from higher energy states. In the limit that we consider here, vibrational relaxation is considered fast in comparison to any other process, so that the various channels for escape from each excited state can be treated using stationary state kinetic treatments. We also assume that the energy difference between states is large enough so that back intersystem crossing can be treated as a minor perturbation ($k_{\mathrm{isc}} \gg k_{\mathrm{bisc}}$). With these assumptions, and for the quantum yield of product Y given by

$$\phi(\mathrm{Y}) = \eta_{\mathrm{isc}} k_{\mathrm{Y,L}} \tau_{\mathrm{L}} p_{\mathrm{Y,L}} + k_{\mathrm{Y,U}} \tau_{\mathrm{U}} p_{\mathrm{Y,U}} \tag{5}$$

so that

$$\begin{aligned}\Delta V^{\ddagger}_{\phi(\mathrm{Y})} = {} & \left[f_{\mathrm{L}}\ \Delta V^{\ddagger}_{\mathrm{Y,L}} + f_{\mathrm{L}}\ \Delta V^{\ddagger}_{\tau(\mathrm{L})} + f_{\mathrm{L}}\ \Delta V^{\ddagger}_{p(\mathrm{Y,L})} \right] + f_{\mathrm{L}}\ \Delta V^{\ddagger}_{\mathrm{isc}} \\ & + \left[f_{\mathrm{U}}\ \Delta V^{\ddagger}_{\mathrm{Y,U}} + \Delta V^{\ddagger}_{\tau(\mathrm{U})} + f_{\mathrm{U}}\ \Delta V^{\ddagger}_{p(\mathrm{Y,U})} \right]\end{aligned} \tag{6}$$

in which f_{L} and f_{U} are the fractions of product formed from the lower and upper states, respectively ($f_{\mathrm{L}} + f_{\mathrm{U}} = 1$).

If population of all but the highest energy state occurs by means of a sequential cascade through states of decreasing energy, then eqn. (6) can be generalized in order to consider n states (the state populated by absorption being designated by $j = 1$)

$$\Delta V^{\ddagger}_{\phi(\mathrm{Y})} = \sum_{j=1}^{n} f_j \left[\Delta V^{\ddagger}_{\mathrm{Y},j} + \Delta V^{\ddagger}_{\tau(j)} + \Delta V^{\ddagger}_{\tau(j-1)} + \Delta V^{\ddagger}_{(j-1)\to j} + \Delta V^{\ddagger}_{p(\mathrm{Y},j)} \right] \tag{7}$$

where eqn. (7) is used for $\Delta V^{\ddagger}_{\tau(j)}$, $\Delta V^{\ddagger}_{(j-1)\to j}$ is the volume of activation for crossing from the ($j - 1$)th state to the jth state

$$\Delta V^{\ddagger}_{0\to 1} = 0,\ \Delta V^{\ddagger}_{\tau(0)} = 0 \text{ and } \sum_{j=1}^{n} f_j = 1$$

(c) Two photoactive excited states with only a single channel for relaxation of the lower state

Most discussions of the behavior of the lowest energy doublet state of Cr(III) have postulated a single channel for escape from the doublet state (see below). Equation (5) reduces to

$$\phi(\mathrm{Y}) = \eta_{\mathrm{isc}} p_{\mathrm{Y,L}} + k_{\mathrm{Y,U}} \tau_{\mathrm{U}} p_{\mathrm{Y,U}} \tag{8}$$

in this limit, since $\tau_L^{-1} = k_{Y,L}$, and assuming competitive kinetics apply to the upper state; $p_{Y,L}$ in eqn. (8) is to be interpreted as the probability of product formation once the barrier for escape from the lower state has been passed. Equation (8) leads to

$$\Delta V^{\ddagger}_{\phi(Y)} = \left[f_L\ \Delta V^{\ddagger}_{p(Y,L)}\right] + f_L\ \Delta V^{\ddagger}_{isc} + \left[f_U\ \Delta V^{\ddagger}_{Y,U} + \Delta V^{\ddagger}_{\tau(U)} + f_U\ \Delta V^{\ddagger}_{p(Y,U)}\right] \quad (9)$$

and

$$\Delta V^{\ddagger}_{\tau(L)} = -\Delta V^{\ddagger}_{Y,L} \quad (10)$$

The important feature of this limit is that $\Delta V^{\ddagger}_{\phi(Y)}$ mainly reflects properties of the upper state while $\Delta V^{\ddagger}_{\tau(L)}$ contains only terms describing the channel for escape from the lower state.

(d) More complex situations

Two possible variations in behavior should be mentioned: (a) two photoactive states with the upper and lower states in equilibrium; (b) two photoactive states with fast reaction behavior in the upper state.

(1) Equilibrium between the upper and lower states. The equilibrium coupling of the upper and lower states would result in a single lifetime characterizing both states, and the kinetic pathways of the upper and lower states would be coupled via the equilibrium. For K, the ratio of lower to upper state populations

$$\phi_Y = \tau\left[K k_{Y,L} p_{Y,L} + k_{Y,U} p_{Y,U}\right]/(1 + K)$$

In this limit, the observed pressure dependence of the quantum yield will contain a substantial contribution originating from the difference in partial molar volumes in the upper and lower states.

(2) Fast kinetic behavior of the upper state. In this limit τ_U is undefined and one can only define probabilities of the various processes ($p_{i,U}$). This would result in

$$\Delta V^{\ddagger}_{\phi(Y)} = f_L\ \Delta V^{\ddagger}_{Y,L} + f_L\ \Delta V^{\ddagger}_{\tau(L)} + f_L\ \Delta V^{\ddagger}_{p(Y,L)} + f_L\ \Delta V^{\ddagger}_{isc} + \left[\sum_i \Delta V^{\ddagger}_{p(i,U)}\right] f_U$$

if competition kinetics were appropriate to the lower state. Interpretation of the $\Delta V^{\ddagger}_{p(i,U)}$ terms is bound to be very difficult.

(vii) The role of chemical intermediates

The cleavage of a metal–ligand bond results in the formation of a new chemical species. Similarly, a new chemical species is formed if an entering ligand binds to the metal before the leaving group departs. The changes in coordination which are characteristic of ligand-field photochemistry must, by definition, involve chemical intermediates at some stage along the excited-state-to-product reaction coordinate. The intermediates are not necessarily "innocent"; i.e., their lifetimes may be long enough so as to allow some of the observed chemical changes to take place in the chemical intermediates rather than in the electronic excited states of the original compound. In evaluating the potential role of intermediate chemical species, it is very important to keep in mind that the intermediates formed from high energy excited states may well behave differently from the intermediates involved in the chemical reactions of thermally equilibrated ground states. The detection of intermediate species can also be a problem. Free radical intermediates, as generated in photoredox reactions, tend to decay by means of second order kinetic pathways so that their lifetimes are often sufficiently long enough so as to permit their direct observation. Substitutional intermediates which differ in coordination number from the thermally equilibrated complexes, decay by means of first order kinetic pathways and are likely to have lifetimes so short that direct detection becomes very difficult.

Extensive studies of nominally pentacoordinate intermediates generated by various means from ground state cobalt(III) complexes, have, by and large, indicated that the detailed chemistry of these intermediates depends on their means of generation. This implies that such species are so short lived that, generally, they do not have time to achieve the equilibrium geometry (e.g., trigonal bipyramid or square pyramid) appropriate to the five coordinate species [40–44]. Such transient intermediates are not well-defined chemical species.

(viii) Summary and scope

This section has sketched the basic requirements for a discussion relating transition metal excited state structure to photochemical reactivity. All the required information is rarely available, even in the most studied systems. In this review we examine the photochemical events which follow excitation of the metal-centered, *d–d* (ligand field) chromophores that are characteristic of transition metal complexes. The approaches sketched are applied, insofar as available information permits, in order to elucidate those structural features which dictate the probability of evolution of the excited system into various photoproducts. This is still a very ambitious goal.

B. LIGAND FIELD PHOTOCHEMISTRY

The redistribution of electron density in metal-centered *d*-orbitals generates "ligand field excited states" which are generally many orders of magnitude more labile towards substitution than is the electronic ground state. The solvolysis reactions of ligand field excited state species are often remarkably selective, and are often accompanied by seemingly well-defined stereochemical changes. The details of these reactions have been discussed extensively during the past twenty years [45–48]. In addition, the mechanistic aspects have been the subject of several recent reviews [6,49–55].

During the past 18 years most of the stimulus for ligand field photochemistry has derived from Adamson's "empirical rules" [20]:

(1) The substituted ligand is situated on the axis characterized by having the weakest ligand field strength.

(2) Of the two ligands situated on the labilized axis, the leaving ligand is the one exhibiting larger field strength.

In addition to the numerous experimental studies that have been stimulated by these "rules", several theoretical studies, inferring the orbital populations and correlations in electronically excited species, have attempted to find a general theoretical basis for such "rules", and for the apparent exceptions [8–19,56]. Of these approaches, that of Vanquickenborne and Ceulemans has been found to be reasonably useful by many experimenters (see reviews cited above).

For the discussions in this review, we have selected material which bears on the relationship between transition metal complex structure (geometrical or electronic) and photochemical reactivity. More comprehensive coverage of other aspects of the subject may be found in the reviews cited. The philosophy of our approach has been outlined in the preceding section. Because the structural information is relatively well established, we have taken $M(NH_3)_6^{n+}$ complexes as the focal point in the discussion of each class of complexes. Systems with other symmetries, where no actual experimental information is available, are approached in terms of the effects expected due to deviations from hexaamine symmetry. Owing to their photosensitivity and detailed spectroscopy, chromium(III) complexes tend to be paradigmatic of the issues in this area. The issues to be addressed include:

(1) Is there a well defined excited state from which ligand field photochemistry occurs?

(2) If so, what is the electronic configuration and what is the equilibrium geometry of the molecule in this state?

(3) To what extent are the excited state relaxation channels dictated by (i) kinetic (i.e., nuclear reorganizational energies and electronic selection rules) or by (ii) thermodynamic (state energies, etc.) factors?

(4) What is the role of chemical intermediates?

(i) Chromium(III)

The chemical transformations which follow ligand field excitation of chromium(III) complexes generally have the following characteristics (based on Kirk's reviews, [53,54]):

(1) Quantum yields tend to be large (10–40% of the light absorbed usually results in product formation).

(2) Several products result.

(3) Quantum yields of the predominant products vary little for different excitation wavelengths whereas yields of minor products often vary with the excitation wavelength.

(4) The predominant chemical product is usually in accord with Adamson's rules.

(5) Axial labilization is frequently associated with net *trans* → *cis* isomerization.

(6) Some, often more than 50%, of the yield of products is quenched when the long lived phosphorescence doublet is quenched; in a few such studies little difference has been found between the dominant product species originating from the quenchable and unquenchable reaction channels.

The spectroscopic region probed by excitation generally contains spin allowed quartet absorptions (molar absorptivities 10–10^2 M^{-1} cm^{-1}) and spin forbidden doublet absorptions (molar absorptivities less than 1 M^{-1} cm^{-1}). The quartet absorptions at room temperature are broad and the 0–0 vibronic component is difficult to identify. However, in some instances the energy of the equilibrated quartet state is equal to or less than the energy of the doublet state, and a broad fluorescence is observed with an emission maximum which is considerably Stokes shifted [57]. These features of the quartet spectroscopy imply an appreciable difference in equilibrated excited state and ground state molecular geometries; e.g., in $Cr(NH_3)_6^{3+}$ the excited state distortion (relative to the ground state) of the lowest quartet has been identified by Wilson and Solomon [21] as a substantial (12 pm) equatorial expansion associated with a distortion coordinate belonging to the e_g symmetry class and a smaller (a_{1g}) axial contraction (2 pm).

In contrast to quartet state spectroscopy, absorption and emission spectra of the lowest energy doublet states tend to be characterized by collections of very narrow bands, to exhibit little Stokes shift, and to have a readily identifiable 0–0 vibronic transition. As a consequence, the lowest energy doublet state, ^2E_g in the O_h-point group, can often be inferred to have the same molecular geometry as the ground state.

The $^2T_{1g}$ state (O_h point group) usually has slightly greater energy than the ^2E_g. These two doublet states have the same electronic origin (^2G in the free ion) and the same formal orbital populations (t_{2g}^3), but very little is known about the properties of the higher energy doublet states. The energy difference between the lowest energy components of the $^2T_{1g}$ and ^2E_g states changes appreciably with variations in microsymmetry and with ligand field splitting energy [58]. It has been suggested that components of the $^2T_1$ state become lower in energy than the ^2E state for certain π-donor ligands (i.e., F^- and OH^-), that the emission from these components of the $^2T_1$ parent is appreciably broader than one normally finds for the ^2E emission [59], and that these $^2T_1$ emissions are exceptionally sensitive to the nature of the solvent, their maxima being shifted to shorter wavelengths in hydroxylic solvents [60]. These effects have been attributed to variations in the equilibrium nuclear coordinates of the respective ground states and the low-energy components of their $^2T_1$ excited states [59,60].

The unquenchable portion of the observed photochemistry is often described as "prompt" (*Type IA* behavior) and is ascribed to reactions in a quartet excited state. Several detailed limiting mechanisms may be distinguished.

(Q-1) The vibrational modes activated by absorption, predominantly t_{1u} modes, mediate the reaction as the excited system approaches vibrational equilibrium [6,61], since any chemical process which competes with vibrational relaxation must occur too rapidly ($k_p > k_v \geq 10^{11}$ s^{-1}) for the system to achieve the normal mode populations appropriate to the lowest energy transition state.

(Q-2) The excited state orbital population gives rise to an increase in bond lengths; the longer, weaker bonds are correlated with enhanced excited quartet state reactivity [8–18]. This very popular approach can be considered to be equivalent to relaxation of the Franck–Condon excited state (the theoretical descriptions have employed parameters appropriate to the ground state geometry) along a "natural coordinate" of e_g symmetry (correlating with the distortion of the vibrationally equilibrated quartet state), followed by reaction of the equilibrated quartet.

(Q-3) Reaction occurs following internal conversion from the excited quartet to vibrationally excited species on the ground state potential energy surface [62]. The point of entry and the vibrational modes activated upon entry into the ground state surface would dictate whether or not this relaxation pathway resulted in product formation. Entry near a transition state for ground state reactions could be regarded as entry onto the potential energy surface of a reaction intermediate.

The quenchable part of the photoreaction has been the subject of considerable controversy. Two limiting mechanisms have been most frequently discussed:

(D-1) Direct reaction of the doublet state [63–65]. We interpret this to be a reaction giving products which are electronically correlated to the doublet state.

(D-2) Back intersystem crossing from the doublet to the excited quartet state followed by the characteristic quartet state reactions [53,66].

An additional limiting mechanism has been proposed [62] but it has rarely been used:

(D-3) The chemical transformations follow intersystem crossing to the potential energy surface of a ground state intermediate species.

The quenching of these excited complexes tends to involve an intimate mechanism, often with an excited cationic complex and with $Cr(CN)_6^{3-}$ as the quencher. Most limiting mechanisms assume that the quencher does not significantly perturb the potential energy surface of the doublet or quartet states. A more detailed consideration of the mechanistic possibilities is deferred until the discussion of some specific systems. However, it is noteworthy that there has been an increasing focus on the possible role of intermediates in chromium(III) photochemistry, with Vanquickenborne and Ceulemans especially [14–19], throughout their treatment, emphasizing that a dissociative excited state reaction will yield a coordinatively unsaturated transient molecule, and that rearrangements of the transient intermediate could well account for the observed overall *trans* to *cis* isomerizations.

(a) $Cr(NH_3)_6^{3+}$

Ligand field excitations result in a single product, $Cr(NH_3)_5OH_2^{3+}$, with a quantum yield of 0.45 [53,67]. There is no evidence available regarding stereochemical changes. About 75% quenching of products accompanies doublet quenching [68,69], and photoanation has been found to compete with photoaquation [70]. The Arrhenius activation energy for photo-aquation is 4 kJ mol^{-1} [53]. This is about 1/8 the activation energy for relaxation of $(^2E_g)Cr(NH_3)_6^{3+}$.

High resolution, solid state absorption spectroscopy at very low temperatures has been used to map out key features of the lowest excited state potential energy surfaces [21]. The ^2E_g state has the ground state geometry and is 15300 ± 100 cm^{-1} higher in energy than the $^4A_{2g}$ ground state. In the low temperature solid state study, $E(^4T^0_{2g}) - E(^2E^0_g)$ was found to be 4.9×10^3 cm^{-1}; in water at room temperature this energy has been estimated to be 4×10^3 cm^{-1} [71]. These parameters have been used for the ordering of potential energy surfaces in Fig. 1.

The activation energy for thermal hydrolysis of $Cr(NH_3)_6^{3+}$ is 109 kJ mol^{-1} [72]. This value can be used as the dissociation limit for the ground state surface (Fig. 3). Although the mechanism for this process inferred from related complexes, such as $Cr(NH_3)_5OH_2^{3+}$, has been one of associative interchange [73–75], varius claims regarding the degree of dissociative character present have also been made [76]. In any event it is unlikely that there is much difference (probably less than 12 kJ mol^{-1}) in activation

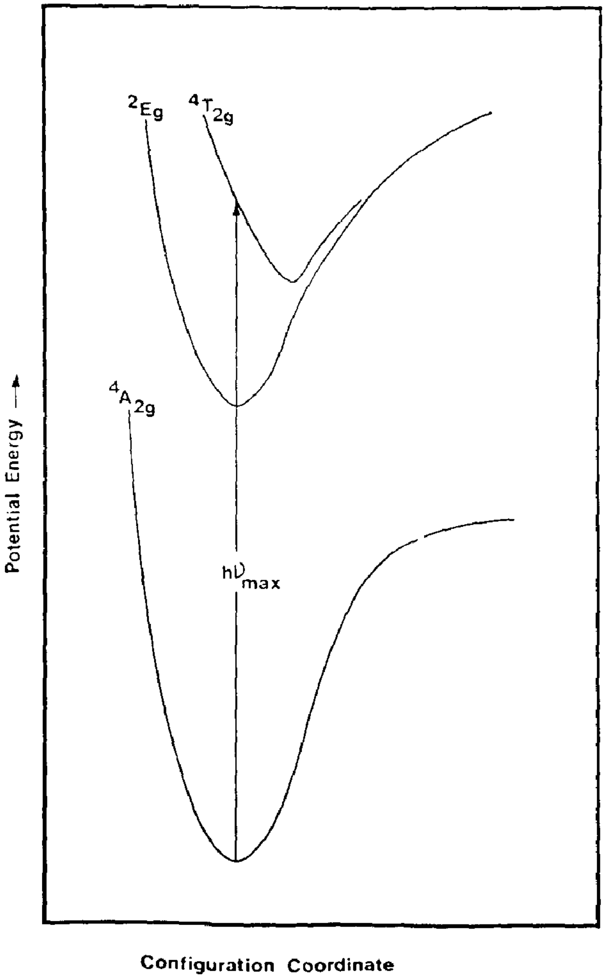

Fig. 3. Qualitative potential energy surfaces for $Cr(NH_3)_6^{3+}$ allowing for a substitutional reaction channel.

energy between the two pathways. It is conceptually a little easier to discuss the dissociative pathway and, hence, photochemists have usually treated the excited state process as being dissociative. For simplicity, and for a more straightforward connection with most photochemical treatments, we initially consider the dissociative pathway.

The dissociative thermal hydrolysis pathway involves the stretching to dissociation of a single $Cr-NH_3$ bond. The net nuclear motion involved is "ungerade", but representation of the motions involved in terms of skeletal vibrational modes requires contribution from many modes [77]. More specifically, deformation modes as well as stretching modes are required. A facile low energy dissociative pathway of the excited state must necessarily result in some distortion of shape of the excited state potential energy surface. The shape of the potential energy surface is reflected in the vibrational frequencies (and force constants). The t_{1u} and t_{2u} modes are promoting modes for *d–d* electronic transitions and may be obtained for the ground and excited states from electronic absorption and emission spectroscopy or from infrared and Raman spectra. The available information is summarized in Table 1. It is clear that the t_{1u} and t_{2u} normal vibrational modes are of similar energy in the $^4A_{2g}$ and ^2E_g states of $Cr(NH_3)_6^{3+}$; for the stretch, buckle and twist respectively, the average values from Table 1 are 470 ± 2, 264 ± 3, 210 ± 2 cm^{-1} for $^4A_{2g}$ and 472 ± 6, 263 ± 5, 209 ± 7 cm^{-1} for ^2E_g. The similarity of these vibrational parameters and the similar equilibrium bond lengths suggest that the activation barriers for simple dissociative Cr–NH_3 hydrolysis (not involving changes in electronic configuration) must also be similar in the $^4A_{2g}$ and ^2E_g states of $Cr(NH_3)_6^{3+}$.

Since $(^4T_{2g}^0)Cr(NH_3)_6^{3+}$ is distorted predominately along an e_g vibrational coordinate [21], any configurational mixing of the $^4T_{2g}$ and ^2E_g states is likely to be manifested in the e_g vibrational mode of the lower energy state. That the e_g mode appears to contribute to the combination bands of several vibronic progressions of the $^2E_g \rightarrow {}^4A_{2g}$ emission is evidence of such configurational mixing [23]. However, similar values of ν_{e_g} are inferred for the ground state and ^2E_g potential energy surface near its minimum. Bigger differences would be expected in the overtone frequencies.

The similarities in the molecular geometry and vibrational parameters of the ^2E_g and $^4A_{2g}$ states of $Cr(NH_3)_6^{3+}$ indicate that their respective potential energy surfaces are parallel and render unlikely simple substitution reactions producing electronically correlated products on this excited state surface. Owing to the alterations of bond length ($\sim$ 12 pm) and vibrational frequencies in the thermally equilibrated $^4T_{2g}$ state, similar considerations do lead to a smaller activation barrier for substitution on this particular potential energy surface. Owing to the differences in orbital occupation, an associative pathway could be relatively more important for the $^4T_{2g}^0$ than for the $^2E_g^0$ or $^4A_{2g}^0$ states.

It is clear that the above considerations *do not* lead to a meaningful description of the photoreaction coordinate for $Cr(NH_3)_6^{3+}$. Nevertheless, the overall quantum yield is very large, $\phi(Y) = 0.45$, and even population of the doublet state results in appreciable product formation [61]: quenching of 75% of the reactivity when the doublet is quenched implies $0.34 \leq \eta_{i,D} \leq 1.0$ and $1\ s^{-1} < (k_{i,D} \times 10^{-5}) < 5\ s^{-1}$. Thus, the effective "activation" barrier must be 100 kJ mol^{-1} smaller in the ^2E_g than in the $^4A_{2g}$ state. "Back intersystem crossing", $^2E_g^0 \rightarrow {}^4T_{2g}^0$, seems an energetically unfavorable possibility; even if one allows for some "down shifting" of $E(^4T_{2g}^0)$ between 5 and 300 K (over this range $E(^4T_{2g}^0)$ of ruby decreases ~ 300 cm^{-1}; [31]), $E(^4T_{2g}^0) - E(^2E_g^0)$ must be at least 4×10^3 cm^{-1}. The mechanisms for the

TABLE 1

Comparison of vibrational and structural parameters for different $Cr(NH_3)_6^{3+}$ electronic states

Electronic state	Method [a]	Conditions	Cr–N bond length (pm)	Vibrational mode [b] (frequencies in cm^{-1})					
				a_{1g}	e_g	t_{1u} (stretch)	t_{1u} (buckle)	t_{2g}	t_{2u} (twist)
$^4A_{2g}$	IR/Raman [c]	Solid; 273 K	206 [d]	465	412	468.5	268	270	
	Emission [e]	Solid; 80 K (ClO_4^-)			422 [f]	476	264**		212*
		Solid; 80 K (PF_6^-)			427 [f] (395) [g]	470	258**		194*
	Emission [h]	DMF soln; 230 K				~ 465	259**		212*
^2E_g	Absorption [i]	Solid; 6 K	206 [i]			478	267*		225*
	Emission [e]	Solid; 80 K (ClO_4^-)				466 [j]	252* [j]		191* [j]
		Solid; 80 K (PF_6^-)			(401) [f,g]	459 [j]	250		183*
	Emission [h]	DMF soln; 230 K					258*		215*
$^4T_{2g}$	Absorption [i]	Solid; 6 K	218, 204 [i]	403	403				

[a] Assignments based on: (i) solid state infrared, solution Raman coupled with normal coordinate analysis for "IR/Raman" [130]; (ii) vibronic structure of ^2E emission for "Emission"; and (iii) vibronic structure of $^4A_{2g} \rightarrow {}^2E_g$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ absorptions for "Absorption". [b] Dominant promoting modes indicated ** (strongest), * (next strongest). [c] [130]. [d] [131]. [e] [23]. [f] Based on the vibronic progressions in emission [23]. [g] For $Cr(ND_3)_6^{3+}$ [23]. [h] [95]. [i] [21]. [j] Measured at room temperature [23].

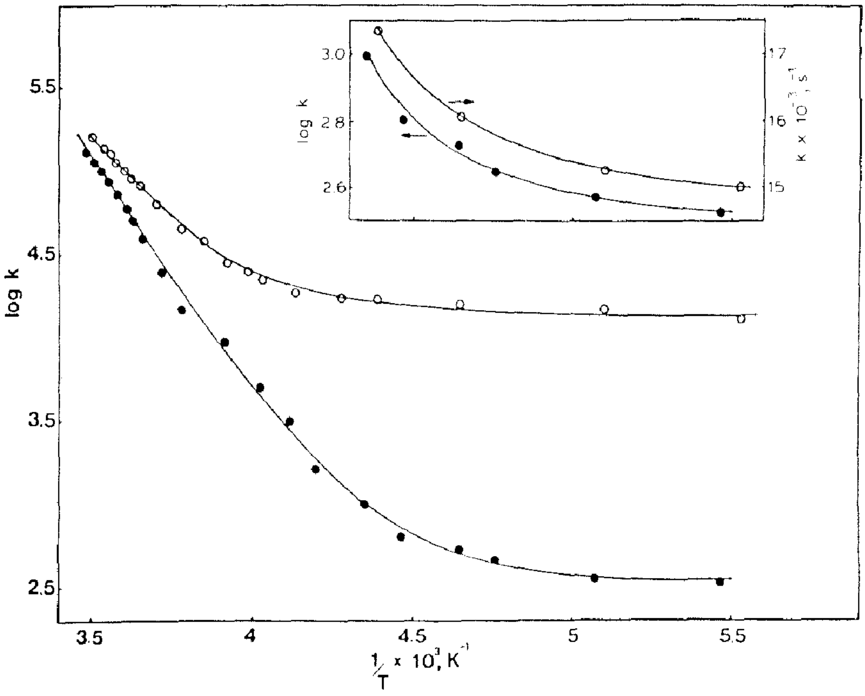

Fig. 4. Temperature dependencies of the ^2E_g lifetimes for $[Cr(NH_3)_6](ClO_4)_3$ (open circles) and $[Cr(ND_3)_6](ClO_4)_3$ (closed circles) in DMF–$CHCl_3$ solution. Inset expands the rate constant scale in the low temperature regime. From [79].

excited state substitution process almost certainly must involve a "jump" to a ground state potential energy surface, i.e., some conversion of electronic excitation energy to vibrational excitation energy. The detailed mechanism of this process is not yet clear, but the observation of significantly smaller values of k_{nr} for $(^2E_g)Cr(ND_3)_6^{3+}$ than for $(^2E_g)Cr(NH_3)_6^{3+}$ (Fig. 3; [78,79]) probably indicate an important contribution from nuclear tunneling and also a strong coupling [80] mechanism for relaxation of the ^2E_g state under conditions where the photoreactions occur. The implications of these observations are explored more fully in sections B(i) (e) and B(i) (f).

Two different surface crossings should be considered: (a) $^2E_g \rightarrow {}^4A_{2g}$ relaxation ("hot ground state"); and (b) ^2E_g relaxation to a potential energy surface of some "intermediate" different from the $Cr(NH_3)_6^{3+}$ ground state. One expects that the nested ^2E_g and $^4A_{2g}$ $Cr(NH_3)_6^{3+}$ potential energy surfaces are only weakly coupled, and that any crossing between these surfaces should be relatively inefficient. Such an inefficient (or weakly coupled) crossing appears to dominate the excited state relaxation in the low temperature regime where k_{nr} becomes nearly temperature independent (e.g. Fig. 4), and where the photochemical reactions are also quenched.

Direct $^2E_g \rightarrow {}^4A_{2g}$ relaxation, (a) (above), is the limiting low temperature relaxation process. There are a number of Cr(III) complexes with macrocyclic ligands in which this pathway is the dominant doublet excited state relaxation mode even in water at 25°C (see below). There are certain to be a number of systems in which the (a) and (b) pathways are competitive.

The second possibility, (b), is more interesting from a photochemical point of view. Some related suggestions have been made by Krause and Wasgestian [70,81]. The limiting intermediates to consider are the $Cr(NH_3)_5^{3+}$ and $Cr(NH_3)_6S^{3+}$ (S, a solvent molecule) species such as would be generated in limiting dissociative and associative substitutional pathways, respectively, of the ground state. The relationship between these limiting intermediates and their excited state precursors is discussed in some detail in section B(i) (e). Since thermally generated, five coordinate complexes seem to be too short lived to be treated as well defined chemical species [40–44], the excited state relaxation pathways associated with these limiting intermediate structures might be best considered to correspond to the respective chemically induced relaxation trajectories. For convenience, we shall refer to the species generated along these "chemically induced relaxation trajectories" as "intermediates" but we do not intend to imply that such "intermediates" must be considered as chemically well defined species in the sense of being at vibrational equilibrium with the medium.

Since the ^2E_g and the $^4A_{2g}$ states are nested, and since the respective potential energy surfaces of $Cr(NH_3)_6^{3+}$ appear to be similar in shape (at least near their equilibrium nuclear configurations), one would expect that the dominant substitution pathways on these surfaces would be parallel (or approximately nested). Thus, there is no obvious basis for strong coupling between the corresponding reaction coordinates. However, intermediates with accessible energies most often have quartet spin multiplicities (see section B(i) (e), and a chemically induced relaxation trajectory must involve spin relaxation and some contribution from excited quartet state configuration coordinates [77].

Any model accounting for the ambient temperature behavior of $(^2E_g)Cr(NH_3)_6^{3+}$ must take into account the medium dependence of the excited state relaxation rate [82]. This is most dramatically illustrated in the contrast between the doublet state lifetimes in solution and in the dilute solid state (Fig. 5). That the solid state lifetime near ambient temperatures is little different from the low temperature limiting lifetime demonstrates that the solvent plays a dynamic role in quenching the $(^2E_g)Cr(NH_3)_6^{3+}$ excited state. It is difficult to see how a limiting dissociative pathway, whether or not it involves back intersystem crossing, can account for such a strong medium dependence of the lifetime: i.e., a facile bond breaking process should quench the excited state regardless of the environment. On the other

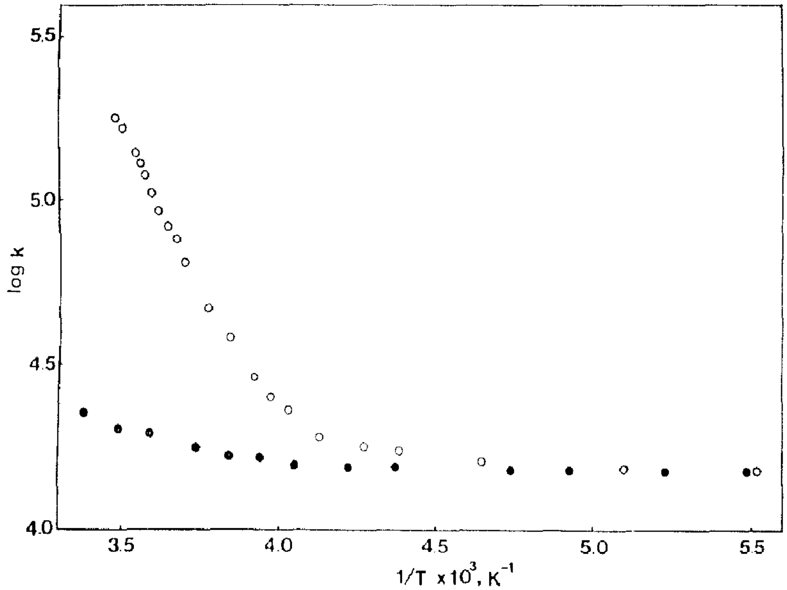

Fig. 5. Contrast in $(^2E_g)Cr(NH_3)_6^{3+}$ lifetimes in fluid DMF/CHCl$_3$ solutions (open circles) and in the crystalline solid $[Cr(NH_3)_6]Cl_3$ doped into $[Ru(NH_3)_6]Cl_3$ with Cr:Ru = 1:30; closed circles). From [79].

hand, studies of photoanation indicate that this process must occur after the excited state enters the relaxation trajectory (i.e., photoanation is not accompanied by ^2E_g state quenching [70,81,83]). While the partitioning of non-radiative processes between reactive and non-reactive relaxation of $(^2E_g)Cr(NH_3)_6^{3+}$ is not well documented in the different media, the rate constants for non-radiative relaxation at room temperature run around 5×10^5 s^{-1} [82], at least comparable in magnitude to the photosubstitution rate.

A successful model for the photochemistry and photophysics of $Cr(NH_3)_6^{3+}$ in fluid solution must be consistent with the pressure dependence of the photochemical and photophysical parameters. For this complex in water at 25°C, $\Delta V^{\ddagger}_{\phi(Y)}$ is reported to be -6.7 ± 0.5 cm^3 mol^{-1} [84] and $\Delta V^{\ddagger}_{\tau}$ is reported to be -4.3 ± 0.4 cm^3 mol^{-1} [85]. The difference in the partial molar volumes of the lowest energy quartet and doublet electronic excited states has been estimated to be 3–4 cm^3 mol^{-1} for $Cr(NH_3)_6^{3+}$ [85]. These observations can be used along with the various models of excited state behavior to give some insight into the nature of the possible excited state relaxation channels.

In the limit of there being a single channel for relaxation of the doublet state, $\Delta V^{\ddagger}_{\tau(D)}$ and $\Delta V^{\ddagger}_{\phi(Y)}$ can be loosely viewed as activation volumes for the relaxation channels characteristic of the doublet and quartet electronic states, respectively. Thus, it appears that transition states for relaxation of the doublet require an expansion of volume, while relaxation of the quartet requires a decrease.

For the direct reactions model (D-1) we have

$$\phi(\mathrm{Y}) = \eta_{\mathrm{isc}} p_{\mathrm{Y,D}} = k_{\mathrm{Y,Q}} \tau_{\mathrm{Q}} p_{\mathrm{Y,Q}}$$

If we assume $p_{\mathrm{Y,D}} = p_{\mathrm{Y,Q}} = 1$ then the values of $\Delta V^{\ddagger}_{\mathrm{Y,Q}}$ and $\Delta V^{\ddagger}_{\mathrm{Y,D}}$ are -50 ± 20 and $+4.3$ cm^3 mol^{-1} respectively (see summary in Table 2). Thus this model would appear to require an associative pathway for quartet reaction and a dissociative pathway for doublet reactions.

For the back intersystem crossing model (D-2) we must allow for multiple passes of the electronically excited system through the two excited states; thus

$$\phi(\mathrm{Y}) = \eta_{\mathrm{Y,Q}} p_{\mathrm{Y,Q}} \left(1 + \sum_{n=1}^{\infty} \eta^{n}_{\mathrm{isc}} \right)$$

If we assume $p_{\mathrm{Y,Q}} = 1$, then the experimental parameters result in $\eta_{\mathrm{isc}} = 0.75$, $\eta_{\mathrm{Y,Q}} = 0.12$, and $\Delta V^{\ddagger}_{\mathrm{Y,Q}} = -13 \pm 4$ cm^3 mol^{-1} (in obtaining this estimate we have allowed $\Delta V^{\ddagger}_{\mathrm{ic}}$ and $\Delta V^{\ddagger}_{\mathrm{isc}}$ to vary between 0 and -4 cm^3 mol^{-1}). Thus, the back intersystem crossing model is only consistent with a strongly associative reaction pathway. This very negative value of $\Delta V^{\ddagger}_{\mathrm{Y,Q}}$ is definitely not consistent with a dissociative pathway such as that proposed by Vanquickenborne and Ceulemans [14,15,17–19].

The third single channel mechanism (D-3) proposes surface crossing to a ground state reaction intermediate. If back intersystem crossing is neglected, then

$$\phi(\mathrm{Y}) = \eta_{\mathrm{isc}} p_{\mathrm{Y,D}} + \eta_{\mathrm{Y,Q}} p_{\mathrm{Y,Q}}$$

If we assume that the quartet and doublet reaction channels result in formation of the same transition state (i.e., that $\Delta V^{\ddagger}_{\mathrm{Y,D}} = \Delta V^{\ddagger}_{\mathrm{Y,Q}} + 3.5$ cm^3 mol^{-1}) and that the ground state and product species are formed by a partitioning of the trajectories after the transition state has been formed in both the quartet and doublet states, then the pressure effects are attributed to a small volume increase along the thermally activated pathway for $(^2E_g)\mathrm{Cr(NH_3)_6^{3+}}$ relaxation and a small decrease of p_{Y} with increasing pressure.

If there are several kinetically competitive channels for relaxation of the doublet state, the analysis of the observed pressure effects becomes correspondingly more complex. It has been common practice to assume that only two channels dominate doublet state relaxation (non-radiative relaxation to the ground state and reaction), and this assumption, coupled with the

TABLE 2

Mechanistic implications of the effect of pressure variations on $Cr(NH_3)_6^{3+}$ photochemistry and photophysics under ambient conditions

Experimental parameters		Single channel models			Multiple channel model
		(1) Direct reaction	(2) B.I.S.C.	(3) Crossing to intermediate	
$\Delta V^{\ddagger}_{\phi(Y)}$, cm^3 mol^{-1}	-6.7 ± 0.5 [a]				
$\Delta V^{\ddagger}_{\tau(D)}$, cm^3 mol^{-1}	-4.3 ± 0.4 [b]				
f_Q	0.25 [c]				
f_D	0.75 [c]				
$\phi(Y)$	0.45 [d]				
Calculated (or assumed) [e] parameters					
$\eta_{Y,Q}$		0.12	0.12	0.25 [j]	0.12
η_{ic}		0.55	0.13	0.25 [j]	(0)
η_{isc}		0.33	0.75	0.75	0.88
$\eta_{Y,D}$		[f]	[f]	[f]	0.34
η_{nr}		[f]	[f]	[f]	0.66
$p_{Y,Q}$		(1)	(1)	0.45 [h]	(1)

$p_{Y,D}$	(1)	[f]	0.45 [h]	(1)
$\Delta V^{\ddagger}_{Y,Q}$, cm^3 mol^{-1}	-50 ± 20	-13 ± 2 [g]	[i]	-7.3 ± 2 [j]
$\Delta V^{\ddagger}_{ic}$, cm^3 mol^{-1}	-1.5 ± 3	0	[i]	
$\Delta V^{\ddagger}_{isc}$, cm^3 mol^{-1}	-1.5 ± 3	0.8 ± 0.9	[i]	(-4)
$\Delta V^{\ddagger}_{Y,D}$, cm^3 mol^{-1}	$+4.3$	[f]	$+4.3$ [f]	-3.8 ± 2 [j]
$\Delta V^{\ddagger}_{nr}$, cm^3 mol^{-1}	[f]	[f]	$+4.3$ [f]	$+8.3 \pm 2$
$\Delta V^{\ddagger}_{p(Y,Q)}$, cm^3 mol^{-1}	(0)	(0)	-7 ± 1 [h]	(0)
$\Delta V^{\ddagger}_{p(Y,D)}$, cm^3 mol^{-1}	(0)	(0)	-7 ± 1 [h]	(0)

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[a] [84]. [b] [85]. [c] [68]. [d] [67]. [e] Values listed in parentheses have been assumed to establish limiting conditions. [f] Only one channel is defined for relaxation of the doublet state. [g] For $\Delta V^{\ddagger}_{ic} = 0$ cm^3 mol^{-1}. [h] In this model it is assumed that return to the ground state and formation of products occur after entry into the relaxation channel, so $\eta_{r,Q} = \eta_{Y,Q} + \eta_{ic}$ and $\eta_{r,D} = \eta_{Y,D} + \eta_{nr}$; where $\eta_{r,i}$ is the total relaxation efficiency of the state i. For purpose of this calculation we have assumed a common intermediate is generated from the doublet and the quartet states. [i] Competing contributions to this term approximately cancel in this limit. [j] For these estimates it was assumed that the same intermediate is formed from the quartet and doublet states so that $\Delta V^{\ddagger}_{Y,D} = \Delta V^{\ddagger}_{Y,Q} + 3.5$ cm^3 mol^{-1}.

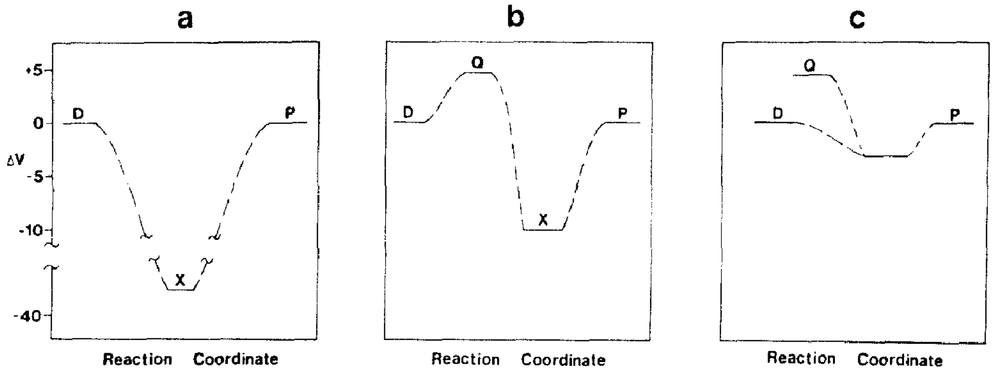

Fig. 6. Volume profiles for several models of $Cr(NH_3)_6^{3+}$ excited state behavior: (a), direct reaction of the doublet state in the single channel limit (D-1); (b), back intersystem crossing as the only channel for doublet state relaxation (D-2); (c), two kinetically competitive channels available for relaxation of the doublet state. The possibility of surface crossing to an intermediate is not illustrated since the construction of this model used in Table 2 did not permit evaluation of $\Delta V^{\ddagger}_{Y,Q}$.

additional assumptions that back intersystem crossing can be neglected and that $p_{Y,D} = p_{Y,Q} = 1$, leads to

$$\begin{aligned}\Delta V^{\ddagger}_{\Phi(Y)} = {} & f_D(1-\eta_{Y,D})\,\Delta V^{\ddagger}_{Y,D} + (f_Q-\eta_{Y,Q})\,\Delta V^{\ddagger}_{Y,Q} \\ & -f_D\eta_{nr}\,\Delta V^{\ddagger}_{nr} - \eta_{ic}\,\Delta V^{\ddagger}_{ic} + (f_D-\eta_{isc})\,\Delta V^{\ddagger}_{isc} \qquad (11)\end{aligned}$$

$$\Delta V^{\ddagger}_{\tau(D)} = -\eta_{Y,D}\,\Delta V^{\ddagger}_{Y,D} - \eta_{nr}\,\Delta V^{\ddagger}_{nr} \qquad (12)$$

If we adopt a model in which the quartet and doublet relaxation channels involve the same transition state and in which $\eta_{ic} = 0$, then (11) and (12) can be combined to give $\Delta V^{\ddagger}_{Y,Q} \approx -7.3$ cm^3 mol^{-1} and $\Delta V^{\ddagger}_{nr} \approx 8.3$ cm^3 mol^{-1} as summarized in Table 2.

Volume profiles for these different models of the photophysical behavior of $Cr(NH_3)_6^{3+}$ are illustrated in Fig. 6.

While neither the spectroscopic studies nor the pressure effects reviewed above unambiguously support any one model for the excited state behavior of $Cr(NH_3)_6^{3+}$ over any other model, these studies do place significant constraints on the viable mechanisms. Of the proposed limiting mechanisms for single channel relaxation of the $(^2E)Cr(NH_3)_6^{3+}$ excited state:

(a) Direct substitution in $(^2E)Cr(NH_3)_6^{3+}$ to give an electronically correlated intermediate (D-1) is energetically prohibitive along a dissociative reaction coordinate and an associative reaction is inconsistent with the sign of $\Delta V^{\ddagger}_{\tau(D)}$, so this does not seem to be a viable mechanistic alternative.

(b) Back intersystem crossing as the single channel for doublet relaxation (D-2) is qualitatively consistent with the observed pressure effects if the products are formed along an associative pathway; however, a dissociative pathway has been assumed in the majority of discussions concerning this model (e.g., [14,17,18,53,54]). Some other problems with the back intersystem crossing model are: (i) the isotope effect observed in the fluid solution, high temperature region suggests a nuclear tunneling contribution to k_{nr} requiring a significant nuclear reorganizational barrier, but the Arrhenius activation energy of k_{nr} is slightly less than $E(^4T_{2g}^0) - E(^2E_g^0)$ and is therefore inconsistent with back intersystem crossing plus a significant reorganizational barrier; (ii) the quartet–doublet energy gap is not very sensitive to the environment so the environmental dependence of k_{nr} is hard to explain.

(c) Most features of the $(^2E_g)\mathrm{Cr(NH_3)_6^{3+}}$ chemical behavior and electronic relaxation can be accounted for using a strongly coupled surface crossing to form an unstable intermediate species in its ground electronic state (model D-3); however few definitive statements about this model are possible at present, since crucial features of the excited state and intermediate potential energy surfaces are not known.

The possibility of more than one channel for $(^2E_g)\mathrm{Cr(NH_3)_6^{3+}}$ relaxation cannot be definitively assessed with the information now available. In fact, the available information is somewhat contradictory since the Arrhenius temperature dependence for τ_D suggests a single channel while the small temperature dependence reported for product formation, unfortunately a composite of quartet and doublet contributions, might be construed as evidence for competitive channels.

(b) Other octahedral and nearly octahedral complexes

In regard to the energy differences between quartet and doublet band origins (or differences in the 0–0 energy levels), $\mathrm{Cr(CN)_6^{3-}}$ on the one hand and $\mathrm{Cr(urea)_6^{3+}}$ on the other, represent limiting cases: the quartet–doublet energy gap is far too large for back intersystem crossing to contribute to the photochemical or photophysical properties of the doublet state in the first compound and the energy gap is so near to zero in the other that the nominal distinction between doublet and quartet states may lose much of its meaning. Among $\mathrm{Cr^{III}L_6}$ compounds there are dramatic variations in doublet lifetimes, but only small variations in photoactivity (see Table 3). Back intersystem crossing is not a viable pathway for $\mathrm{Cr(CN)_6^{3-}}$ and the photoaquation yield of 0.08 in water, has been assigned to a "prompt" quartet state reaction [53,54,86]. The efficiency of populating the doublet, η_{isc}, has been reported to be ~ 0.4 [87,88]. Since, $\phi(\mathrm{Y}) = \eta_{isc}\eta_{Y,D}p_D + \eta_{Y,Q}p_Q = 0.08$ and $\eta_{isc} + \eta_{Y,Q} + \eta_{ic} = 1.0$, these observations indicate that η_{ic} could be as large as 0.5: alternatively, only 13% of the photochemical intermediates in this system may give rise to products; a possibility for an associative, but not for a dissociative reaction process.

TABLE 3

Comparison of excited state properties for some $Cr^{III}L_6$ complexes [a]

Complex	$E(^2E^0)$ [b] $cm^{-1}/10^4$	$E(^4T_{2g})_{max}$ $cm^{-1}/10^4$	$E(^4T_{2g}^0)$ [c] $cm^{-1}/10^4$	τ (μs)		$\phi_{product}$
				298 K (H_2O)	77 K	
$Cr(NH_3)_6^{3+}$	1.523 [d]	2.164 [d]	1.97	2.2 [e]	78	0.45 [f]
$Cr(OH_2)_6^{3+}$	1.475 [g] (1.59) [h]	1.74 [h]	1.64 [h]	0.0018 [i]	~16 [j]	0.01–0.03 [k]
$Cr(OD_2)_6^{3-}$	1.48 [g]				130 [g]	
$Cr(urea)_6^{3+}$	1.42 [l] (1.44) [l]	1.61 [m]	1.45 ± 0.03 [l]		150 [l]	0.10 [m]
$Cr(CN)_6^{3-}$	1.237 [n] (1.241)	2.64 [o]	2.4	0.12 [p]	3950 [q]	0.17 [r]
$Cr(NCS)_6^{3-}$	1.286 [s] (1.36) [s]	1.78 [t]	1.53	~ 0.01 [u]	2380 [g]	0.27 [m]
CrF_6^{3-}	1.57 [t]	1.49 [t]				
$Cr(phen)_3^{3+}$	1.37 [v,w,x] (1.43) [x]	2.39 [x]	2.1	330 [v,x]	5300 [x]	0.006 [y]
$Cr(bpy)_3^{3+}$	1.37 [v,x] (1.44) [x,z]	2.20 [y]	2.07	73 [v]	5000 [f] 6500 [x]	0.13 [y] 0.18 [aa]
$Cr(en)_3^{3+}$	1.50 [ab]	2.19 [w]	1.94	1.85 [e]	100 [ac] 120 [d]	0.37 [ad]
$Cr(ox)_3^{3}$	1.445 [ae] (1.54) [ae]	1.740 [ae]	1.5		900 [af]	0.08 [ag]
$Cr(acac)_3$	1.28 [j]	1.79 [j] 1.84 [ah]	1.54	2.4 [j]	~ 475 [ai]	0.01 [aj]
$Cr(sep)^{3+}$	1.50 [ak]	2.17 [ak]	1.92	1.74 [ak]		< 0.03 [ak]
$Cr(chda)_3^{3+}$	1.48 [al]	2.17 [al]	1.92	0.9 [al]	96 [al]	0.13 [al]
$Cr([9]aneN_3)_2^{3+}$	1.46 [al]	2.28 [am]	2.02	11.4 [al]	400 [al]	< 0.002 [al]
$Cr(tpy)_2^{3+}$	1.30 [x,an] (1.41) [x]	~ 2.11 [x,an]		~ 0.05 [am]	540 [al]	

[a] For additional information on hexaamine type complexes see Table 4. [b] $E(^2T_1)$ in parentheses. [c] Estimate based on assumed 2500 $cm^{-1} = E(^4T_{2g})_{max} - E(^4T_{2g}^0)$ except as noted otherwise. [d] [94]. [e] [114]. [f] [67]. [g] [132]. [h] [24]. [i] [107]. [j] [70]. [k] [133]. [l] [134]; 5 K. [m] [135]. [n] [136]. [o] [137,138]. [p] [139]. [q] [140]. [r] [83,141]. [s] [142]. [t] [143]. [u] [89]. [v] [103]. [w] [71,94]. [x] [144]. [y] [145]. [z] [146]. [aa] [147]. [ab] [122]. [ac] [71]. [ad] [148]. [ae] [91]. [af] [149]. [ag] [53]. [ah] [150]. [ai] [118]. [aj] [151]. [ak] [78]. [al] [95]. [am] [152]. [an] [153]. [ao] [154].

For $Cr(urea)_6^{3+}$ the $(^2E_g^0 - ^4T_{2g}^0)$ energy gap (≤ 500 cm^{-1}) is small enough for spin–orbit coupling to result in considerable mixing of states. The "intersystem" crossing rate is likely to be considerably greater than the rate of non-radiative relaxation, at least for $Cr(urea)_6^{3+}$.

The $Cr(NCS)_6^{3-}$ complex is apparently an intermediate case with $E(^4T_{2g}^0) - E(^2E_g^0) \sim 2.5 \times 10^3$ cm^{-1}. The large photoaquation yield and the very short lifetime are indicative of very rapid excited state processes: $k_{nr} \sim 10^8$

s^{-1}, $k_p \sim 10^7$ s^{-1}, since about 70% of the photoreaction appears to occur from the doublet state [53].

It is a very significant observation that τ_D is strongly solvent dependent for $Cr(NCS)_6^{3-}$ [65,89,90], while the intersystem crossing efficiencies appear to be nearly independent of solvent composition [88,90]. Since η_{isc} and the energies of the LF excited states are not significantly solvent dependent, these observations imply that there is some channel for doublet state relaxation which does not involve population of the quartet states [88,90].

Many chelate complexes exhibit small (≤ 200 cm^{-1}) trigonal distortions from O_h symmetry, and these distortions should lead to a small splitting of the ($^4T_{2g}$) state. Such a splitting would tend to lower the energy of the excited quartet state origin. A 200 cm^{-1} splitting has been reported for $Cr(ox)_3^{3-}$ [91]. In this complex there seems to be little energy difference between the excited quartet and doublet states. However, the small energy gap does not result in a large product yield.

That the ^2E_g excited state and $^4A_{2g}$ ground state surfaces are nested and apparently similar in shape might be expected to lead to similar substitution reaction patterns. However, this is not the case. The slightly larger activation barrier and the one or two orders of magnitude smaller hydrolysis rate found for $Cr(NH_3)_6^{3+}$ [92,93] compared to $Cr(en)_3^{3+}$ [72] in their ground states has no parallel whatsoever in the excited state chemistry. Rather, the excited states of these complexes exhibit nearly identical photochemical and photophysical behavior. It seems unlikely, given the variety of behavior found in chromium(III) compounds, that such similar behavior is merely fortuitous. It seems more likely that these similarities in photochemical behavior have their origin in the similar electronic structure and metal–ligand bonding within these complexes. One possible means of resolving the apparent dilemma is in terms of an excited state reaction channel which involves crossing to a lower energy potential energy surface, a process more dependent on electronic properties of the system than are the typical substitutional processes.

A great deal of photophysical and photochemical information is becoming available for hexaaminechromium(III) complexes with small, but systematic differences from O_h microsymmetry (Table 4) [78,79,94–98]. These complexes vary in their quantum efficiency ranging from being photolabile, as in $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$, to being virtually photoinert, as in $Cr(sep)^{3+}$ [78], $Cr(diamsar)^{3+}$ and $Cr(sar)^{3+}$ [99], $Cr([9]aneN_3)_2^{3+}$ [95,97,100] and *trans*-$Cr([14]aneN_4)(NH_3)_2^{3+}$ [96]. The *cis*- and *trans*-$Cr([14]aneN_4)(NH_3)_2^{3+}$ complexes exhibit rather unique behavior in that the photoreactive *cis*-complex ($\phi = 0.2$) has a somewhat shorter lifetime (1.7 μs in water at 20°C) than the photoinert *trans*-complex ($\phi < 10^{-3}$; 55 μs in water at 20°C) [96]. A similar, but more dramatic contrast in lifetime behavior has been found for

TABLE 4

Excited state properties of some hexaamine and cyano-amine chromium(III) complexes

Complex	$E(^2E^0)$ (cm^{-1}/10^4)	$E(^4T_{2g})_{max}$ (cm^{-1}/10^4)	τ (μs) 298 K	τ (μs) 77 K	ϕ_{phos} (77 K)	E_A ^{a} (kJ mol^{-1})	Medium ^{b}
$Cr(NH_3)_6^{3+}$	1.523 ^{c}	2.164 ^{c}	4 ^{d}	78 ^{d}		47 ^{d}	DMF + $CHCl_3$
				70 ^{c}	0.0031 ^{c}		DMSO + glycerol
			2.2 ^{c}			42 ^{c}	H_2O
						42 ^{g}	H_2O + LiCl
$[Cr(NH_3)_6]Cl_3$			14 ^{d}	38 ^{d}		4 ^{d}	crystalline powder
			45 ^{d}	71 ^{d}		5 ^{d}	doped into $[Ru(NH_3)_6]Cl_3$; crystalline powder
$Cr(ND_3)_6^{3+}$	1.52 ^{d}	2.16 ^{d}	4.2 ^{d}	3500 ^{d}		48 ^{d}	DMF + $CHCl_3$
			3.0 ^{c}			52 ^{c}	H_2O
$[Cr(ND_3)_6](ClO_4)_3$			546 ^{d}	598 ^{d}			crystalline powder
$Cr(en)_3^{3+}$	1.496 ^{c}	2.188 ^{c}		120 ^{c}	0.009 ^{c}	41 ^{d}	DMSO + glycerol
			1.2 ^{f}	97 ^{f}		41 ^{f}	DMSO + $CHCl_3$
						42 ^{g}	H_2O + LiCl
$[Cr(en)_3](ClO_4)_3$			17 ^{f}	52 ^{f}		49 ^{f}	crystalline powder
$Cr(d_4\text{-en})_3^{3+}$			1.4 ^{f}	2560 ^{f}		43 ^{f}	DMF + $CHCl_3$
$[Cr(d_4\text{-en})_3](ClO_4)_3$			25 ^{f}	1780 ^{f}		50 ^{f}	crystalline powder
$Cr(tn)_3^{3+}$	1.502 ^{c}	2.157 ^{c}		133 ^{c}	0.0065 ^{c}		DMSO + glycerol
						38 ^{h}	MeOH + H_2O + glycol
$Cr(chda)_3^{3+}$	1.48 ^{f}	2.174 ^{f}	0.9 ^{f}	96 ^{f}		37 ^{f}	DMF + $CHCl_3$
$[Cr(chda)_3](ClO_4)_3$			4.5 ^{f}	82 ^{f}		38 ^{f}	crystalline powder
trans-$Cr(dien)_2^{3+}$	1.449 ^{f}	2.174 ^{f}	0.3 ^{f}	90 ^{f}		33 ^{f}	DMF + $CHCl_3$
$Cr(dien)_2^{3+\,i}$	1.465 ^{c}	2.17 ^{c}		97 ^{c}	0.0134 ^{c}		DMSO + glycerol
$Cr([9]aneN_3)_2^{3+}$	1.47 ^{j}	2.278 ^{j}	40 ^{j}	(340) ^{j,k}	0.027 ^{j}	42 ^{j}	DMSO + H_2O
			11 ^{f}	400 ^{f}		47 ^{f}	DMF + $CHCl_3$
$[Cr([9]aneN_3)](ClO_4)_3$			74 ^{f}	222 ^{f}			crystalline powder
$Cr(d_3\text{-}[9]aneN_3)_2^{3+}$	1.47 ^{j}	2.278 ^{l}	51 ^{l}	(3200) ^{j,k}	0.27 ^{k}	47 ^{j}	DMSO + D_2O
$Cr(DTNE)^{3+}$	1.38 ^{l}	2.08 ^{m}	6×10^{-3} ^{l}	50 ^{l}		18 ^{l}	DMSO + H_2O
trans-$Cr([14]aneN_4)(NH_3)_2^{3+}$	~ 1.5 ^{n,o}	2.25 ^{n}	136 ^{n,p}	180 ^{n}		67 ^{n}	DMSO + H_2O
		(2.38) ^{n}					
			108 ^{n,p}	169 ^{n}			DMF
			55 ^{n,p}			79 ^{n}	H_2O
trans-$Cr(d_4\text{-}[14]aneN_4)(ND_3)_2^{3+}$			1620 ^{n,p}	3720 ^{n}			DMSO + D_2O
			810 ^{n,p}	3660 ^{n}			DMF
			165 ^{n,p}			73 ^{n}	D_2O

cis-Cr([14]aneN$_4$)(NH$_3$)$_2^{3+}$	~1.5 ^{n,p}	2.14 ^{n}	1.0 ^{n,p}	116 ^{n}			DMSO + H$_2$O
			0.8 ^{n,p}				DMF
			1.7 ^{n,p}			42 ^{n}	H$_2$O + HClO$_4$
[*cis*-Cr([14]aneN$_4$)(NH$_3$)$_2$](PF$_6$)$_2$NO$_3$			19 ^{n,p}	73 ^{n}			crystalline powder
cis-Cr(d$_4$-[14]aneN$_4$)(ND$_3$)$_2^{3+}$			1.2 ^{n,p}	1580 ^{n}			DMSO + D$_2$O
			2.1 ^{n,p}				D$_2$O
[*cis*-Cr(*d*$_4$-[14]aneN$_4$)(ND$_3$)$_2$](PF$_6$)$_2$NO$_3$			65 ^{n,p}	800 ^{n}			crystalline powder
cis-Cr([14]aneN$_4$)en^{3+}	1.48 ^{c}	2.15 ^{c}		136 ^{c}	0.0167 ^{c}		DMSO + glycerol
			3 ^{p,q}			44 ^{q}	DMF
Cr(sen)$^{3+}$	1.48 ^{l}	2.22 ^{l}	0.02 ^{l}	120 ^{l}			DMF + CHCl$_3$
Cr(sep)$^{3+}$	1.50 ^{r}	2.17 ^{r}	1.74 ^{r}			51 ^{r}	DMF + CHCl$_3$
Cr(sar)$^{3+}$	1.46 ^{s}	2.22 ^{s}, 2.19 ^{s}	< 0.01 ^{s}	60 ^{s}	0.02 ^{s}		frozen water
Cr(diamsar)$^{3+}$	1.46 ^{s}	2.24 ^{s}, 2.20 ^{s}	< 0.01 ^{s}	65 ^{s}	0.02 ^{s}		frozen water
Cr(NH$_3$)$_5$CN^{2+}	1.466 ^{q}	2.217 ^{u}	14 ^{q}		0.002 ^{t}	52 ^{q}	H$_2$O + HCF$_3$SO$_3$ (pH 4)
	1.471 ^{t,u}						
				79 ^{q}			DMF + EtOH
Cr(ND$_3$)$_5$CN^{2+}			14 ^{q}				D$_2$O
				9662 ^{q}		54 ^{q}	DMSO + D$_2$O
trans-Cr(en)$_2$(CN)$_2^{+}$		2.315 ^{v}	1 ^{p,w}				H$_2$O
			1 ^{p,w}	210 ^{w}			DMSO
cis-Cr(en)$_2$(CN)$_2^{+}$		2.310 ^{v}	2 ^{p,w}				H$_2$O
cis-Cr(*d*$_4$-en)$_2$(CN)$_2^{+}$			11 ^{p,w}	3000 ^{w}			DMSO
trans-Cr(NH$_3$)$_4$(CN)$_2^{+}$	1.433 ^{x}	2.273 ^{x}	33 ^{t}			28 ^{t}	H$_2$O (pH 3)
	1.490 ^{x,y}						
cis-Cr(NH$_3$)$_4$(CN)$_2^{+}$	1.429 ^{x}	2.294 ^{x}					
trans-Cr([14]aneN$_4$)(CN)$_2^{+}$	1.395 ^{q}	2.416 ^{z}	361 ^{l}			38 ^{v}	H$_2$O (pH 4.3)
				355 ^{w}			DMSO
trans-Cr(*d*$_4$-[14]aneN$_4$)(CN)$_2^{+}$			1499 ^{q}				D$_2$O
				3060 ^{w}			DMSO
trans-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)(CN)$_2^{+}$	1.426 ^{q}	2.347 ^{q}	429 ^{q}				H$_2$O + HCF$_3$SO$_3$ (pH 5)
			380 ^{q}	379 ^{q}			DMSO + H$_2$O
trans-Cr(N-*d*$_4$-*ms*-(5,12)-Me$_6$[14]aneN$_4$)(CN)$_2^{+}$			1752 ^{q}				D$_2$O
				5600 ^{q}			DMSO + D$_2$O
cis-Cr(*rac*-(5,12)-Me$_6$[14]aneN$_4$)(CN)$_2^{+}$	1.379 ^{q}	2.164 ^{q}	2.1 ^{q}			50 ^{q}	H$_2$O (pH 3)
				208 ^{q}			DMF + EtOH
cis-Cr(N-d$_4$-*rac*-(5,12)-Me$_6$[14]aneN$_4$)(CN)$_2^{+}$			2.0 ^{q}		1854 ^{q}		46 ^{q}DMSO + D$_2$O
cis-(*rac*-(5,12)-Me$_6$[14]aneN$_4$)en^{3+}	1.47 ^{l}	2.01 ^{l}	$2 \times 10^{-3,l}$	91 ^{l}		42 ^{l}	DMSO + H$_2$O

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[a] Arrhenius activation energy for τ. [b] Lifetimes in fluid or glassy solutions except as indicated. [c] [94]. [d] [79]. [e] [114]. [f] [95]. [g] [82]. [h] Value reported in [82] based on data in [115]. [i] Isomer not identified in [94]. [j] [97]. [k] 95 K. [l] [100]. [m] [155]. [n] [96]. [o] Emission spectrum poorly resolved. [p] 295 K. [q] [156]. [r] [78]. [s] [99]. [t] [157]. [u] [158]. [v] [159]. [w] [160]. [x] [161]. [y] Second electronic origin. [z] [162].

cis- and *trans*-$\mathrm{Cr(N_4)(CN)_2^+}$ complexes (see section B(i) (d); $\mathrm{N_4}$ = tetraazamacrocyclic ligand). In spite of this, the photoinert complex $\mathrm{Cr(sep)^{3+}}$ has a ^2E lifetime comparable to that of the photoreactive $\mathrm{Cr(en)_3^{3+}}$ in DMF under ambient conditions [78] and similar cage complexes are reported to be even shorter lived [99]. Some of these observations suggest that ligand systems which are strained in the ground state may facilitate excited state relaxation. Preliminary observations on some other systems with strained ligands seem to bear this out: (a) encapsulation of one trigonal face of $\mathrm{Cr(en)_3^{3+}}$ by a neopentyl moiety (to form $\mathrm{Cr(sen)^{3+}}$) results in an approximately 100 fold decrease in the room temperature lifetime [100]; (b) coupling of the triazanonane rings of $\mathrm{Cr([9]aneN_3)_2^{3+}}$ with an ethylene moiety (to form $\mathrm{Cr(DTNE)^{3+}}$) results in an approximately 10^5-fold decrease in lifetime [100]. These observations support the argument that the steric constraints which prevent substitution into the coordination sphere are not identical with those that control entry into the ^2E quenching channel; they also suggest that access to the quenching channel (or channels) can be mediated by steric constraints imposed by the ligands. The contrasting behavior of the $\mathrm{Cr([14]aneN_4)(NH_3)_2^{3+}}$ isomers seems to support the view that some coordination sphere rearrangement is necessary for easy entry into the quenching channel. Nuclear reorganizational barriers, as required in the formation of approximately trigonal bipyramidal or of 7-coordinate intermediates, could be implicated.

A complicating feature in studies of Cr(III)–amine excited states is that nearly all of the ^2E states are quenched by base, especially by $\mathrm{OH^-}$ [54,59,81,94,101]. The ^2E excited state quenching is often accompanied by partial or total quenching of the product yield. A remarkable aspect of this observation is indicated by comparison to base hydrolysis of the ground state species: the conjugate base intermediate, $\mathrm{Cr^{III}(NH_3)_4(NH_2)X}$ would frequently be as labile as (possibly more labile than) the $(^2E)\mathrm{Cr^{III}(NH_3)_5X}$ excited state. If the hydroxide quenching proceeds by means of deprotonation of a coordinated amine, the quenching of products seems surprising. The fact that hydroxide quenches both the excited state and photoproducts suggests that hydrogen bonding is not likely to be the mechanism for the thermally activated, solvent dependent quenching of excited states which is accompanied by product formation.

Values of $\Delta V^{\ddagger}_{\phi(\mathrm{Y})}$ are reported to be slightly positive for $\mathrm{Cr(NCS)_6^{3-}}$ and $\mathrm{Cr(CN)_6^{3-}}$ [102] (see Table 5), in contrast to the negative values found for several cationic complexes [84]. Unfortunately, the $\Delta V^{\ddagger}_{\tau(\mathrm{D})} = -3.3\ \mathrm{cm^3\ mol^{-1}}$ value for $\mathrm{Cr(en)_3^{3+}}$ [85] cannot be usefully interpreted in the absence of the corresponding value of $\Delta V^{\ddagger}_{\phi(\mathrm{Y})}$. Since photochemical reactivity is a minor feature of the behavior of $\mathrm{Cr(bpy)_3^{3+}}$ [103], a value of $\Delta V^{\ddagger}_{\tau(\mathrm{D})} = +0.9\ \mathrm{cm^3}$ $\mathrm{mol^{-1}}$ [104] may indicate an associative pathway for doublet state relaxation (k_{nr}) in this complex.

Among this family of complexes, $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$ seem to be the exceptions with $k_{nr} \sim k_p$. For the other complexes, k_{nr} seems to be an order of magnitude or more greater than k_p. Coupling of the reactive and non-reactive doublet decay channels is plausible, but the partitioning between pathways would have to vary from system to system. Since k_{nr} is usually strongly medium dependent, information about the solvent dependency of product yield, coupled with lifetime data, could provide more definitive information about the coupling of reactive and nonreactive doublet decay channels in each system. In some instances the small yield of products from the doublet state may have more to do with the efficiency of competing processes than with the rate of doublet reaction. Thus, the apparent lack of doublet reactivity in $Cr(CN)_6^{3-}$ may be a consequence of the efficient non-reactive decay rate ($k_{nr} \sim 10^8$ s^{-1} in water) rather than a reflection of the substitutional reactivity of the doublet state in the normal kinetic sense. Of course, there is no simple kinetic picture which would predict orders of magnitude of greater lability in a hexacyano than in a hexaammine complex in molecules with similar electronic configurations.

The hexaamminechromium(III) complexes exhibit a spectacular variation in ^2E lifetimes under ambient conditions (Table 4): τ (298 K) is reported to vary from $\sim 10^{-4}$ s for *trans*-$Cr([14]aneN_4)(NH_3)_2^{3+}$ [95,96] to less than 10^{-8} s for certain cage complexes [99]. Furthermore, these lifetimes are distinctly dependent on the environment, with the room temperature lifetimes of most complexes varying by factors of at least one order of magnitude when crystalline solids and fluid solutions are considered. In contrast, the low temperature lifetimes tend to approach a limit that is medium independent for each complex. The relatively short solid state lifetimes observed at low temperatures in pure crystalline solids appear to originate from a unique solid state process: the intermolecular migration of excitation energy to defect sites in the crystal lattice [23]. When this process is repressed, for example, by doping the $Cr(NH_3)_6^{3+}$ complex into a host lattice with no low energy acceptor states, similar lifetimes are observed in the solid state and in glasses at low temperature (Fig. 5; [79]).

We can make some tentative generalizations about the observations in Table 4: (1) excluding the extreme systems (*trans*-$Cr([14]aneN_4)(NH_3)_2^{3+}$, *trans*-$Cr([14]aneN_4)_4(CN)_2^{+}$ and the cage complexes) the fluid solution room temperature lifetimes of the hexaamine complexes are ca. $3 \times 10^{-6 \pm 1}$ s; (2) the medium dependence of the ambient lifetimes indicates that the solvent plays an active role in quenching the ^2E excited state [82]; (3) only a small part of the variation in ambient condition lifetimes is reflected in variations in the Arrhenius activation energy. This last point is most strikingly illustrated by the behavior of *trans*-$Cr([14]aneN_4)(NH_3)_2^{3+}$. The exceptionally long lifetime of this complex is largely a consequence of the

TABLE 5

Pressure dependence of Cr(III) and Rh(III) photochemical and photophysical parameters [a]

Complex	$\Delta V^{\ddagger}_{\phi(\mathrm{X}^-)}$	$\Delta V^{\ddagger}_{\phi(\mathrm{NH_3})}$	$\Delta V^{\ddagger}_{\tau}$	$\Delta V^{\ddagger}_{\mathrm{X}^-}$ [b]	$\Delta V^{\ddagger}_{\mathrm{NH_3}}$ [b]	$\Delta V^{\ddagger}_{\mathrm{nr}}$ [c]
$Cr(NH_3)_6^{3+}$		-6.7 ± 0.5 [d]	-4.3 ± 0.4 [e]		~ -13 (Q; D-1)	
					~ -50 (Q; D-2)	
					$+4.3$ (D; D-3)	$+4.3$ (D; D-3)
					-7.3 (Q; CK)	
					-3.8 (D; CK)	$+8.3$ (D; CK)
$Cr(NH_3)_5NCS^{2+}$	-9.8 ± 0.2 [d]	-6.4 ± 0.1 [d]	-6.9 ± 0.1 [e]			
$Cr(NH_3)_5Cl^{2+}$	-13.0 ± 0.5 [d]	-6.0 ± 0.4 [d]		-19 [f] (Q)	-11 [f] (Q)	~ (-2) [g] (Q)
$Cr(NH_3)_5Br^{2+}$	-12.2 ± 0.3 [d]	-6.5 ± 0.1 [d]		-18 [f] (Q)	-12 [f] (Q)	~ (-2) [g] (Q)
$Cr(NCS)_6^{3-}$	$+2.1 \pm 0.4$ [h]					
$Cr(CN)_6^{3-}$	$+2.7 \pm 0.2$ [h]					
$Cr(en)_3^{3+}$			-3.3 ± 0.5 [e] $(1.6 \pm 1.0$ [i]$)$			
$Cr(bpy)_3^{3+}$			$+0.9$ [i]			
$Rh(NH_3)_6^{3+}$		3.6 [j]			3.9 ± 0.5 [j]	(0) [g,j]
$Rh(NH_3)_5Cl^{2+}$	-5.2 ± 0.5 [k]	12.7 ± 1.2 [k]	(3.4) [k,g]	-8.6 ± 1.6 [k]	9.3 ± 1.9 [k]	(-2.6) [k,g]
	-4.6 ± 0.7 [l,m]	4.2 ± 0.9 [l,m]	$+0.3 \pm 0.4$ [l,m]	-4.9 ± 1.1 [l]	3.9 ± 1.3 [l]	0.2 ± 0.5 [l]
		6.3 ± 0.9 [l,n]	-1.3 ± 0.2 [l,n]		7.6 ± 1.1 [l]	0.7 ± 0.3 [l]
	-7.8 ± 1.8 [l,o]	4.4 ± 0.9 [l,o]	$+1 \pm 1$ [l,o]	-8.9 ± 2.7 [l]	3.3 ± 1.8 [l]	-1 ± 1 [l]

$Rh(ND_3)_5Cl^{2+}$	-4.2 ± 0.5 [k,p]	9.5 ± 1.6 [k,p]	3.5 ± 1.1 [k,p]	-7.7 ± 1.6 [k]	6.2	-2.6
$Rh(NH_3)_5Br^{2+}$	-10.3 ± 1.2 [k]	4.6 ± 0.6 [k]	(-3.5) [k,g]	-6.8 ± 1.6 [k]	8.1	(2.5) [k,g]
$Rh(ND_3)_5Br^{2+}$	-9.4 ± 1.5 [k,p]	3.4 ± 0.5 [k,p]	-4.1 ± 0.6 [k,p]	-5.3 ± 1.8 [k]	7.5	2.5
$Rh(NH_3)_5I^{2+}$		0.2 [j]			1.4 ± 0.9 [j]	(0) [g,j]
$Rh(NH_3)_5SO_4^+$				-3.9 ± 0.6 [j,q]		(0) [g,j]
cis-$Rh(NH_3)_4Cl_2^+$	-2.24 [r]			-3.5 ± 0.3 [s]		(0) [g,s]
trans-$Rh(NH_3)_4Cl_2^+$	2.5 [r]			2.8 ± 0.6 [s]		(0) [g,s]
cis-$Rh(NH_3)_4(OH_2)Cl^{2+}$	-0.11 [r]			0.0 ± 0.4 [s]		(0) [g,s]
cis-$Rh(NH_3)_4Br_2^+$	-1.73 [r]	8.95 [r]		-2.3 ± 0.3 [s]	9.3 ± 0.8 [s]	(0) [g,s]
trans-$Rh(NH_3)_4Br_2^+$	3.41 [r]			$+2.9 \pm 0.7$ [s]		(0) [g,s]
cis-$Rh(NH_3)_4(OH_2)Br^{2+}$	-0.49 [r]			-1.0 ± 0.4 [s,t]		(0) [g,s]

[a] In water at 25°C except as indicated. Activation volumes in units of cm^3 mol^{-1}. [b] For Cr(III) see Table 2 and the accompanying discussion; abbreviations: Q, for quartet state process; D, for doublet state process; alternative models D-1, D-2, D-3 and CK (competition kinetics) are described in the text. For Rh(III), a single photoactive state is assumed and equations (2)–(4) are employed. [c] Abbreviations as in Note b; for the quartet state of Cr(III), $\Delta V^{\ddagger}_{nr} = \Delta V^{\ddagger}_{ic}$. [d] [103]. [e] [85]. [f] Estimate assuming all reactions are from quartet and $\Delta V^{\ddagger}_{\phi(Y)} \approx \Delta V^{\ddagger}_{Y} - \eta_{ic}\, \Delta V^{\ddagger}_{ic} - \eta_{NH_3}\, \Delta V^{\ddagger}_{NH_3} - \eta_{X^-}\, \Delta V^{\ddagger}_{X^-}$. [g] Assumed value. [h] [102]. [i] [104]; 16–18°C. [j] [238]. [k] [229]. [l] [230]. [m] FMA solvent. [n] DMF solvent. [o] DMSO solvent. [p] D_2O solvent. [q] 14 ± 1°C. [r] Determined by the least squares method ($\ln \phi$ vs P) from data in [231]. [s] [231]. [t] H_2O exchange.

onset of a strong temperature dependency only under near ambient conditions rather than at the very low temperatures (200–250 K) characteristic of most other complexes [80,83,94,95,100]. These issues will be discussed in greater detail below.

(c) $Cr^{III}(NH_3)_5X$ *complexes*

A large amount of both the experimental and theoretical study of chromium(III) photochemistry has centered on complexes of CrA_5X and CrA_4XY stoichiometries. This work has largely been motivated by the frequently observed "anti-thermal" nature of the dominant photochemistry. Most of the observations on these systems are concisely summarized in Adamson's rules, but with a striking prevalence of *cis*-products. The proposed theoretical treatments of these reactions describe orbital occupations in the Franck–Condon excited states, and they use orbital correlations of excited states (or intermediates) with various products to generate rules regarding the dominant reaction processes and the course of stereochemical changes [8–10,12,14,15,17–19].

Table 6 summarizes information about excited state energies and reactivity. The complexes exhibit predominantly ammonia photoaquation in large yield (note that several of the complexes listed in Table 5 have not been subjected to photochemical examination and also that the possibility of water labilization has not been investigated in $Cr(NH_3)_5OH_2^{3+}$). By comparison with $Cr(NH_3)_6^{3+}$, $Cr(en)_3^{3+}$, $Cr(NH_3)_2(NCS)_4^-$ and $Cr(en)_2(NCS)_2^+$, it might be presumed that the larger quantum yields are similarly composites of doublet (~ 50–70%) and quartet contributions; however, proof of this assumption is sparse. Finally, excited state lifetimes are known for only a few of these complexes under photochemical conditions, but there does seem to be a range of several orders of magnitude in the ^2E state lifetimes with halide complexes exhibiting lifetimes of, at most, tens of ns contrasting with the microsecond lifetimes characteristic of hexaamines in fluid solution at room temperature. It is significant that quantum yields do not change enormously over this range of lifetimes, although the extent to which the shortest lived doublet states contribute to the net product yields has not been established.

The Vanquickenborne and Ceulemans model [14–19] uses the angular overlap approach to estimate orbital populations in the Franck–Condon excited state and to generate a set of parameters, $I^*(M\text{–}L)$, which are considered to be roughly proportional to metal–ligand bond strength. These parameters for the individual axial (ax.; $A = NH_3$, X = non-amine ligand) and equatorial (eq.) bonds in several $Cr^{III}(NH_3)_5X$ complexes are included in Table 5. The leaving group is predicted to be an axial ammonia in every case except $Cr(NH_3)_5OH_2^{3+}$ (for which H_2O and NH_3 are equally probable

TABLE 6

Photochemical reactivity and energetics of $Cr^{III}(NH_3)_5X$ complexes

X	Excited state energies ($cm^{-1}/10^4$)						I^*(M–L)($cm^{-1}/10^3$)			τ (77 K), μs [f]	$\phi(NH_3)$	$\phi(X^-)$
	$^2E^0$(obsd) [a]	$^2T_1^0$(obsd) [a]	^4E(obsd) [b]	$^4E^0$(estd) [c]	$^4E^0$(calcd) [d]	$^4B_2$(calcd) [d]	$(M-X)_{ax}$ [e]	$(M-NH_3)_{ax}$ [e]	$(M-NH_3)_{eq}$ [e]			
H_2O	1.506 [g]	1.526	(2.08)	1.83	2.05	2.16	8.61	8.59	11.86	60 (51 [i])	0.19 [h]	
I^-	1.464	1.494	1.85 (2.13)	1.6	1.85	2.16	7.20 [j]	8.22 [j]	12.13 [j]		0.28 [u]	~ 0 [u]
Br^-	1.476	1.498	1.91 (2.14)	1.65	1.90	2.16	9.26	8.42	11.94	59 (54 [i])	0.36 [k]	0.010 [k]
Cl^-	1.481 [g]	1.498	1.94 (2.21)	1.7	1.93	2.16	9.27	8.48	11.91	41 (40 [i])	0.37 [l]	0.007 [l]
NCS^-	1.45 [m]	~1.54 [d]	(2.05)	1.8	2.06	2.16	8.94	8.74	11.79	97 (70 [i])	0.47 [n]	0.025 [n]
CN^-	1.47 [o,p]	1.49 [q]	(2.22) [o]	1.97	2.27	2.16	18.12	14.36	8.98	100 [r]	0.33 [p]	< 0.0005 [p]
F^-	1.45		1.99	1.74	2.01	2.16	15.33	9.12	11.60		0.43 [s]	0.004 [s]
$CF_3CO_2^-$	1.502	1.513	2.07	1.82							0.36 [t]	< 0.01 [t]
$-ONO^-$	1.489	1.504	(2.08)	1.83						24 [i]		
NO_3^-	1.495	1.516	2.01	1.76								
N_3^-			2.01 [d]	1.76	2.02	2.16				52		

[a] [163] except as indicated. [b] Absorption maxima for the lowest quartet; presumed to be the ^4E state except for $Cr(NH_3)_5CN^{2+}$. Data from [72] and references therein. Energy of $^4B_2$ state in parentheses. [c] Estimate of thermalized energy of lowest quartet obtained as $^4E^0(\text{estd}) \sim [^4E^{max}(\text{obsd}) - 0.25] \times 10^4\ cm^{-1}$. [d] Absorption maxima calculated by Perumareddi [108]. [e] From [19] except as indicated. [f] DMF–$CHCl_3$ glasses; ref. [95] except as indicated. [g] $\tau(^2E) < 5$ ns at 20°C in H_2O [116]. [h] [164]. [i] Ethylene glycol–H_2O (2 : 1, v/v) glasses, except Me_2SO–H_2O glass (1 : 1, v : v) for $Cr(NH_3)_5OH_2^{3+}$ [117] or [165]. [j] Calculated using parameters from [14,19]. [k] [166]. [l] [167,168]. [m] $\tau(^2E) = 0.26\ \mu s$ at 20°C in H_2O [114]. [n] [53]. [o] [155]. [p] [169]. [q] [156]. [r] [100]. [s] [170]. [t] [171]. [u] [172].

as leaving groups) and $Cr(NH_3)_5I^{2+}$ (even for $Cr(NH_3)_5Br^{2+}$ the numerical values of $I^\star(M-Br)$ and $I^\star(M-NH_3)$ are so similar that one might be surprised at the dominance of ammonia loss). These predictions are in reasonable accord with those based on Adamson's rules except for $Cr(NH_3)_5I^{2+}$.

In the approach of Vanquickenborne and Ceulemans, the stereomobility accompanying photolabilization of Cr(III) complexes is attributed to a dominant reaction pathway in which *cis*-attack in a trigonal bipyramidal intermediate correlates with the ground state product orbital configuration. The origin of the leaving group is difficult to establish for the pentaammines, and definitive information about stereomobility is correspondingly rare.

Kirk [53] has drawn attention to the similarities in the yield ratios for the quenchable and unquenchable portions of Cr(III) photoreactions. This similarity has been cited [53] as support for the hypothesis that all the photoreactivity can be attributed to very rapid quartet state decomposition, with the doublet state acting as a reservoir in labile communication with the reactive quartet. Such yield comparisons are currently available for very few systems, and they are only meaningful for those complexes in which the different photoprocesses compared have no dependence on excitation energy. Since the yields from minor processes in many chromium complexes are reported to be excitation energy dependent [61], the similarity of yield ratios for doublet and quartet photoreactions may not be very general.

The information summarized in Table 6 can be used in a more careful consideration of forward and back intersystem crossing. The spectroscopic data indicate that the ${}^4T_{2g}^0$ state of $Cr(NH_3)_6^{3+}$ is distorted mostly along an e_g symmetry coordinate [21]. The inferred small change in bond lengths (e.g., compared to the average difference of ~ 20 pm in $Cr(OH_2)_6^{3+}$ and $Cr(OH_2)_6^{2+}$ bond lengths [105]) is consistent with the charge on the metal and the orbital occupation. The rate of the ${}^4T_{2g} \rightarrow {}^2E_g$ crossing will be largely dictated by the Franck–Condon factors (λ) resulting from this difference in molecular geometry and modified by $\delta\epsilon = E({}^4T_{2g}^0) - E({}^2E_g^0)$. The apparent activation energy of the surface crossing will be given by $E_a \simeq \lambda(1 - \delta\epsilon/\lambda)^2/4$ [80]. Assuming potential energy surfaces that are effectively parabolic for the intersystem crossing process, the intrinsic Franck–Condon parameters associated with the two states, $\lambda({}^4T_{2g})$ and $\lambda({}^2E_g)$, are simply the vibrational energies associated with a 12 pm change in bond length of the four $Cr-NH_3$ bonds. In the classical limit this is $\lambda_i = 2f(\Delta Q)^2$ (f the force constant and Q the nuclear coordinate), so $\lambda({}^4T_{2g}) \simeq 2.3 \times 10^3\ cm^{-1}$ and $\lambda({}^2E_g) \simeq 2.5 \times 10^3\ cm^{-1}$. For $Cr(NH_3)_6^{3+}$, $\delta\epsilon \simeq 4 \times 10^3\ cm^{-1}$ so $E_A \sim 240\ cm^{-1}$. For $k_{isc} \simeq \nu_q \exp(-2E_A/\hbar\omega_{ave} \coth\gamma)$ [79] with $\gamma = \hbar\omega_{ave}/2k_BT$ and $\nu_q \sim 6 \times 10^{12}\ s^{-1}$ (assuming the surface coupling to be strong enough so that the crossing is fully adiabatic), $k_{\mathrm{isc}} \sim 2 \times 10^{12}$ s^{-1}. The value of k_{isc} based on a more rigorous Franck–Condon model, and allowing for some electronic constraints (based on Buhks et al., [32]) gives $10^{11\pm1}$ s^{-1}. Fonger and Struck [31] used a different Franck–Condon model to estimate $k_{\mathrm{isc}} = 1.5 \times 10^{13}$ s^{-1} in ruby at 4.4 K. These various theoretical estimates may be compared to $k_{\mathrm{isc}} < 10^{11}$ s^{-1} determined for $\mathrm{Cr(acac)_3}$ and for some amine–$\mathrm{NCS^-}$ complexes [28–30,106]. Given the assumptions involved in the various theoretical models, these observations seem in accord with the expectation of very rapid ${}^4T_{2g} \rightarrow {}^2E_g$ intersystem crossing in chromium(III) complexes, at least where $E({}^4T_{2g}^0) > E({}^2E_g^0)$, and $\lambda \sim 2 \times 10^3$ cm^{-1}. As $E({}^4T_{2g}^0)$ approaches $E({}^2E_g^0)$, for similar values of λ, one expects a decrease in k_{isc}; based on Franck–Condon factors only, this could result in $k_{\mathrm{isc}} \sim 10^8$ s^{-1} when $\delta\epsilon \sim 0$. However, the increase in spin–orbit coupling, expected for decreasing $\delta\epsilon$, would tend to facilitate the surface crossing.

Based on $\delta\epsilon \sim 4 \times 10^3$ cm^{-1} and the estimate of $k_{\mathrm{isc}} \sim 2 \times 10^{12}$ s^{-1}, the back intersystem crossing rate for $\mathrm{Cr(NH_3)_6^{3+}}$ is much too small ($\sim 5 \times 10^3$ s^{-1}) at room temperature to contribute to the observed photochemistry.

Product yields among the pentaammines are remarkably similar in numerical value, and, as above, there is no significant correlation of the yield with variations in $E({}^4T_{2g}^0) - E({}^2E_g^0)$.

Negative values of $\Delta V_{\phi(i)}^{\ddagger}$ have been found for the photoaquation of X and $\mathrm{NH_3}$ in $\mathrm{Cr(NH_3)_5X^{2+}}$ complexes (Table 5) [84]. On the basis of these values, an "associative interchange" mechanism has been proposed for the photoaquation in these complexes. It should be noted, that the experiments did not distinguish the quenchable from the non-quenchable components of the photoreactions, so they may be presumed to reflect some composite of fast (or quartet state) reactions and slow (possibly doublet state) reactions. Only for $\mathrm{Cr(NH_3)_5NCS^{2+}}$ are both $\Delta V_{\phi(i)}^{\ddagger}$ (-9.8 and -6.4 $\mathrm{cm^3\ mol^{-1}}$ respectively for $i = \mathrm{NCS^-}$ and $\mathrm{NH_3}$ [84]) and $\Delta V_{\tau(\mathrm{D})}^{\ddagger}$ (-6.9 $\mathrm{cm^3\ mol^{-1}}$ [85]) known. These are similar to values of $\Delta V_{\phi(\mathrm{NH_3})}^{\ddagger}$ and $\Delta V_{\tau(\mathrm{D})}^{\ddagger}$ reported for $\mathrm{Cr(NH_3)_6^{3+}}$, and the inferences drawn from these observations are largely the same as those discussed in section B(i) (a).

(d) $\mathrm{Cr^{III}A_4XY}$ complexes

A large variety of complexes of this stoichiometry have been synthesized and their photochemical behavior investigated. Much of this work has focused on the applicability of Adamson's rules and the various theoretical models, and this aspect has been recently reviewed [53]. In this section we focus on only a few compounds, selected for the structural implications of their excited state behavior. Pertinent information is collected in Table 7.

Relatively detailed information is available for the thiocyanate complexes.

TABLE 7

Photochemical reactivity and excited state energetics of $Cr_4^{III}AXY$ complexes

trans-Complex (except as indicated)	Excited state energies ($cm^{-1}/10^4$)				$I^*(M-L)(cm^{-1}/10^3)$		$\tau(^2E)$, μs		$\phi(Am)$[e]	$\phi(X^-)$[e]
	$^2E^0$(obsd), ($^2T_1$)	^4E(obsd)	$B^4_{2(obsd)}$	$^4E^0$(estd)[a]	(M–A)[b]	(M–X)[b]	298 K[c]	77 K[d]		
$Cr(NH_3)_4Cl_2^+$	1.45[d]	1.70[f]	2.13[f]	1.45	12.12	8.94	< 0.005[g]	30	0.003[h]	0.44[h]
$Cr(en)_2Cl_2^+$	1.44[i] (1.47)[i]	1.74[f]; 1.73[j]	2.20[f]; 2.21[j]	1.49	12.32	8.90		50	$< 10^{-3}$[k]	0.32[k]
$Cr([14]aneN_4)Cl_2^+$	1.40[t] (1.44)[m]	←	1.76[n] →	1.51	–	–	0.010[o]	88[m]	$< 10^{-3}$[l]	6.9×10^{-4}[l]
cis-$Cr([14]aneN_4)Cl_2^+$	1.42[m]	←	1.89[n] →				0.01[m]	52[m]		$< 5 \times 10^{-4}$[l]
cis-Cr(*rac*-(5,12)-$Me_6[14]aneN_4)Cl_2^+$		←	1.67[p] →					94[m]		
$Cr(en)_2F_2^+$	1.31[q]	1.89[f]; 1.85[r]	2.14[f]; 2.17[r]	1.64	11.71	15.42	1.9[d]	35	0.35[s]	≤ 0.08[s]
$Cr(en)_2(OH_2)F^{2+}$	1.39[d]	←	1.90[t] →	1.65	11.75	14.40 (F) 8.81 (H_2O)	0.025[t]	67		
$Cr(en)_2(NCS)F^+$	1.38[u]	←	1.94[t] →	1.69	11.91	11.50 (F) 9.01 (NCS)	0.325[t]		0.07	0.27[v]
$Cr(NH_3)_4(NCS)_2^+$	1.39[w]	1.95[t]	2.16[t]	1.7			0.56[g]			
$Cr(en)_2(NCS)_2^+$	1.37[u,x]	←	2.02[s] → (1.98)[t]	1.83[x] (1.73)	12.09	8.68	6[g]; 4.4[t]		0.07[x]	0.18[x]
$Cr([14]aneN_4)(NCS)_2^+$	1.41[m]	←	2.07[n] →	1.7	–	–	80[m]	> 80[m]		
Cr(*ms*-(5,12)–$Me_6[14]aneN_4)(NCS)_2^+$	1.41[m]	←	2.00[p] →					> 108[m]		
cis-Cr(*rac*-(5,12)–$Me_6[14]aneN_4)(NCS)_2^+$	1.38[m]	←	1.90[p] →					56[m]		
$Cr(tn)_2(NCS)_2^+$	1.38[t]	←	1.96[t] →	1.71	11.90	8.74	1.5[t]			
$Cr(en)_2(OH_2)NCS^{2+}$	1.42[t]	←	1.93[t] →	1.68	11.97	8.43 (H_2O) 8.62 (NCS)	0.012[t]			

$Cr(tn)_2(OH_2)NCS^{2+}$	1.43[t]	←	1.92[t] →	1.67	11.97	8.43 (H_2O) 8.62 (NCS)	0.01[t]			
$Cr(NH_3)_4(OH_2)NCS^{2+}$	1.44[t]	←	1.96[y] →	1.71	11.96	8.43 (H_2O) 8.62 (NCS)	0.0025[t]		0.43[z]	0.02
$Cr(en)_2(NCS)Br^+$		←	1.82[t] →	1.57	12.085	8.320 (Br) 8.420 (NCS)	0.002[t]			
$Cr(NH_3)_2(NCS)_4^-$	1.34[w] (1.38)[w]	1.92[w]	1.76[w]	1.5[aa]	9.150	14.360	0.005[g] 0.016[ab]			0.31[ac]
$Cr(NH_3)_4(CN)_2^+$		←	2.27[ab] →	1.9[aa]	8.980	17.540	33[ab]		0.24[ad]	< 0.005[ad]
$Cr(en)_2(CN)_2^+$		←	2.315[ab] →	2.2[aa]	9.10	17.540	1[ae]	210[ae]	0.58[af]	< 0.05[af]
$Cr(tn)_2(OH_2)_2^{3+}$	1.49[t]	←	1.87[t] →	1.62	12.035	8.330	0.003[t]			
cis-$Cr(tn)_2(OH_2)NCS^{2+}$	1.44[t]	←	1.92[t] →	1.7	$14.370(tn)_{ax}$ $8.980(tn)_{cq}$	8.930 $(H_2O)_{eq}$ 9.155 $(NCS)_{eq}$	0.03[t]			
cis-$Cr(en)_2(OH_2)NCS^{2+}$	1.42[t]	←	1.94[t] →	1.7	$14.370(en)_{ax}$ $8.980(en)_{eq}$	8.930 $(H_2O)_{eq}$ $9.155(NCS)_{eq}$	0.02[t]			
cis-$Cr(tn)_2(OH_2)_2^{3+}$	1.48[t]	←	1.88[t] →	1.6	$14.370(tn)_{ax}$ $8.980(tn)_{eq}$	8.930 $(H_2O)_{eq}$	0.0035[t]			
cis-$Cr(en)_2(OH_2)_2^{3+}$	1.47[t]	←	1.90[t] →	1.7	$14.56(en)_{ax}$ $9.10(en)_{eq}$	10.13 $(H_2O)_{eq}$	0.0024[t]			
cis-$Cr(tn)_2(OH_2)Cl^{2+}$	1.45[t]	←	1.81[t] →	1.6	$14.370(tn)_{ax}$ $8.980(tn)_{eq}$	$9.680(Cl)_{eq}$ 8.930 $(H_2O)_{eq}$	0.0013[t]			

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[a] Presumed to be the lowest energy quartet state in *trans*-arrangement when pertinent, except as indicated; $^4E^0 \simeq [^4E^{\max} - 0.25] \times 10^4$ cm^{-1}. [b] From [14]. [c] Doublet lifetimes in aqueous solution at room temperature. [d] [165]; ethyleneglycol–H_2O (2 : 1, v/v). [e] *cis* products except as indicated. [f] [72]. [g] [114]; 20 °C. [h] [171]. [i] [173]. [j] [174]. [k] [175,176]. [l] [177]. [m] [100]; Me_2SO–H_2O (1 : 1, v/v). [n] [178]. [o] [179]; 4.5 °C. [p] [180]. [q] [120]. [r] [181]. [s] [53,182]. [t] [107]. [u] "Emission maximum" reported in [66,107]. [v] [183]. [w] [108]. [x] [66]. [y] [184]. [z] *Quantum yield for trans → cis isomerization.* [aa] Lowest quartet is probably $^4B_2$; we have used the splittings calculated by Perumareddi [108] to obtain an estimate of $E(^4B_2^0)$. [ab] [160]. [ac] [135]. [ad] [185]. [ae] [160]. [af] [186].

We consider *trans*-Cr(en)$_2$(NCS)$_2^+$ to be an extensively studied, characteristic example of the behavior of compounds of this class [53,54]. The products of electronic excitation of this compound are *cis*-Cr(en)$_2$(OH$_2$)NCS^{2+} and Cr(en)(enH)$^+$(OH$_2$)(NCS)$_2^{2+}$ ($\phi = 0.18$ and 0.07, respectively) [66]. About 80% of the photoreaction can be quenched with Cr(CN)$_6^{3-}$, but the ratio of photoproducts is comparable for the quenchable and unquenchable portions of the photoreaction. The product yields are independent of excitation energy through the ligand field absorption region (560–365 nm), but the phosphorescence quantum yield appears to drop by about 20% for the longer wavelength excitations [66].

A single, reasonably symmetrical, low energy ligand field absorption band is observed for *trans*-Cr(en)$_2$(NCS)$_2^+$ ($\lambda_{\text{max}}^{\text{obsd}} = 20.2 \times 10^3$ cm^{-1} [66,107]), even though a parameterized ligand field calculation [108], predicts an appreciable splitting of this band ($\lambda_{\text{max}}^{\text{calcd}} = (20.7$ and $19.4) \times 10^3$ cm^{-1}, with the ^4E_g component being lowest in energy). On the basis of the calculated splitting, and allowing a 2.5×10^3 cm^{-1} difference in energy between the absorption maximum and the energy of the band origin, one finds $^4E_g^0 \sim 16.9 \times 10^3$ cm^{-1}. A high resolution study of the *trans*-Cr(en)$_2$(NCS)$_2^+$ emission is not available, but the emission is centered at about 13.7×10^3 cm^{-1} [66,107], and a plausible estimate of the band origin would be $^2E_g^0 \simeq 14 \times 10^3$ cm^{-1}. Since the differences between the quartet and doublet state energies must roughly parallel any variations in ligand field stabilization energy, and since this difference is 1650 cm^{-1} for Cr(OH$_2$)$_6^{3+}$ and 4500 cm^{-1} for Cr(NH$_3$)$_6^{3+}$ (see Table 3), the value inferred for *trans*-Cr(en)$_2$(NCS)$_2^+$ is $\delta\epsilon = E(^4E_g^0) - E(^2E_g^0) \simeq 2900$ cm^{-1}.

The rate of population of ^2E_g, following quartet excitation of *trans*-Cr(en)$_2$(NCS)$_2^+$, has been the subject of some dispute [28–30], but two different groups have obtained $k_{\text{isc}} \geqslant 2 \times 10^{11}$ s^{-1} in water at 25°C [28,30]. The rate of this process is reported to be strongly solvent dependent [30], possibly consistent with a previously postulated solvent limited, "prompt" intersystem crossing rate [29,40,47,101]. However, one recent picosecond study [30] reports a single rate for the population of the ^2E state, thus suggesting that there is no reason why this rate should compete with vibrational relaxation within the quartet state. More rapid relaxation of the high frequency metal–ligand modes than the low frequency solvent modes is plausible, and the quartet configuration could be "trapped" by a small solvent reorganizational barrier and the low frequency solvent modes. The information currently available does not allow resolution of this issue. The back intersystem crossing rate, based on the estimated energy gap and k_{isc}, is $k_{\text{bisc}} \gtrsim 5 \times 10^5$ s^{-1}. This can be compared to the rate of doublet decay $\tau_D^{-1} = 2 \times 10^5$ s^{-1}. Thus back intersystem crossing could be a viable relaxation–reaction pathway for (^2E_g)*trans*-Cr(en)$_2$(NCS)$_2^+$.

More generally, $\delta\epsilon$ should increase in the order $F \leq Cl < NCS \ll CN$ among the *trans*-$Cr^{III}A_4X_2$ complexes. There is no correlation of product yields within this ordering, but the doublet lifetimes of ammine and amine complexes do seem to correlate with variations in LFSE or with $\delta\epsilon$ (see discussion in section B(i) (f)). While the ^2E lifetimes of $Cr^{III}A_4XY$, $Cr^{III}A_5X$, and $Cr^{III}A_6$ ($A = NH_3$ or an amine) are roughly correlated to some LFSE-related energy gaps, the quantum yields for products exhibit considerable variation depending on the type of amine coordinated. Within a given family of complexes (i.e., for $Cr^{III}(NH_3)_4XY$ complexes, or $Cr^{III}(en)_2XY$ complexes, or $Cr^{III}([14]aneN_4)X_2$ complexes, etc.), the product yields are remarkably similar while the lifetimes vary a great deal. This kind of observation has led to proposals that there is a single, dominant channel for ^2E relaxation, and that reactive and non-reactive processes occur after entry into this channel. Steric features of the ligands could dictate the partitioning between the formation of products or return to the ground state once the system has entered the relaxation channel. Alternatively, competing reaction and relaxation channels could account for these observations.

The *cis*- and *trans*-$Cr^{III}(N_4)XY$ complexes, containing macrocyclic (N_4) ligands, are beginning to emerge as useful steric probes of excited state behavior. Thermally activated, solvent mediated doublet relaxation pathways are relatively unimportant in the *trans*-$Cr^{III}(N_4)(CN)_2^+$ and *trans*-$Cr^{III}(N_4)(NH_3)_2^{3+}$ complexes, but these pathways so dominate the ambient temperature, fluid solution behavior of the *cis*-isomers that, as a result, they exhibit photochemical and photophysical behavior comparable to their ammine analogs [100]. In striking contrast, this discrimination between the *cis*- and *trans*-isomers disappears for very short lived doublet states of the $Cr(N_4)Cl_2^+$ complexes [100]. Since steric constraints on the ligands are not important features of the dominant pathway in these macrocyclic chloro-complexes, there may be a channel for relaxation which is available for them, but not for the analogous cyano or ammine complexes.

(e) Some observations concerning possible photogenerated substitutional intermediates

During the past decade there has been an increasingly explicit discussion of the intermediate species which may mediate the substitution reactions of ligand field excited states. While there is still no evidence that such "intermediate" species can survive large numbers of collisions with the solvent, the energy requirements of the various limiting species do provide insight into the reaction and/or deactivation channels available to the electronic excited states. Furthermore, since the electronic excited states often appear to meet the energy requirements of several possible substitutional intermediates, an understanding of the factors governing discrimination between these reaction channels may eventually enable the trapping and chemical utilization of some new, reactive, intermediate species to be undertaken. Owing to the paucity of relevant experimental information and to uncertainties in theoretical arguments, material in this section is of necessity highly speculative.

The limiting dissociative and associative pathways correspond to 5- and 7-coordinate intermediates, respectively. There have been reports of isolable 5- and 7-coordinate Cr(III) complexes [109–111], lending credence to the existence of such intermediates in photosubstitution reactions. The limiting geometries for identical ligands are square pyramidal (C_{4v}) and trigonal bipyrimidal (D_{3h}) for five coordinate, and pentagonal bipyramidal (D_{5h}), face capped octahedral (C_{3v}) and face capped trigonal prismatic (C_{2v}) for the seven coordinate species. The most stable geometry for a given coordination number seems to depend largely on steric factors. Interconversion between the limiting geometries (of a given coordination number) involves simple nuclear motions and is generally presumed to be facile unless there are steric constraints. However, one does expect small nuclear reorganizational barriers for such changes in geometry and these are likely to be important in dictating the relaxation pathways for the vibrationally excited molecules generated by surface crossings from electronic excited states.

It is possible to use simple (diagonal terms only, no configuration interaction) angular overlap model (AOM) arguments to obtain estimates of the accessible intermediate pathways. The very approximate approach which we have employed uses the ground state σ-parameters from six coordinate complexes to estimate energies in species with different coordination numbers. This approach greatly underestimates repulsion terms, and to compensate for this we have: (a) assumed ground state bond lengths and constant repulsions for any given geometry; (b) set the electronic state with the lowest energy for each geometry equal to the activation energy for ground state substitution (109 kJ mol^{-1} or 9×10^3 cm^{-1}; this is clearly the least possible energy for any substitutional intermediate); and (c) reduced the energies of Jahn–Teller distorted intermediate excited states by (2 to 3) $\times 10^3$ cm^{-1} to approximate the reduced repulsion accompanying coordination sphere expansion. Figure 7 summarizes these estimates of the relative energies of the intermediate excited states. Excited intermediate electronic states could mediate the relaxation process when some of the 7-coordinate intermediates are produced (associative pathways), but the electronically excited intermediates seem to be too high in energy to be important for the dissociative pathways. The actual energies of the intermediate ground electronic states are expected to vary a great deal, and some are undoubtedly higher in energy than the lowest energy quartet and doublet electronic excited states of $Cr(NH_3)_6^{3+}$. For example, first order AOM energies span a range of about 15×10^3 cm^{-1} for the intermediate ground electronic states

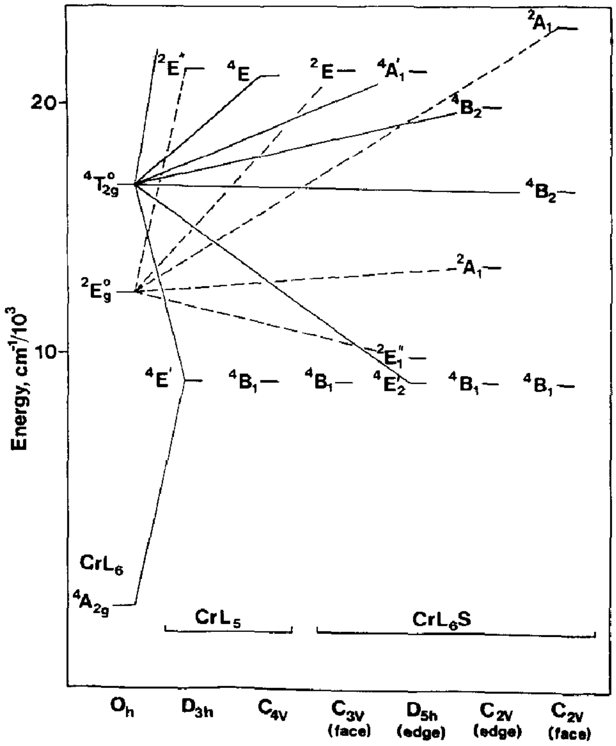

Fig. 7. Comparisons of the estimated energies of several substitutional intermediates and the vibrationally equilibrated electronic states of $Cr(NH_3)_6^{3+}$. The ground state electronic configuration for each hypothetical intermediate geometry has been set equal to the activation energy for hydrolysis of $(^4A_{2g})Cr(NH_3)_6^{3+}$. Since the thermal processes tend to be stereoretentive, this provides a lower limit for the energy of all but the $(^4B_1)Cr(NH_3)_5^{3+}$ intermediate. For a given intermediate geometry, the relative energies of electronic states are based on ground state AOM parameters, but allowing 3×10^3 cm^{-1} lower energy for Jahn–Teller distorted states. Those intermediate electronic states which are electronically correlated with $(^4T_{2g}^0)Cr(NH_3)_6^{3+}$ are indicated by solid lines, and those which are correlated with $(^2E_g)Cr(NH_3)_6^{3+}$ are indicated by dashed lines. Similar electron pairing energies are assumed for $Cr(NH_3)_6^{3+}$ and the various intermediates.

in the order: $D_{3h}(CrL_5) \sim D_{5h}$(edge; Cr_7) > $C_{4v}(CrL_5)$ > C_{2v}(face) > C_{2v}(edge; Cr_6S) > C_{3v}(face). Coordination sphere repulsions would increase the energies of the 7-coordinate intermediates in this series, but it is not easy to assess the balance between repulsions and favorable bonding angles to ligands. One would expect any repulsions to be especially large for the incoming ligand entering at an octahedral edge of the original complex, and the energies of the ^2E_g and ground state (^4E_g) configurations for the D_{5h} intermediate geometry may be energetically inaccessible from the $(^2E_g)Cr(NH_3)_6^{3+}$ species. Thus, there is no obvious spin conservative pathway for relaxation or reaction of the $(^2E_g)Cr(NH_3)_6^{3+}$ excited state. Doublet–quartet spin relaxation probably accompanies reaction or relaxation of this low energy state.

Figure 7 illustrates a fundamental concern associated with any mechanism which rationalizes product distributions in terms of the chemical behavior that is predicted by being based upon population of intermediate electronic excited states: these states are generally too high in energy to be populated from the vibrationally equilibrated doublet or (lowest energy) quartet excited states of the 6-coordinate parent complex. However, these excited states are near enough in energy that one would expect considerable mixing, especially as the system moves across the reaction (or relaxation) trajectory.

A final and very important point to be considered in relation to crossings from parent ($Cr^{III}L_6$) excited electronic states to intermediate potential energy surfaces is that such surface crossings must generally involve some kinetic constraints. This point is illustrated in Fig. 8 for the crossing from the potential energy surface of $(^2E_g)Cr^{III}L_6$ to the potential energy surface

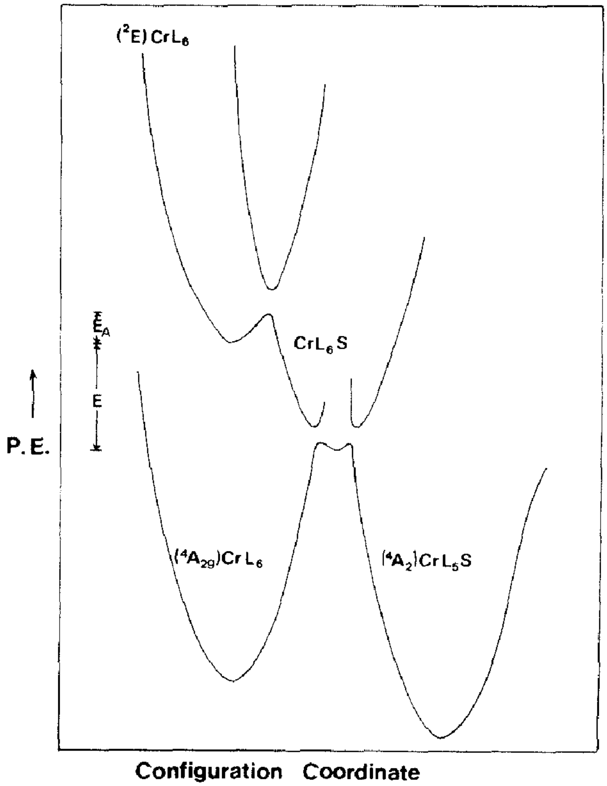

Fig. 8. Parabolic potential energy surfaces illustrating the strong coupling and crossing between excited state and substitutional intermediate surfaces. For this illustration, associative intermediate and parabolic potential energy surfaces have been assumed. As noted in the text, the $^2E \rightarrow$ intermediate crossing is undoubtedly more complicated than implied in such a simple illustration.

of a 7-coordinate intermediate in its ground electronic state, assuming a conventional surface crossing. The nuclear reorganizational barriers to surface crossing between the $Cr^{III}L_6$-excited state and the ground electronic state of an intermediate can be expected to play a significant role in dictating chemically important details of the relaxation pathway. For example, the classical expression [32,80,112,113] $E_a = (\lambda/4)(1 - \Delta E/\lambda)^2$ has been combined with an estimate of reorganizational parameters (λ) for degenerate ligand exchange reactions of $Cr^{III}L_6$ and the trigonal bipyrimidal (TBPY) $Cr^{III}L_4X$ intermediates, to show that the reorganizational barriers expected for $(^2E)Cr(NH_3)_5Cl^{2+}$ to TBPY surface crossings are consistent with observed product distributions [77], and that the crossings to TBPY intermediates tend to have smaller barriers than do crossings to SPY intermediates. However, the $^2E \rightarrow$ intermediate transition is not readily described as the intersection of the respective potential energy surfaces. Rather, this process must have many features of an avoided crossing, with the kinetic parameters reflecting electronic as well as nuclear constraints.

It is clear that the systematic consideration of photosubstitutional intermediates is at a very early stage. Experiments with perdeuterated amine complexes [79,96,97] indicate that $(^2E)Cr(III)$ excited state relaxation processes involve strong coupling and significant nuclear reorganizational barriers for crossing to the potential energy surfaces of intermediate species. As yet the photochemical intermediates have eluded direct detection, but model compounds with Cr(III) in 5- and 7-coordinate environments are becoming available [109–111]. A better theoretical understanding of the electronic structures of these species would help establish which excited state relaxation channels are energetically accessible, and which are not. The information currently available leads to the expectation that surface crossing from excited states results in intermediates in (or near) their ground electronic states. Even if the intermediate electronic excited states were nearer to the parent excited states than we have estimated, the intrinsic nuclear reorganizational barriers (λ) must be appreciable for all surface crossings involving intermediates and the pathways generating the lowest energy intermediates will tend to be favored by $E_a = (\lambda/4)(1 - \Delta E/\lambda)^2$.

It is to be noted that the "surface crossings" considered are electronically complex. An intersection between the ^2E excited state potential energy surface and the surface of an intermediate would require some distortion, at least for higher quanta, in the ^2E surface. Mixing with higher energy states could provide a mechanism for such distortions.

(f) Summary and conclusions

In recent years the interpretation of chromium(III) photosubstitutional chemistry has been dominated by three, not entirely exclusive themes: (a) the course of photochemical reaction is dictated by the electronic orbital occupation in the initial Franck–Condon excited state [8–19]; (b) a large percentage of the photoproducts result from dissociation of the lowest energy quartet excited state following back intersystem crossing from the lowest energy doublet state [53]; (c) a large percentage of the photoproducts occur by direct reaction from the thermally equilibrated, lowest energy doublet state [65,113]. Other views advanced can be combined in order to postulate that the reaction and relaxation of the electronic excited states in fluid solutions involve surface crossing, activated by nuclear rearrangements, to form a reactive intermediate [62,70,77–79,81]. The chemical behavior of the substitutional intermediates, postulated in these various mechanistic views, has come to be regarded as a major factor in dictating the observed product distributions.

Reactions of the higher energy ligand field excited states must occur very rapidly [28–30], possibly in competition with intersystem crossing and/or vibrational relaxation [6,61]. However, the wavelength independence of the yields of the predominant products suggests that $k'_p \leq k'_v$ in most Cr(III) systems. The solvent dependence reported for the intersystem crossing rates [30] suggests a dynamic role for the solvent in either (or both) the reaction or (and) intersystem crossing channel from the electronically excited quartet states in at least some systems. The issues raised by the fragmentary pieces of information now available may be resolved when the results of more direct and systematic investigations of excited quartet state behavior are available.

In contrast to the situation for the quartet excited states, there is almost too much information available about the behavior of the lowest energy Cr(III) doublet excited state. Nevertheless, the basic mechanistic questions have also not been resolved. We have outlined relevant information about doublet excited state structure and reactivity in the preceeding sections of this review and we have drawn attention to the specific mechanistic implications of this information. Some general features of doublet state photophysics are examined in the following section, before we attempt a summary of the overall mechanistic situation.

(1) Doublet state photophysics in Cr(III) complexes. The electronic relaxation of the lowest energy doublet excited state of chromium(III) is accompanied by the formation of products ($k_{Y,D}$) or regeneration of the original ground state (k_{nr}). Product formation is associated with the thermally activated regime for non-reactive relaxation, and the behavior of the electronically excited system in this temperature regime seems to be solvent induced (see Fig. 5). In the photochemical regime, the product yields tend to increase slightly with temperature [53], so there may often be a slightly

larger activation barrier for product formation than for non-reactive relaxation. Nevertheless, $Cr^{III}(NH_3)_5X$ complexes with very short excited state lifetimes ($< 10^{-7}$ s) have product yields not much different from those of pentaammine complexes with much larger ($> 10^{-5}$ s) doublet excited state lifetimes. Similar observations hold for most other classes of Cr(III) complexes. Thus, one hypothesis to be considered is that a single doublet excited state decay channel results in both the reactive and non-reactive processes. Three such single channel mechanisms have been considered in this review: (D-1) direct reaction; (D-2) back intersystem crossing; and (D-3) crossing to the potential energy surface of a substitutional intermediate. These are considered further in the section below.

The lifetimes of "thermally equilibrated" chromium(III) doublet states exhibit complex temperature and solvent dependencies. The temperature dependence may be approximately separated into two regions: (a) a limiting, nearly temperature and medium independent lifetime at very low temperature (usually less than 100 K); and (b) a high temperature region in which the lifetime decreases rapidly with increasing temperature [71,82,115].

The transition temperatures (T^0) between the limiting low temperature, temperature independent lifetime (τ^0), and temperature dependent lifetime regime occur over a very wide range varying with both the complex and the medium. Thus $T^0 < 77$ K for $Cr(OH_2)_6^{3+}$ [71], but $T^0 > 298$ K for *trans*-$Cr([14]aneN_4)(CN)_2^+$ (in water at pH 4) [79].

In the low temperature limit, variations in τ^0 reflect variations in the tunneling probability between the nested ^2E excited state and the $^4A_2$ ground state potential energy surfaces. A factor in this tunneling probability is the number of high frequency acceptor modes [80], and in these complexes the N–H stretching modes seem to function as the most effective acceptor modes, giving rise to the large isotope effects. Thus τ^0 tends to increase as the number of N–H groups decreases [94,98,116,117].

A complex description is required for the temperature dependence of the lifetime in the high temperature regime, where the complexes are photoactive. The usual practice has been to quote Arrhenius activation energies for the lifetimes in fluid solution ($E_A \sim 30$ to 70 kJ mol^{-1}). However, data obtained over an extended temperature range often result in Arrhenius plots with systematic curvature [79,95]. As a consequence, the inferred Arrhenius activation energies must be viewed with caution. The curvature can be accomodated using two exponentials to fit the complex temperature dependence [118], or by using a complex exponential function which takes account of the quantization of vibrations involved in the surface crossing [80]. The first approach assumes competing reaction and/or non-reactive decay channels, while the latter assumes a single relaxation channel and that the branching to form products or to return to the ground state occurs after entry into this channel.

The single channel view expresses the rate of excited state decay as the sum of a unimolecular term (based on the tunneling between weakly coupled ^2E and ground state surfaces) and a solvent dependent term (based on strong coupling between ^2E and an intermediate potential energy surface): e.g.,

$$k_{\mathrm{nr}} = (\tau^0)^{-1} + C(k_{\mathrm{B}}T^\star)^{-1/2} \exp(-E_{\mathrm{a}}/k_{\mathrm{B}}T^\star) \qquad (13)$$

where the effective temperature is given by,

$$k_{\mathrm{B}}T^\star = \tfrac{1}{2}\hbar\omega_{\mathrm{ave}} \coth(\hbar\omega_{\mathrm{ave}}/2k_{\mathrm{B}}T)$$

C is a combination of constants and electronic matrix element terms, and ω_{ave} is the mean frequency of the vibrational modes involved in the strongly coupled surface crossing. A considerable strength of this interpretation is that the deuterium isotope effects observed at high temperatures have a very natural explanation in terms of the small effects of nuclear tunneling expected when $\hbar\omega_{\mathrm{ave}} \geq 2k_{\mathrm{B}}T$ and in terms of the different vibrational quanta observed for the M–N skeletal frequencies in *N*-proteo and *N*-deutero ammine (or amine) complexes [22]. This approach has a very severe deficiency in that the inferred activation barriers are extremely large, (7–12) $\times 10^3$ cm^{-1} (values of E_{a} in Table 1 of ref. 79 are about a factor of 2 too small), and this leads to huge pre-exponential factors, 10^{14}–10^{20} s^{-1}. For a bond breaking or bond making reaction coordinate one would expect pre-exponential factors of $\sim 10^{13}$ s^{-1}. While many features of the single channel approach are appealing, eqn. (13) does not appear to provide an appropriate description of the reaction coordinate. This may indicate that this surface crossing is too complex to be approximated by quadratic potential energy functions or that a many channel model is required, or, alternatively, that the surface crossing should be formulated in terms of free energies so that the pre-exponential factor contains an entropy contribution.

Under high temperature conditions, the doublet lifetimes have been observed to roughly parallel the ligand field stabilization energy [114]; however, this seems to be the case mainly for amine (ammine) complexes (see Fig. 9). The approximate correlation of τ_{D} with LFSE could in principle reflect: (a) vairations in $\delta\epsilon = E(^4E^0$ or $^4T^0_{2g}) - E(^2E^0)$; (b) the variations in activation barrier for direct substitutional chemistry of the electronically excited doublet; or (c) the variatons in the energy gap to some low energy intermediate chemical species. Thus the correlation of excited state lifetimes for a selected group of *cis*- and *trans*-Cr$^{\mathrm{III}}$A$_4$XY complexes has been cited by Linck et al. [107] as evidence for the back-intersystem crossing model for excited state relaxation. However, when an extended collection of complexes is considered, the estimated energy gaps, solvent dependencies, isotope effects, etc., would seem to be inconsistent with back intersystem crossing.

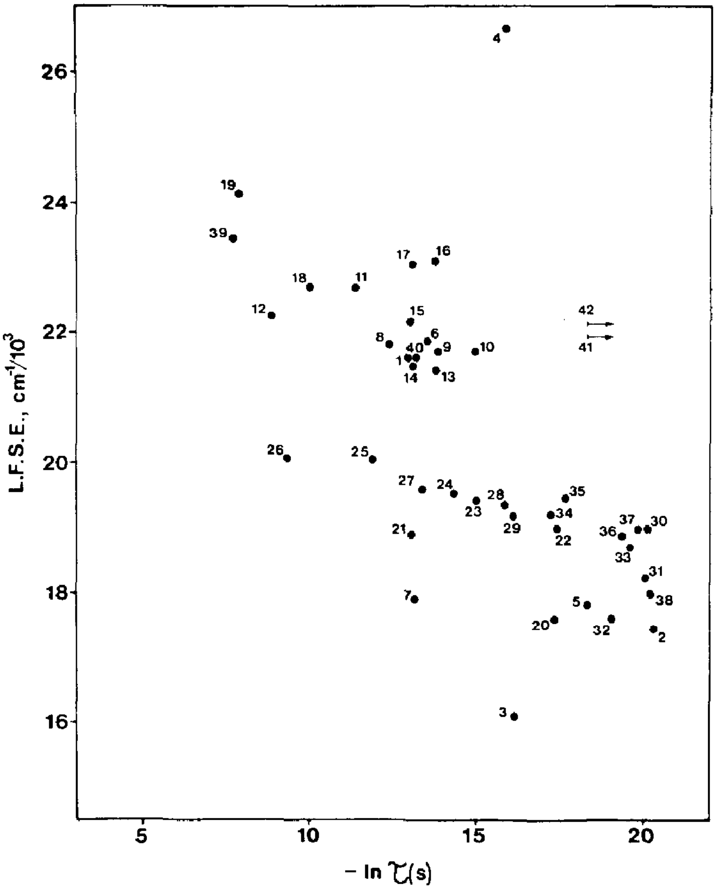

Fig. 9. Correlation of ligand field stabilization energy (LFSE) with the mean ^2E decay time (in aqueous solution at 25°C except as indicated) for several Cr(III) complexes. Energy of lowest LF absorption used for LFSE. Data from Tables 3, 4, 6 and 7. Key to points: 1, $Cr(NH_3)_6^{3+}$. 2, $Cr(OH_2)_6^{3+}$. 3, $Cr(urea)_6^{3+}$. 4, $Cr(CN)_6^{3-}$. 5, $Cr(NCS)_6^{3-}$. 6, $Cr(en)_3^{3+}$. 7, $Cr(acac)_3$. 8, $Cr(sep)^{3+}$ (in DMF). 9, $Cr(chda)_3^{3+}$ (in DMF). 10, $Cr(dien)_2^{3+}$ (in DMF). 11, $Cr([9]aneN_3)_2^{3+}$. 12, *trans*-$Cr([14]aneN_4)(NH_3)_2^{3+}$. 13, *cis*-$Cr([14]aneN_4)(NH_3)_2^{3+}$. 14, *cis*-$Cr([14]aneN_4)en^{3+}$. 15, $Cr(NH_3)_5CN^{2+}$. 16, *trans*-$Cr(en)_2(CN)_2^{+}$. 17, *cis*-$Cr(en)_2(CN)_2^{+}$. 18, *trans*-$Cr(NH_3)_4(CN)_2^{+}$. 19, *trans*-$Cr([14]aneN_4)(CN)_2^{+}$. 20, *trans*-$Cr([14]aneN_4)Cl_2^{+}$. 21, *trans*-$Cr(en)_2F_2^{+}$. 22, *trans*-$Cr(en)_2(OH_2)F^{2+}$. 23, *trans*-$Cr(en)_2(NCS)F^{+}$. 24, *trans*-$Cr(NH_3)_4(NCS)_2^{+}$. 25, *trans*-$Cr(en)_2(NCS)_2^{+}$. 26, *trans*-$Cr([14]aneN_4)(NCS)_2^{+}$. 27, *trans*-$Cr(tn)_2(NCS)_2^{+}$. 28, *trans*-$Cr(en)_2(OH_2)NCS^{2+}$. 29, *trans*-$Cr(tn)_2(OH_2)NCS^{2+}$. 30, *trans*-$Cr(NH_3)_4(OH_2)NCS^{2+}$. 31, *trans*-$Cr(en)_2(NCS)Br^{+}$. 32, *trans*-$Cr(NH_3)_2(NCS)_4^{-}$. 33, *trans*-$Cr(tn)_2(OH_2)_2^{3+}$. 34, *cis*-$Cr(tn)_2(OH_2)NCS^{2+}$. 35, *cis*-$Cr(en)_2(OH_2)NCS^{2+}$. 36, *cis*-$Cr(tn)_2(OH_2)_2^{3+}$. 37, *cis*-$Cr(en)_2(OH_2)_2^{3+}$. 38, *cis*-$Cr(tn_2)(OH_2)(Cl)^{2+}$. 39, *trans*-(*ms*-(5,12)-$Me_6[14]aneN_4)(CN)_2^{+}$. 40, *cis*-Cr(*rac*-(5,12)-$Me_6[14]aneN_4)(CN)_2^{+}$. 41, $(Cr(sar)^{3+}$ (upper limit for τ). 42, $Cr(diamsar)^{3+}$ (upper limit for τ).

The similarities in bond length and vibrational frequencies of the lowest doublet and the ground electronic states suggest strongly, that direct doublet state reactions (to form electronically correlated products) should not be significantly faster than the corresponding substitution reactions in the ground state. Furthermore, the facts that (a) only amine complexes seem to have room temperature lifetimes approximately correlating with the LFSE,

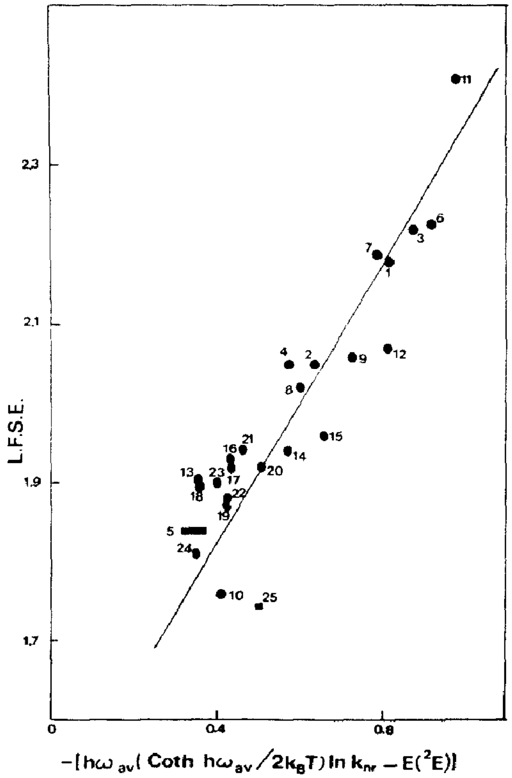

Fig. 10. Correlation of ^2E excited state lifetimes of $\mathrm{Cr^{III}}$–amine complexes in aqueous solution and LFSE based on a simple strong coupling surface crossing model using $\hbar\omega_{\mathrm{ave}} = 400\ \mathrm{cm^{-1}}$ and the energy of lowest LF absorption maximum ($^4T_{2g}$ in O_h or the mean of ^4E and ^4B components in lower symmetry) has been used for LFSE (energies in $\mathrm{cm^{-1}}/10^4$). The correlation is based on eqn. 13 with $\lambda \gg \Delta E$, $E_a \sim \lambda/4 - \Delta E/2$, $\hbar\omega_{\mathrm{ave}} \sim 400\ \mathrm{cm^{-1}}$, and

$$\hbar\omega_{\mathrm{ave}}(\coth \hbar\omega_{\mathrm{ave}}/2k_BT)\ln k_{\mathrm{nr}} \sim A + E(^2E^0) - \Delta E$$

where A is presumed to be approximately constant through a series of complexes. This correlation suggests that a strong-coupling-type of energy gap law is important in determining lifetimes of $\mathrm{Cr^{III}}$–amine complexes in the thermally activated regime. The "quality" of the correlation is not very sensitive to the value of $\hbar\omega_{\mathrm{ave}}$ used and the implied intercept is unrealistic (see text). Key to points: 1, $\mathrm{Cr(NH_3)_6^{3+}}$. 2, $\mathrm{Cr(NH_3)_5NCS^{2+}}$. 3, $\mathrm{Cr(NH_3)_5CN^{2+}}$. 4, *trans*-$\mathrm{Cr(NH_3)_4(NCS)_2^+}$. 5, *trans*-$\mathrm{Cr(NH_3)_2(NCS)_4^-}$. 6, *trans*-$\mathrm{Cr(NH_3)_4(CN)_2^+}$. 7, $\mathrm{Cr(en)_3^{3+}}$. 8, *trans*-$\mathrm{Cr(en)_2F_2^+}$. 9, *trans*-$\mathrm{Cr(en)_2(NCS)_2^+}$. 10, *trans*-$\mathrm{Cr([14]aneN_4)Cl_2^+}$. 11, *trans*-$\mathrm{Cr([14]aneN_4)(CN)_2^+}$. 12, *trans*-$\mathrm{Cr([14]aneN_4)(NCS)_2^+}$. 13, *trans*-$\mathrm{Cr(en)_2(OH_2)F^{2+}}$. 14, *trans*-$\mathrm{Cr(en)_2(NCS)F^+}$. 15, *trans*-$\mathrm{Cr(tn)_2(NCS)_2^+}$. 16, *trans*-$\mathrm{Cr(en)_2(OH_2)NCS^{2+}}$. 17, *trans*-$\mathrm{Cr(tn)_2(OH_2)NCS^{2+}}$. 18, *trans*-$\mathrm{Cr(NH_3)_4(OH_2)NCS^{2+}}$. 19, *trans*-$\mathrm{Cr(tn)_2(OH_2)_2^{3+}}$. 20, *cis*-$\mathrm{Cr(tn)_2(OH_2)NCS^{2+}}$. 21, *cis*-$\mathrm{Cr(en)_2(OH_2)NSC^{2+}}$. 22, *cis*-$\mathrm{Cr(tn)_2(OH_2)_2^{3+}}$. 23, *cis*-$\mathrm{Cr(en)_2(OH_2)_2^{3+}}$. 24, *cis*-$\mathrm{Cr(tn)_2(OH_2)Cl^{2+}}$. 25, $\mathrm{Cr(OH_2)_6^{3+}}$.

and (b) that the probability of product formation seems to have little relevance to this correlation, indicate that the high temperature decay channel is not contingent upon chemical reaction. The strong temperature dependence of the doublet lifetime indicates a strong coupling mechanism for non-radiative relaxation. That the rates correlate with some ligand field-like energy gap parameter for amine, but not some other complexes, suggests that the configuration coordinates of the surface crossing involve some specific class of vibrational mode; i.e., the crude correlation would seem to implicate some kind of NH or Cr–NH_3 reorganizational motion among the amine complexes.

The crude correlations of LFSE with excited state lifetimes (Figs. 9 and 10) are suggestive of a gap law for the excited state decay process. A qualitative correlation between LFSE and decay rate would be expected if the decay process can be described by a strongly coupled crossing from the ^2E potential energy surface into the potential energy surface of a reaction intermediate in its electronic ground state. This is illustrated in Fig. 11 where it is assumed that the barrier to ground state substitution increases with LFSE [119], so that the $^2E \rightarrow$ intermediate energy gap decreases as LFSE increases. In the strong coupling limit one expects the rate to increase as the energy gap increases.

Furthermore, there is an appreciable scatter even for amine complexes, and the behavior of *cis*- and *trans*-$Cr^{III}(N_4)X_2$ ($X = CN^-$ or NH_3) does not correlate well with the other data in Fig. 10. Despite its limitations, the approximate correlation is suggestive of a "reactant-product" (here, ^2E-intermediate) energy gap dependence of the kind that one expects for a strongly coupled surface crossing.

(2) Mechanistic issues and problems. The major mechanistic issues of Cr(III) photochemistry and photophysics remain a challenge. The problems, concerns and evidence are conveniently summarized in terms of four principle issues.

(1) Issue 1. Is there a unique, single channel for doublet state relaxation?

(a) Single channel. As noted above, most of the photo-mechanistic hypotheses have been based on single channel arguments. The principle evidence in favor of a single relaxation channel is: (i) Arrhenius plots of τ_D in the thermally activated regime are usually close to linear; (ii) product yields and product stereochemistry are usually very nearly independent of the excitation wavelength and have been found to be the same for some quenchable and unquenchable photoreactions; (iii) the predominant products and product stereochemistries are nearly always consistent with a simple set of rules (e.g. those of Adamson or those of Vanquickenborne and Ceulemans).

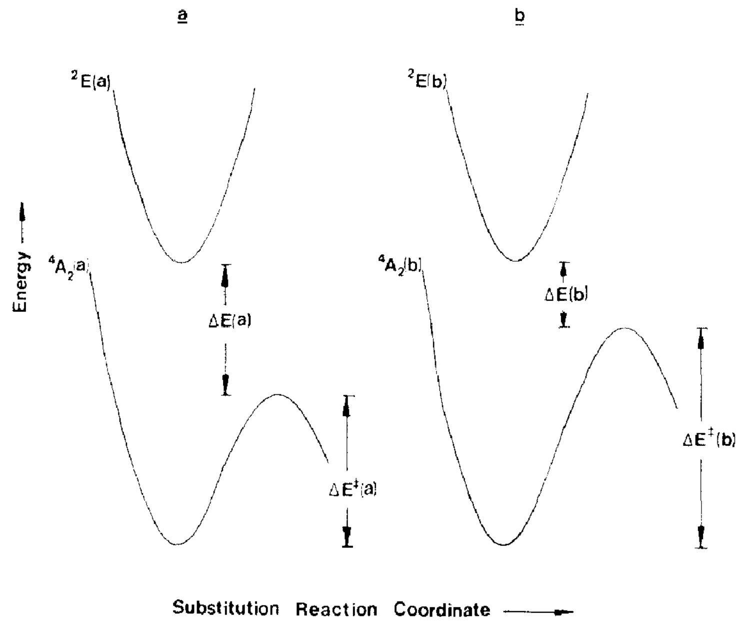

Fig. 11. Qualitative illustration of the expected increase in $\Delta E = E(^2E) - E$(substitutional intermediate) with LFSE. For relatively small LFSE, figure (a) the activation energy for substitution is expected to be relatively small and the doublet state energy is expected to be relatively large: i.e., for LFSE(a) < LFSE(b), $\Delta E^{\ddagger}(a) < \Delta E^{\ddagger}(b)$, $E[^2E(a)] > E[^2E(b)]$, so $\Delta E(a) > \Delta E(b)$.

(b) Multiple channels. A number of experimental observations indicate that more than one channel exists, at least for non-radiative relaxation of the doublet state: (i) product quantum yields are often weakly temperature dependent; (ii) Arrhenius plots for τ_D are sometimes curved; (iii) different solvent effects are found for cations than for anions; (iv) sensitivity of τ_D to steric constraints of the ligands; (v) the repression of the sensitivity of τ_D to the *cis-* or *trans-*macrocyclic ligand isomer when Cl^- is coordinated.

The discovery that some complexes exhibit limiting low temperature (or weakly coupled) lifetime behavior, while for most τ_D is strongly temperature dependent in fluid solution near ambient conditions, clearly requires that more than one relaxation channel be considered. Even aside from this consideration, the range of photophysical behavior noted is very difficult to reconcile with single channel behavior. This issue needs to be examined more extensively than it has been in the past.

(2) Issue 2. If there is a predominant mechanism for doublet decay (i.e., a single channel), what is it?

(a) Back intersystem crossing to populate the lowest energy quartet state, followed by characteristic quartet state reactions. There are a number of observations which support this as being a predominant mechanism for the

doublet state reactions: (i) the values of the Arrhenius activation energy observed in many (but not all) systems are comparable to the estimated doublet–quartet energy gaps; (ii) in a few systems it has been possible to demonstate that the same products are obtained from the quenchable and non-quenchable photoreaction pathways; (iii) the rough correlations of τ_D with LFSE; (iv) the generally recognised usefulness of the Vanquickenborne and Ceulemans model; (v) values of $\Delta V^{\ddagger}_{\phi(Y)}$ and $\Delta V^{\ddagger}_{\tau(D)}$ for $Cr(NH_3)_6^{3+}$ and $Cr(NH_3)_5NCS^{2+}$ are qualitatively consistent with this model if the quartet reaction is associative (thus not consistent with the Vanquickenborne and Ceulemans model). Observations which do not fit neatly into this model include: (vi) the observations that τ_D is sensitive to amine (or ammine) deuteration even in the thermally activated regime; (vii) the sensitivity of τ_D to the solvent matrix in the thermally activated regime; (viii) the variatons of τ_D with steric constraints imposed by coordinated ligands; (ix) the magnitude of the inferred value of $\Delta V^{\ddagger}_{Y,Q}$.

(b) Direct reaction to give electronically correlated products. Several observations can be cited as support for such a model: (i) the most reactive systems are often (but not always!) the shortest lived; (ii) the isotope, environmental and ligand–steric effects on τ_D can be accomodated using this kind of model; (iii) the very approximate correlation of τ_D with LFSE. However, there are many features of Cr(III) photochemistry and photophysics which argue against this model; (iv) the Arrhenius activation energies are too small for a dissociative reaction, while the sign of $\Delta V^{\ddagger}_{\tau(D)}$ is incorrect for an associative reaction; (vi) binding of Cr(III) in clathro-chelate ligands quenches the photoreaction, but can result in very small values of τ_D; (vii) no good correlation of $\phi(Y)$ with τ_D exists; (viii) where information is available, only a fraction of the ^2E relaxation events produce products [69].

(c) Relaxation through a channel strongly coupling the doublet state to the potential energy surface of some intermediate species in its ground electronic state. This approach is flexible enough to account for most observations, but in the absence of sufficiently detailed information about the shapes of excited state and product potential energy surfaces, it currently lacks the predictive features which would make it useful.

(d) Relaxation mediated by population of high energy, distorted doublet state. The attribution [59,60] of broadened emissions, in certain Cr(III) complexes, to distorted components of $^2T_{1g}(O_h)$ electronic states raises the possibility that these states play a significant photochemical role. On the other hand, high resolution absorption, emission and excitation spectroscopy of low symmetry Cr(III) complexes indicates that the components of both $^2E_g(O_h)$ and $^2T_{1g}(O_h)$ states tend to have very narrow bands [120–128], and τ_D does not appear to be unusually small [53,107] for these complexes.

(3) Issue 3. What kinds of intermediates are formed and what role do they play in dictating the product distribution? There are many aspects of this issue which need to be resolved; e.g., are such intermediates in any sense thermally equilibrated? Can they be detected? Are solvent cage effects important? As yet there is no clear experimental information available which bears up on this issue. Certainly one expects either 5- or 7-coordinate intermediates to be very short lived under ambient conditions, but arguments based on intermediates generated thermally are probably misleading since different vibrational modes will be activated along the thermal and photochemical reaction coordinates.

(4) Issue 4. Is the quartet state bound under ambient, fluid solution conditions? The somewhat limited picosecond flash photolysis evidence seems to suggest that vibrational equilibration is rapid compared to intersystem crossing in the quartet state for *trans*-$Cr(en)_2(NCS)_2^+$ [30] but that these processes may actually be competitive in most other Cr(III) complexes [106]. There are some reports that product yields decrease at very long wavelengths [61,66,101], consistent with a weakly bound quartet state. However, quantum yields are very difficult to measure under conditions of weak light absorption, and other, very sensitive studies, have indicated that, at least for $Cr(en)_3^{3+}$, the production of products and stereoisomers is not significantly dependent on excitation wavelength [129].

(3) Closing observations. All the mechanistic models mentioned in this section probably contain some element of "truth", but not one is likely to be absolutely correct for all Cr(III) systems. Among the single channel models, the forbidden surface crossing model, D-3, has many attractive features despite its lack of detailed structure. The postulated surface crossing would be to a potential energy surface for some substitutional intermediate in its electronic ground state. Any such crossing must be complex since: (a) the ^2E excited state and the $^4A_2$ ground state surfaces are nested near their respective equilibrium nuclear positions; and, (b) the most likely intermediates have quartet electronic states so one expects some contribution of an electronic matrix element term to the overall crossing probability. The nuclear coordinates of the crossing point and the vibrational modes activated in the crossing would tend to determine whether the crossing would generate substitutional products or the original ground state. Thus, one would expect that only crossings with nuclear coordinates near to some saddle point of a ground state reaction surface would generate a chemically distinct intermediate species; i.e., a species which could survive a few collisions with the solvent. Steric constraints introduced by complex ligand systems could promote or restrict such crossings. The relatively long lifetimes of *trans*-$Cr^{III}(N_4)X_2$ complexes could be attributed to such a restriction, the rela-

tively short lifetimes of Cr(III) complexes (in which the ligands are trigonally distorted in the ground state) could be attributed to a crossing promoted by relaxation of ligand strain. However, these effects do not often show up neatly in Arrhenius activation energies, rather, they appear more often to determine the temperature range at which the transition between temperature independent and temperature dependent lifetime behavior occurs. The formal description of this situation requires either (or both): (a) a vibrationally quantized crossing between anharmonic surfaces; or, (b) a selection rule for the possible nuclear motions involved in the crossing. From a strictly intuitive point of view, the restriction on surface crossings implied for *trans*-$Cr^{III}(N_4)X_2$ complexes can be rationalized by postulating that the crossing is to the potential energy surface of a trigonal bipyramidal-type of intermediate, and that this crossing requires inversion of an amine nitrogen of the N_4 macrocyclic ligand. There are, of course, other possibilities. The use of sterically constrained ligands to promote or restrict the nuclear rearrangements available to an excited state is likely to prove a very powerful probe of the mechanistic possibilities.

(ii) d^6*-Metal complexes*

For no other metal do we have the wealth of photochemical and spectroscopic information which is available for chromium(III). However, there have been a substantial number of studies of cobalt(III), rhodium(III), iridium(III), iron(II), and ruthenium(II) complexes. Taken as a class of compounds, there is more information available concerning the structure and reactivity of the ligand field excited states of these d^6 complexes than for any except for the d^3 class of complexes. While there are gross spectroscopic similarities among the low spin compounds, there is no single pattern of photochemical behavior that can be readily associated with this electronic configuration. Rather, there is considerable variation from metal to metal, with the most striking contrast being that of the near photoinertness of cobalt(III) amine (or ammine) complexes ($\phi < 10^{-3}$) and the greater photoactivity of the heavier metal complexes and $Co(CN)_6^{3-}$, following ligand field excitations.

The low spin d^6 complexes differ from d^3 complexes in that all their excited electronic states involve population of orbitals which are antibonding. As a consequence all the excited states undergo changes in metal–ligand bond lengths upon thermalization. These bond length changes may be moderately large ($\geqslant 10$ pm; e.g., [22,25,187]) and all luminescence from the ligand field states is appreciably Stokes shifted. The ground electronic states are singlets, and while states of triplet spin multiplicity probably play important roles in all the photoinduced behavior, the lowest energy excited state for many cobalt(III) amines (or ammines) is probably a quintet. Each excited electronic configuration is likely to have different metal–ligand bond lengths and coordination symmetry (e.g., see [22,25]), and one would, on this basis alone, predict differences in chemical behavior. A final issue of concern is that for the heavy metal complexes and $Co(CN)_6^{3-}$, the lowest energy excited state has an energy significantly in excess of the energy requirements for substitution in the ground state, while among most cobalt amines (or ammines) it is very likely that the lowest energy excited state does not meet the energy requirements for substitution in the ground state. It has been proposed that this relative ordering of thermalized excited states and transition states is a major feature in the overall photoreactivity [62]. However, these patterns of photoreactivity have also been rationalized in terms of the orbital population of Franck–Condon states and in terms of Adamson's rules [188].

(a) Cobalt(III) amine (ammine) complexes

These complexes seem to form the best documented example of *Type IA* (fast reaction) photochemical behavior. Their behavior is thus in distinct contrast to, at the least, that found for the slow component of chromium(III) photochemistry or the major components of the photochemistry of rhodium(III) and of iridium(III). Quantum yields of products tend to be very small and to be excitation wavelength dependent for irradiations of the Co(III) ligand field absorption bands. Even the ratios of products turn out to be dependent on the wavelength of excitation. This is clearly a warning against the use of overly simple models to describe these systems.

An additional feature which can complicate study of some of the cobalt complexes is the ubiquitous photoinduced redox process (forming Co(II) and an oxidized ligand species). While the threshold energies for those processes are in the near ultraviolet or high energy visible regions for most cobalt(III) ammines [188], the photoredox threshold can be of very low energy (near red), for $Co^{III}(N_4)XY$ complexes [189–191]. Since these macrocyclic ligands tend to remain coordinated to Co(II) under photochemical conditions [192,193], and since the $Co^{II}(N_4)$ complexes can catalyse substitution in $Co^{III}(N_4)XY$ complexes [194], failure to take account of small amounts of photoredox can lead to errors in the assessment of photosolvation yields. These $Co^{II}(N_4)$ complexes are usually easily oxidized, so that net yields of $Co(OH_2)_6^{2+}$ are of little value either in determining the significance of the redox process or in evaluating the catalytic effects of small amounts of $Co^{II}(N_4)$.

The most thoroughly studied complex of this class is $Co(NH_3)_5Cl^{2+}$. Irradiation of this complex in its lowest energy ligand field absorption band results in competitive ammonia and chloride aquation, with quantum yields

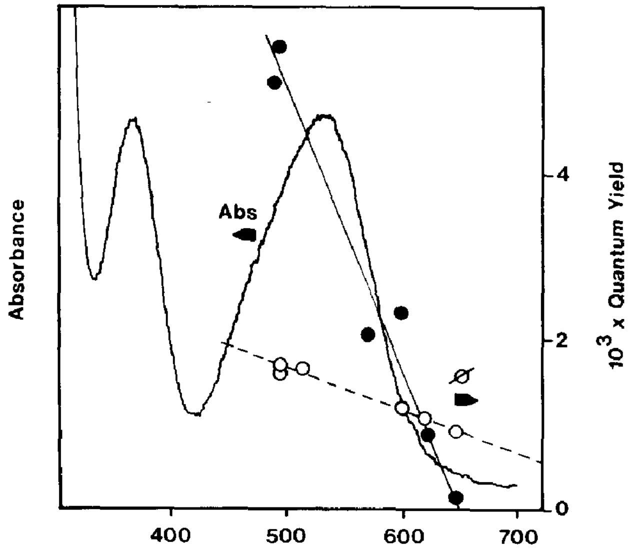

Fig. 12. Relationship between product yields and the spectroscopic transition excited state for $Co(NH_3)_5Cl^{2+}$. Quantum yields for the photoaquation processes are plotted on the right: solid circles for NH_3 aquation forming $Co(NH_3)_4(OH_2)Cl^{2+}$; open circles for Cl^- aquation forming $Co(NH_3)_5OH_2^{3+}$.

varying between (1 and 55) $\times 10^{-4}$ depending on the excitation wavelength [188,195,196]. The yields of both products, $Co(NH_3)_4OH_2Cl^{2+}$ and $Co(NH_3)_5OH_2^{3+}$, decrease as the excitation energy decreases. However, the photoaquation of NH_3 (to give $Co(NH_3)_4OH_2Cl^{2+}$) decreases the most rapidly and changes from the dominant process for excitations near the absorption maximum, to the minor one for $\lambda_{excit} > 600$ nm [195,196]. Langford has attributed this behavior to state specific chemistry; i.e., to chemistry dependent on the vibronic state populated, and therefore to reactions which are competitive with vibrational relaxation [61]. The photochemical behavior is compared to the absorption spectrum and the electronic state assignment in Fig. 12.

The lowest energy, vibrationally equilibrated, excited triplet electronic state of $Co(NH_3)_5Cl^{2+}$ is ^3E, this being electronically degenerate it will distort along an e_g normal vibrational mode. The result is an expansion of the Co–ligand bonds in either the **X**–**Z** or the **Y**–**Z** planes (where the Co–Cl bond defines the **Z**-axis) [22,197]. The electronically excited system will fluctuate between the two distorted structures with a frequency of the order of $5 \times 10^{10 \pm 1}$ s^{-1} (based on a simple harmonic oscillator estimation of the nuclear reorganizational barrier using the parameters in [22]). This excited state fluctuation amounts to a pseudorotation around the **Z**-axis. With respect to any chemical reaction that occurs more slowly than the rate of this pseudorotation, the electronically excited system will behave as if the NH_3–Co–Cl (**Z**-axis) has relatively long and weak bonds. This distortion of the equilibrated triplet excited state could be regarded as consistent, on the average, with the predictions of models based on orbital populations of Franck–Condon excited states [8–19], if the excited state reactions are sufficiently slow.

Any reactions of the vibrationally equilibrated triplet or quintet states must proceed by pathways involving transition states with total energy (or, more correctly, free energy) greater than or equal to that of the transition state for the corresponding ground state reaction. Some of the arguments employed above in discussing the quartet and doublet excited states of chromium(III) are qualitatively applicable to d^6 systems. However, there are likely to be some chemical consequences resulting from the fact that the lowest energy excited state and the ground state potential energy surfaces are nested for d^3 systems, but displaced along some nuclear coordinate for the d^6 systems. The limited spectroscopic evidence [22,186,198,199], indicates that the triplet and quintet states in Co(III) can be described in terms of reasonable, bound Born–Oppenheimer surfaces, at least for the lower vibrational quanta. Furthermore, the minimum energy position on these surfaces is near to or lower than the activation enthalpy for the ground state substitutional processes (see Fig. 12). The proximity of these excited electronic states and the transition states for thermal reactions must give rise to a complex web of possible crossings into product surfaces: the singlet, triplet and quintet excited electronic states of $Co(NH_3)_5Cl^{2+}$ all have A and B components at slightly different energies and one should consider both the dissociative (shown in Fig. 13) and the associative (presumably at somewhat higher energy) pathways for ground state substitution; even the simplest consideration of these possibilities leads to about a fivefold increase in the number of crossings over that shown in Fig. 13. Since these crossing points are an expression of the mixed state description of the wave function at the energies of the component crossings, such multiple crossings are in accord with strongly wavelength dependent, or "state specific", photochemical behavior. This contrasts markedly to descriptions of the (^2E)Cr(III) systems, in which it is commonplace to consider one surface crossing of an equilibrated excited state.

The vibrational coordinate associated with excited state thermalization, ν_{e_g} is different from the ungerade coordinate associated with ligand replacement. This results in displacement of the excited state potential energy surfaces with respect to the reaction channels for thermal substitution and raises the possibility that some surface crossings are more likely to regenerate the starting material than to generate reaction products. While surface

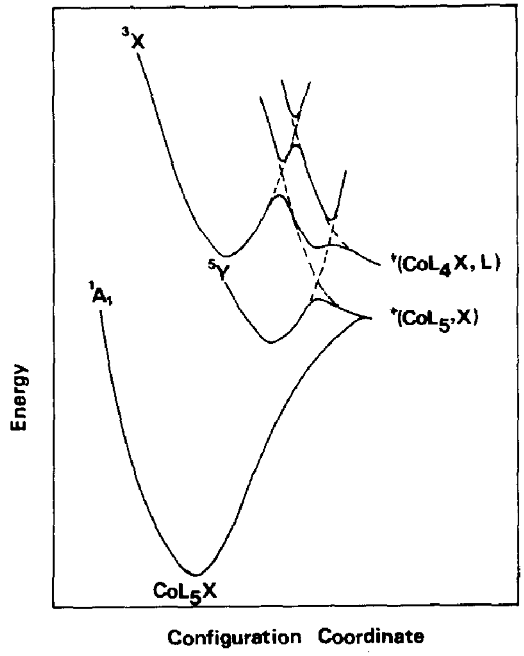

Fig. 13. Qualitative potential energy surfaces for $Co(NH_3)_5Cl^{2+}$ illustrating the multiple crossings between the low energy ligand field excited states and a single substitutional intermediate. For convenience of illustation the figure has been greatly simplified by neglecting the contributions arising from the non-degeneracy of the lowest energy states, the fact that the triplet and quintet should have two components each, and the possibility of crossings to more than one substitutional intermediate (e.g., associative as well as dissociative).

crossing to a substitutional intermediate provides a plausible rationalization for the strongly wavelength dependent quantum yields found for cobalt(III) ammines, there is as yet no simple way of predicting products (or product ratios) with any confidence.

Despite the noted conceptual difficulties and the theoretical complexities of the cobalt ammine systems, some simple features do occur in the behavior of $Co(NH_3)_5Cl^{2+}$: extrapolation, to $\phi = 0$, of plots of quantum yield vs. excitation energy, yields the threshold energies for ligand hydrolysis, $E_{th}(NH_3) \sim 167 \pm 17$ kJ mol^{-1} and $E_{th}(Cl^-) \sim 109 \pm 8$ kJ mol^{-1}. Thus the minimum photonic energy required to induce substitution of Cl^- is comparable to the activation energy (100 kJ mol^{-1}) [118] found for thermal substitution in $Co(NH_3)_5Cl^{2+}$. This implies that $\phi(Cl^-)$ is a fairly simple function of $E_{excit} - E_{th}$; i.e., the probability for fast (or "prompt") vibronic excited state to intermediate (or transition state) surface crossing must increase approximately linearly with the difference in energy between the Franck–Condon state and the substitutional transition state. The greater threshold energy for photoinduced substitution of NH_3 is as expected, based on the larger activation barrier for thermal hydrolysis of ammonia than chloride. It will be interesting to find out whether these patterns of behavior are characteristic of *Type IA* photochemistry in Co(III) complexes. If further experimental study does find this to be a general pattern of behavior, then photochemical selection rules will most likely be found to dictate the slopes of dependence of ϕ on $E_{\mathrm{excit}} - E_{\mathrm{th}}$.

It is to be emphasized that the discussion in this section pertains to the mechanism for a very minor process in the photochemistry of cobalt(III) amines: the overwhelming majority of ligand field excitations results in no chemical reaction. The obvious difference between these "photoinert" cobalt(III) complexes and their photoactive d^6 analogs ($\mathrm{Co(CN)}_6^{3-}$, Ru(II), Rh(III), etc.) is that the lowest energy excited states tend to have energies smaller than required for thermal substitution in the former complexes but not in the latter, as pointed out some time ago [62,200] and discussed at length by Hollebone et al. [6]. In order that surface crossing from a vibrationally thermalized excited state does not dominate the photochemistry, processes which compete with that surface crossing must be relatively efficient (e.g., $k_{\mathrm{nr}} \gg k_{\mathrm{p}}$). Such a situation is consistent with, but does not require, extremely short excited state lifetimes. Excited states of simple Co(III) complexes have usually eluded detection, but Langford and coworkers [201] have recently detected transient absorbancies, which they attribute to ligand field excited states, following excitations of *trans*-$\mathrm{Co(en)_2(NO_2)_2^+}$ and *cis*-$\mathrm{Co(en)_2(NCS)Cl^+}$. If this assignment is correct, the lowest energy ligand field excited states in these complexes have lifetimes of ~ 150 and ~ 40 ps respectively. There is less direct evidence, based on sequential two-photon photochemistry, that the lowest energy excited state of $\mathrm{Co(NH_3)_6^{3+}}$ could have a lifetime as long as 10^{-9} s [202]. In neither case is there any evidence that the observed transients are responsible for the substitutional photochemistry of the parent complexes.

(b) Cobalt(III) cyano complexes

There have been a few relevant studies of hexacyano- and halopentacyanocobaltate(III) complexes. The excited $\mathrm{Co(CN)}_6^{3}$ complex exhibits a broad, Stokes-shifted emission centered around 13.5×10^3 cm^{-1} [203–205]. The emitting excited state of this complex is reasonably long lived [204] and presumed to be the lowest energy triplet state and populated with high efficiency [206]. Band shape analysis of the excited state emission has been interpreted in terms of a uniform expansion of the six Co–CN bonds (an a_{1g} expansion, nearly preserving the O_h symmetry) [204] and in terms of a Jahn–Teller distorted excited state [205]. The latter seems most plausible, especially in view of the similar distortions inferred for related Co(III) and Rh(III) complexes.

The $Co(CN)_5X^{3-}$ (X = CN or halogen) and *trans*-$Co^{III}(CN)_4(SO_3)X^{n-}$ ($X = SO_3^{2-}$, OH^- or OH_2) complexes are photoactive. The dominant process is photosolvolysis of X, with yields in the range of 0.1–0.3 [48,207–209]. The photochemical processes have been postulated to be dissociative, and a nanosecond flash photolysis study of the initial products from photolysis of $Co(CN)_6^{3-}$ provided evidence for a five coordinate intermediate similar in chemical behavior to the thermally generated solvolysis intermediate [210].

(c) Rhodium(III) complexes

There has been a great deal of study of rhodium(III) complexes and the mechanistic situation for photosubstitution is relatively clear in these systems. Many, perhaps most, rhodium(III) complexes exhibit excited state luminescence [211]. Unfortunately, the luminescence attributed to ligand field excited states tends to be very broad and there is only one detailed analysis of the vibrational structure in these emissons [25]. Sexton et al. [212] have very recently reported a biphasic luminescence from many rhodium(III) ammine complexes in aqueous solution at 25°C. The high energy, fast decay component ($\tau \sim 10^{-10}$ s) has been attributed to a fluorescence decay of the upper singlet state (or states) initially populated by the absorption of radiation. The longer wavelength (centered ~ 700 nm), slow decay component ($\tau \sim 10^{-8}$ s) has been attributed to phosphorescence from the lowest energy excited state, presumably of triplet spin multiplicity [25,50,51,211–214].

Most Rh(III) ammine and aliphatic amine complexes are photolabile and have short excited state lifetimes (tens of ns) in water at room temperature [50,51] (Table 8). An exception is *trans*-$Rh([14]aneN_4)(CN)_2^+$ which is virtually photoinert and has a relatively long lifetime (~ 10 μs) [215]. The small photosubstitution yields of this complex are not surprising since one expects an equatorial ligand displacement in the cyano–Rh(III) complexes [216,217] and this process is effectively blocked by the macrocyclic ligand (see also the discussion below). The relatively long lifetime may indicate that expansion of ligands in the equatorial plane, expected by analogy to *trans*-$Co(NH_3)_4(CN)_2^+$ [187], is restricted by the macrocyclic ligand: a relatively small nuclear displacement of the lowest energy triplet state, coupled with a relatively large singlet–triplet energy gap, could result in weaker coupling between the excited state and ground state surfaces.

The phosphorescence lifetimes are usually ~ 10^3 to 10^4-times longer at 77 K (Table 3) than in fluid solution at room temperature [212,218,219]. This implies an activation-energy controlled relaxation process in the high temperature regime, but there have been no reports which document the temperature dependence of the decay lifetime over the full range. The decay process in the low temperature regime has been interpreted as having the

TABLE 8

Photochemistry and photophysics of some rhodium ammine complexes (25°; aqueous solutions)

Complex	τ(ICS) [a] (ps)	$\tau(^{3}$LF) 298 K [a,b] (ns)	$\tau(^{3}$LF) 77 K [c,d] (μs)	ϕ(X) [c]	ϕ(Am) [c]	$\phi(H_2O)$	ϕ(ISOM) [c]	$10^{-9}k_{isc}$ [f] (s^{-1})	$10^{-6}k_{X^-}$ [f] (s^{-1})	$10\ ^{6}k_{Am}$ [f] (s^{-1})	$10\ ^{6}k_{nr}$ [f] (s^{-1})
$Rh(NH_3)_6^{3+}$		21 [d]	19.1 ± 0.6		0.07					3.3	44
$Rh(NH_3)_5Cl^{2+}$		14.2 [g]	12.2 ± 0.2	0.15 [h]	0.04 [h]				10.5	2.8	57
$Rh(NH_3)_5Br^{2+}$	220	13.0 ± 0.4	10.3 ± 0.3	~ 0.02 [i]	0.18 [i]			4.5	~ 1.6	15	60
$Rh(NH_3)_5I^{2+}$	40 [h]	1.3 ± 0.1 [h]	7.6 ± 0.2	≤ 0.01 [h]	0.79 [h]			25	≤ 8	610	150
$Rh(NH_3)_5CN^{2+}$					0.09 [j]						
$Rh(NH_3)_5OH_2^{3+}$			2.7								
cis-$Rh(NH_3)_4Cl_2^+$	70	1.3 ± 0.3	0.7	0.39 [k]	0.013 [k]		0.33 [k]	14	300	10	460
trans-$Rh(NH_3)_4Cl_2^+$	90	1.8 ± 0.3	7.6	0.14 [l]	< 0.002 [l]		0.025 [d]	11	78	< 1	480
cis-$Rh(NH_3)_4Br_2^+$	60	1.0 ± 0.1	1.0	0.24	0.06		0.24	17	240	64	700
trans-$Rh(NH_3)_4Br_2^+$	90	1.5 ± 0.1	7.7	0.10	0.002		0.00 [m]	11	67	1.3	600
cis-$Rh(NH_3)_4(OH_2)_2^{3+}$			0.2				0.072 [n]				
trans-$Rh(NH_3)_4(OH_2)_2^{3+}$							0.012 [n]				
cis-$Rh(NH_3)_4(OH_2)Cl^{2+}$	60	2.4 ± 0.6	0.5	< 0.01	< 0.001	0.66 [k]	0.54 [k]	17	< 4	< 0.4	140 [o]
trans-$Rh(NH_3)_4(OH_2)Cl^{2+}$	100	2.2 ± 0.6	0.7	< 0.01	< 0.001	0.39 [k]	0.064 [k]	10	< 5	< 0.5	270 [o]
cis-$Rh(NH_3)_4(OH_2)Br^{2+}$	50	1.6 ± 0.6	0.6	< 0.01	~ 0.006	> 0.5 [d]	0.50 [d]	20	< 6	~ 4	< 310 [o]
trans-$Rh(NH_3)_4(OH_2)Br^{2+}$	100	1.7 ± 0.7	0.7	< 0.01	~ 0.003		0.00 [m]	10	< 6	~ 2	~ 350
trans-$Rh(NH_3)_4(OH_2)CN^{2+}$							0.52 [j]				
cis-$Rh(NH_3)_4(OH_2)OH^{2+}$			5.0								
trans-$Rh(NH_3)_4(OH_2)OH^{2+}$							0.59 [n]				

cis-Rh(NH$_3$)$_4$(OH)Cl$^+$	3.2 [d]			~ 0.02		~ 6 [d]		310 [d]
trans-Rh(NH$_3$)$_4$(OH)Cl$^+$	2.7 [d]	3.5		0.21		80 ± 20 [d]		290 [d]
cis-Rh(NH$_3$)$_4$(OH)Br$^+$	2.1 [d]	5.0		0.02		10 [d]		470 [d]
trans-Rh(NH$_3$)$_4$(OH)Br$^+$	2.3 [d]	6.1		0.33		140 ± 40 [d]		290 [d]
cis-Rh(en)$_2$(OH$_2$)$_2^{3+}$					0.26 [p]			
trans-Rh(en)$_2$(OH$_2$)$_2^{3+}$					< 0.002 [p]			
cis-Rh(en)$_2$(OH)$_2^+$					0.005 [q]			
					0.008 [q,r]			
trans-Rh(en)$_2$(OH)$_2^+$					< 0.002 [p]			
cis-Rh(en)$_2$(OH$_2$)OH^{2+}		3.2 [s]			0.052 [p]			
trans-Rh(en)$_2$(OH$_2$)OH^{2+}		~ 2–5 [s,t]			0.62 [p]			
cis-Rh(tn)$_2$Cl$_2^+$		2.0 [s]						
trans-Rh(tn)$_2$Cl$_2^+$		7.3 [s]						
cis-Rh(tn)$_2$Br$_2^+$		2.4 [s]						
trans-Rh(tn)$_2$Br$_2^+$		8.1 [s]						
cis-Rh(tn)$_2$(OH$_2$)OH^{2+}		2.5 [s]						
trans-Rh(tn)$_2$(OH$_2$)OH^{2+}		4 ~ 6 [s,t]						
trans-Rh([14]aneN$_4$)(CN)$_2^+$	8×10^3 [u]	189 [u,v] 292 [u,w]	$< 10^{-4}$ [u]	$< 10^{-4}$ [u]			1.2×10^{5} [u]	$< 1.2 \times 10^{-5}$ [u]
Rh(bpy)$_3^{3+}$	< 15 [m]	2.2×10^3 [x]						
Rh(phen)$_3^{3+}$	18.7 [y]	48×10^3 [x]						

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[a] [212]; fluorescence. [b] [50]. [c] [213]; in 4:1 MeOH–H$_2$O. [d] [239]. [e] [240] except as indicated. For Rh^{III}(Am)$_n$(X$^-$)$_m$ complexes ($n + m = 6$); Am = NH$_3$(or amine); X$^-$ = halide; ISOM for *cis* ↔ *trans* isomerization. [f] Calculated assuming k_X, k_{Am} and k_{nr} correspond to independent decay channels. [g] [219]. [h] [218]. [i] [221]. [j] [216]. [k] [223]. [l] [241]. [m] Not detected. [n] [242]. [o] $k_{H_2O}/10^8 = 2.8$, 1.8 and 3.1 s^{-1} for *cis*- and *trans*-Rh(NH$_3$)$_4$(OH$_2$)Cl^{2+} and *cis*-Rh(NH$_3$)$_4$(OH$_2$)Br^{2+}, respectively [239]. [p] [243]. [q] [244]. [r] *cis-L* to *cis-rac* isomerization. [s] [245]; 1 ~ 4% in KBr pellets. [t] Non-exponential decay. [u] [215]. [v] Measured in DMSO. [w] Measured in DMF. [x] [246]. [y] [247].

characteristics expected for weak coupling of the lowest energy excited state to the ground state [213,214]: excited state lifetimes at 77 K increase dramatically with deuteration of ammine protons (implicating the high frequency N–H vibrations as acceptor modes) and they also appear to increase with an increasing excited state–ground state energy gap.

Excited state lifetimes of rhodium ammine complexes in water at room temperature are slightly increased by perdeuteration: $\tau_D/\tau_H \sim 2$ at 250°C [218–220] compared to ~40 at 77 K [213]. This deuterium effect is consistent with a strong coupling mechanism for non-radiative relaxation under photochemical conditions, provided the implicated surface crossing involves some Rh–N (or NH) nuclear displacements. A similar point was made above in regard to the thermally activated ^2E relaxation of Cr(III) amine complexes, and is consistent with any of several strong coupling models proposed for (^{3}X)Rh(III) excited state behavior (e.g., [16,62,221]). Many features of the luminescence dynamics of these systems are qualitatively reminiscent of the chromium(III) amines: (a) apparently different mechanisms for non-radiative relaxation at very low temperature and near room temperature; (b) small deuterium isotope effects on the room temperature lifetimes; (c) the room temperature relaxation is often accompanied by very large probabilities for substitution into the first coordination sphere; (d) lifetimes which depend on the class of complexes, (e.g., tetraamines vs. pentaammines) as much as any other obvious parameter, with *trans* macrocyclic complexes being especially long lived. Of course, there are many qualitative and quantitative differences in behavior. Most striking are the much shorter lifetimes found for rhodium complexes at room temperature and the remarkable insensitivity of the lifetime in fluid aqueous solutions to the permutations of NH_3, H_2O, Cl^- and Br^- in the rhodium ammine complexes. A possibly more revealing contrast in behavior is found in the consistently more positive volumes of activation found for photoproducts of $Rh(NH_3)_5X^{2+}$ than of $Cr(NH_3)_5X^{2+}$ complexes (see Table 5).

A contrast in principle is that the lowest energy excited state potential energy surface of Cr(III) is nested with the ground state potential energy surface, while the corresponding surfaces must be appreciably displaced for Rh(III); i.e., the promotion of a non-bonding electron to a degenerate set of anti-bonding orbitals results in an appreciable excited state distortion. Owing also to the different orbital populations of ground and excited state rhodium(III), the energy difference between these vibrationally equilibrated states is expected to parallel variations in LFSE. Consequently, the line of reasoning developed for chromium(III) complexes would suggest that excited state surface crossing to the potential energy surface of a substitutional intermediate in its ground electronic state should be relatively insensitive to variatons in LFSE for the rhodium(III) systems.

Ford has suggested a simple parameterization of the quantum yield for products [50,218–220,222]: $\phi(i) = k_i\tau({}^3X)$, where $[\tau({}^3X)]^{-1} = \sum_i k_i$ for the various competitive processes contributing to decay of the excited state. Table 8 presents the rate constants for each reaction process (ammine displacement, halide displacement, isomerization, and non-radiative relaxation). The isomerization process has been ascribed to the behavior of intermediates formed when the system leaves the excited state surface [15–17,19]; the other processes are usually assumed to be kinetically independent excited state reactions. A number of features of this approach have been supported by some elegant isotope labeling studies of Skibsted and co-workers [223–227]. This description of the important features of rhodium(III)–ammine photochemistry can be summarized:

$$({}^1A_1)\mathrm{Rh^{III}(NH_3)_4LP} + h\nu \rightarrow ({}^1Y)\mathrm{Rh^{III}(NH_3)_4LP}$$

$$({}^1Y)\mathrm{Rh^{III}(NH_3)_4LP} \rightarrow \qquad ({}^3X)\mathrm{Rh^{III}(NH_3)_4LP} \quad (\eta_{\mathrm{isc}}, k_{\mathrm{isc}})$$

$$({}^3X)\mathrm{Rh^{III}(NH_3)_4LP} \left[\begin{array}{ll} \rightarrow ({}^1A_1)\mathrm{Rh^{III}(NH_3)_4LP} & (\eta_{\mathrm{nr}}, k_{\mathrm{nr}}) \\ \rightarrow \mathrm{I} + \mathrm{L} & (\eta_{\mathrm{L}}, k_{\mathrm{L}}) \\ \rightarrow \mathrm{I'} + \mathrm{P} & (\eta_{\mathrm{p}}, k_{\mathrm{p}}) \end{array}\right.$$

$$\mathrm{I} + \mathrm{H_2O} \left[\begin{array}{ll} \rightarrow cis\text{-}({}^1A_1)\mathrm{Rh^{III}(NH_3)_4OH_2P} & (\eta_{\mathrm{c}}) \\ \rightarrow trans\text{-}({}^1A_1)\mathrm{Rh^{III}(NH_3)_4OH_2P} & (\eta_{\mathrm{tr}}) \end{array}\right.$$

where Y and X are the initial (or Franck–Condon) and the lowest energy vibrationally equilibrated excited states, respectively, L and P are the ligands photolabilized ($\mathrm{NH_3}$, $\mathrm{H_2O}$ or halide), the k_i are the respective rate constants, the η_i are the probabilities of the processes indicated (e.g., $\eta_{\mathrm{nr}} + \eta_{\mathrm{p}} + \eta_{\mathrm{L}} = 1.0$ for ${}^3X$) and the net product yields are given by $\phi_i = \eta_{\mathrm{L}}\eta_i$ (i = *cis* or *trans*). The ratio $\eta_{\mathrm{c}}/\eta_{\mathrm{tr}}$ has been found to be ca. 0.2 independent of whether the starting material is *cis* or *trans*-$\mathrm{Rh(NH_3)_4Cl_2^+}$ or *cis* or *trans*-$\mathrm{Rh(NH_3)_4(^{18}OH_2)Cl^{2+}}$ [225,226]. This provides very strong evidence for a common, 5-coordinate intermediate, $\mathrm{Rh(NH_3)_4Cl^{2+}}$, obtained by ligand field excitation of any of these four different starting materials. Further implications are that such intermediates are sufficiently long lived so that: (a) the means of generation does not affect their chemistry (at least for $\mathrm{Rh(NH_3)_4Cl^{2+}}$); and (b) the distinction between equatorial and axial positions is lost in $\mathrm{Rh(NH_3)_5^{3+}}$ [227] (possibly implicating a high frequency pseudorotational scrambling of the coordination positions and geometries, analogous to the behavior of $\mathrm{PF_5}$ [228]). This contrasts markedly to the behavior of thermally generated 5-coordinated cobalt(III)-amine intermediates [40–44]. However, the rhodium systems may have some features in common with $Co(CN)_6^{3-}$ for which similar scavenging properties in the photo- and thermally-induced substitutions imply a common 5-coordinate intermediate with at least a 1 ns lifetime [210]. It is interesting that $Co(CN)_5^{2-}$ has been postulated to be in its electronic ground state [210], while many investigators have claimed that the behavior attributed to rhodium(III)–ammine intermediate species is only consistent with excited electronic configurations [15,16,19,50,51].

The dissociative nature of the step which forms the postulated intermediate is consistent with the relatively positive values found for the volumes of activation for photolabilization of the rhodium(III) complexes (Table 3) [229–231]. As a consequence of these studies, rhodium(III) photochemistry must be considered in two parts: (a) the characteristics and decay pathways of the electronically excited species; and, (b) the nature and chemical behavior of the intermediate species.

The basic pattern of excited state dynamics in the rhodium(III) systems does appear to involve very rapid, efficient intersystem crossing ($\eta_{isc} \sim 1$) [221] from the excited state initially populated to the lowest energy excited state. Intersystem crossing rate constants appear to be comparable ($k_{isc} \sim 5 \times 10^9$ to 5×10^{11} s^{-1}; [212,218,232]) to those reported for chromium(III) ($\sim 10^{10}$ s^{-1}; [28–30]). It seems likely that spin–orbit coupling promotes the efficient "singlet"–"triplet" crossing in these heavy metal complexes, where the surfaces involved are probably only slightly displaced. Thus, the comparable magnitudes of interstate crossings for rhodium(III) and chromium(III) complexes are probably attributable to strong coupling of upper and lower surfaces through spin–orbit coupling in the former and large displacements of equilibrium nuclear positions in the latter. Since "triplet" lifetimes are generally very long compared to the rate of intersystem crossing, it is likely that these lowest energy states are vibrationally equilibrated.

The assumption that all the photochemistry of rhodium(III) ammines can be attributed to reactions of a single, vibrationally equilibrated triplet excited state has been called to question by some recent experiments which indicate that some, but not all, of the photoreactions can be quenched by OH^- [218,233,234]. The implications of these observations are not yet clear since OH^- is not necessarily an "innocent" quencher, but could itself participate in some excited state reaction such as the formation of an adduct or an amido–rhodium excited state species with altogether different chemical behavior from that of the initial excited state [218].

The rate parameters in Table 8 do not exhibit obvious, conventional substitutional kinetic patterns. Taken at face value, these rate parameters indicate that Cl^- is more easily substituted than Br^-, and that NH_3 is sometimes more labile than the halides. There is no known precedent for such substitutional patterns in transition metal chemistry [119]; however, substitution in Jahn–Teller distorted systems is not well documented. The observed substitution patterns have often been rationalized in terms of the electronic population occurring in orbitals of the Franck–Condon excited state [8–19], but it is not obvious that these arguments are appropriate to the vibrationally equilibrated excited states. Since there is likely to be an appreciable difference in the metal–ligand bond lengths of the ground and vibrationally equilibrated excited states, neither spectroscopic ligand field parameters, nor ground state radial overlap parameters are likely to be definitive in determining ratios of excited state bond energies.

The excited state distortions inferred from the emission of $(^3T_{1g})$-$Rh(NH_3)_6^{3+}$ [25] are analogous to those inferred for $(^3T_{1g})Co(NH_3)_6^{3+}$ based on ground state absorption [22]. The distortions expected in electronically excited $Rh(NH_3)_5X^{2+}$ should, at sufficiently long times, appear as a greater weakening of the axial X–Rh–NH_3 bonds than of the equatorial Rh–NH_3 bonds; see Section B(ii) (a). There are no easily accessible precedents for this situation in thermal hydrolysis studies. One would expect that bonds sufficiently weakened to remove most of the kinetic barrier to substitution would result in significant changes in luminescence band shape with medium, temperature, etc. It turns out that the excited state lifetimes and the ratios of product yields do change when the solvent is changed [222,235]. Ford and co-workers [219] have postulated that this effect originates from solvent stabilization of charge separation in the substitutional transition state. The existence of this effect does indeed demonstrate that the solvent is as important in dictating product ratios as is the orbital population of the Franck–Condon excited state.

Bergkamp et al. [221,222] have used their stationary state parameterization of the quantum yields and excited state lifetimes to obtain activation energies for the various assumed competitive rate processes. There is a correlation between activation energies and frequency terms obtained from this parameterization, presumably due to error correlation, and no strong mechanistic inference is justified. Activation energies are positive (10–40 kJ mol^{-1}) for the rate parameters and for the unparameterized quantum yields and lifetimes.

There have been several photochemical studies of rhodium(III) amine chelates. Much of this work has documented the predominantly *cis* → *trans* photoisomerization characteristic of rhodium(III). There have been few complementary reports of excited state lifetimes or structures. By and large, the results of this work have been in agreement with the predicted, dominant, bond breaking process based on excited state orbital populations [15–17] and the predicted stereochemical behavior of the resulting electronically excited 5-coordinate intermediate (e.g., [17]). An interesting recent study has inferred, from the correlation of quantum yield ratios with ground state amine basicity, that bonding in the ground state must be similar in its general features to bonding in the thermally equilibrated excited state [236]. This inference is consistent with other inferences, based on spectroscopic parameters, that some bonds are lengthened in the equilibrated excited states, but that there are no dramatic reversals of bond order. In the absence of experimental information about excited state lifetimes and structures, any inference about these systems must be very tentative.

Overall, the information summarized above indicates that the photochemistry of rhodium(III) complexes proceeds almost exclusively from a tetragonally distorted, low energy triplet state. There is considerable evidence that the primary chemical reaction of this excited state generates a five coordinate intermediate which reaches some degree of vibrational equilibrium with its environment. Information about such intermediates is, of necessity, still indirect. The relevant experimental evidence is obtained from: (a) the isotope tracer studies of Skibsted and co-workers described above; (b) the relatively positive values of $\Delta V^{\ddagger}$ (Table 5); and, (c) magnetic field effects on the product yields [237].

In some very interesting recent experiments, Ferraudi has found small, but opposite ($\phi(i)$ increases for NH_3, decreases for the halide) variations in quantum yield for ammonia and halide photoaquation when $Rh(NH_3)_5X^{2+}$ ($X = Cl$, Br) is irradiated in the presence of an intense external magnetic field [237]. These effects indicate some sort of kinetic competition in the formation of the different products; i.e., the halide and the NH_3 aquation processes must originate from either: (a) magnetically different, nearly degenerate excited electronic states with different distortions and different couplings to products; (b) competing reaction channels of a single state yielding different intermediates (as implied in Ford's parameterization [50]), with the magnetic field effects arising from different magnetic properties of the two transition states; or, (c) the magnetically sensitive coupling between the excited state relaxation trajectory and different product species within a single relaxation channel. There is no unequivocal basis for choice among these alternatives. The most interest possibilities from a chemical viewpoint are (b) and (c), since these would attribute the magnetic field effects to spin–orbit coupling between the precursor excited state and the different chemical intermediates. A triplet precursor excited state should be most strongly coupled by this mechanism to intermediates with singlet spin multiplicities. If the ammonia and halide aquation processes were kinetically competitive, Ferraudi's experiments indicate that the strong magnetic fields favor the $Rh(NH_3)_4X^{2+}$ intermediate over $Rh(NH_3)_5^{3+}$ (237). It may be relevant that the lowest electronic states of trigonal bipyramidal intermediates are of triplet spin multiplicity for the latter (D_{3h}) but not necessarily for the former (C_{3V} or C_{2V}). This kind of study may eventually provide some unique insights into very important features of the excited state potential energy surfaces.

The photoisomerization of rhodium(III) complexes is usually discussed in terms of the rapid equilibration of triplet excited state square pyramidal intermediates through a trigonal bypyramidal species [17,50–52,226]. Since there is only about 5×10^3 cm^{-1} energy difference between (^{3}X)Rh(III) and the transition state for substitution in the ground state (certainly the lowest energy substitutional "intermediate" and presumably a singlet state species), it is not at all clear whether triplet excited states of square pyramidal intermediates are energetically accessible from the lowest energy 6-coordinate excited state. Furthermore, the experimental discrimination between *cis*- and *trans*-photoproducts is only about 300 cm^{-1} [225], too small to be confidently assigned to AOM energy differences between electronic states, and there is no obvious requirement that ligand dissociations should lead to a square pyramidal intermediate [77]. The discrimination between different intermediates could be a kinetic property of the relaxing system, resulting from factors such as the nuclear reorganizational barriers to the surface crossing [77] or the vibronic coupling along a decay trajectory [6]. A high energy intermediate need not be invoked and seems less consistent with the available information than does the formation of intermediates in their lowest energy electronic states.

(d) Other d^6 *systems*

A handful of studies of iridium(III) amine complexes [248,249] have indicated very similar patterns of photochemistry to those found for the rhodium(III) analogs. No excited state structural or lifetime information is available.

There have been a substantial number of studies of the luminescence of polypyridyl and tetrapyridine complexes of rhodium(III) and iridium(III) (for a summary, see [211]). Excited state lifetimes of the rhodium(III) polypyridyl complexes tend to be longer [239] than found for the amine analogs at 77 K [246]. The few studies undertaken of the photochemical behavior of these complexes indicate considerable complexity, partly owing to peculiarities associated with the trapping of partially labilized polypyridyl complex intermediates, and partly to the relatively facile oxidation–reduction reactions of polypyridyl species. For example, the photochemical behavior of $Ir(bpy)_3^{3+}$ has been difficult to unravel since the photoproduct contains three bipyridyl ligands, yet differs markedly from the starting material in spectroscopic and in acid–base properties [250]. The remarkable properties of the photoproduct initially led to the formulation, $Ir(bpy)_3OH_2^{3+}$, in which the water was presumed to be coordinated and one bipyridine was presumed to be monodentate. Preliminary X-ray structural studies led Serpone and co-workers [251] to propose an even more remarkable structure for the photoproduct: two normal (Ir–N bonded) bidentate bipyridine ligands, and the third remaining bidentate bipyridine ligand containing one Ir–N bond and one Ir–C bond [250]. This structure has now received substantial confirmation by solution NMR [252,253] and further X-ray work [254]. These observations suggest very complex excited state chemistry for $Ir(bpy)_3^{3+}$: a carbon must deprotonate and one pyridine ring must rotate 180°. An intermediate stage in this sequence of events can be described using a π-allylic type of bond between the electronically excited iridium and the 90°-rotated pyridine ring. It is tempting to postulate a high degree of localization for the excited electron (in a π-antibonding orbital) and the partially vacant orbital (in the t_{2g} or π–d orbital set). Such a formulation would be analogous to the structure proposed by Ford [49,255] for the long-lived intermediate produced [255,256] when $Ru(NH_3)_5py^{2+}$ is irradiated. However, the failure to observe any labilization of the C–H bonds in the Ru(II) system would tend to rule out similar mechanisms for the $Ir(bpy)_3^{3+}$ and $Ru(NH_3)_5py^{2+}$ photoreactions, and, in addition, a major difference between these systems is that the Ru(II) photochemistry follows excitation of a metal-to-ligand-charge-transfer (MLCT) transition, while the iridium photochemistry is presumed to proceed from a ligand field excited state. At present there is no obvious mechanistic relationship between the ligand field photochemistry of $Ir(bpy)_3^{3+}$ and that of any ammine complexes of d^6 metals.

Ruthenium(II) complexes have provided another rich area of photochemical study. Most Ru(II) complexes can be photolabilized, and this has been ascribed to population of ligand field excited states. Even $Ru(bpy)_3^{2+}$ can be photolabilized in the presence of scavengers for the chemical intermediates [257–259]; the apparent photoinertness of this complex under most conditons appears to be more a measure of the tendency of monodentate polypyridyl to recombine, than an absence of excited state chemical reactivity. A most remarkable feature of this system is the photogeneration of the previously unknown *trans*-$Ru^{II}(bpy)_2X_2$ complexes [260]. This nominally *cis–trans* photoisomerization is analogous to that found in rhodium(III) amines and can be rationalized in terms of the behavior of electronically excited, 5-coordinate, d^6-intermediates [261].

Luminescence from ligand field excited states has not been reported for ruthenium(II) complexes, but the most interesting photochemical feature of these systems in the present context is that the substitutional photochemistry is nearly always postulated to occur from a ligand field excited state, even when the ligand field absorptions are obscured by much more intense metal-to-ligand-charge-transfer absorptions. This is most dramatically illustrated by $\mathrm{Ru(bpy)_3^{2+}}$ for which both MLCT absorption and emisson are observed, with the ligand field state postulated to be populated thermally from the slightly lower energy, thermalized MLCT "triplet" state [262]. This interrelation of the photochemistry and the relative energies of MLCT and ligand field states has been extensively investigated in $\mathrm{Ru^{II}(NH_3)_5L}$ complexes by Ford and his co-workers (work reviewed by Ford, [49]). This work has indicated that reasonably large yields of photoinduced substitution products are obtained only if the lowest energy, thermally equilibrated excited state is ligand field rather than MLCT in character; i.e., photosubstitution yields are the largest when $E(\mathrm{LF}^0) \leq E(\mathrm{MLCT}^0)$.

Work with the $\mathrm{Fe(CN)_5en^{3-}}$ complex has demonstrated that product yields with $\mathrm{CN^-}$ loss can be large provided that a scavenger for a labilized site is present in the second coordination sphere: the free end of ethylenediamine served as a scavenger in this complex [263]. If this interpretation holds it is a nice illustration of the role of chemical intermediates, in this instance a presumably solvent cage trapped five coordinate ($\mathrm{Fe(CN)_4en^{2-}}$, $\mathrm{CN^-}$) species, in dictating the net yields of products.

(e) General comments

The photochemical behavior of d^6 complexes is undoubtedly diverse and complicated. A crude classification of the behavior can be obtained by distinguishing those systems in which the lowest energy excited state meets the minimum energy requirements for product formation (e.g., Rh(III), Ru(III)) from those in which it does not (e.g., cobalt(III)–ammines). In the latter complexes the excited system probably relaxes in a rapid cascade through vibronic levels, and in the course of this relaxation the decaying system samples most of the energetically allowed product species available. The rules governing product distribution in such a fast reaction system have not been established.

The systems in which the energy of the lowest energy excited state exceeds the energy requirements for product formation are characterized by a tendency of the final products to have a *trans*-isomeric geometry. This stands in distinct contrast to the prevalence of *trans* → *cis* photo-induced isomerizations often found in chromium(III) systems. The distortions induced in the Jahn–Teller distorted excited states appear to be very similar in d^3 and d^6 complexes [21,22,25,186,187]. The lowest energy, vibrationally equilibrated excited states do differ in structure: $(^2E_g)\mathrm{Cr(NH_3)_6^{3+}}$ has the ground state geometry [21] while the $^3T_{1g}$ states of $\mathrm{Co(NH_3)_6^{3+}}$ and $\mathrm{Rh(NH_3)_6^{3+}}$ are Jahn–Teller distorted with relatively long $\mathrm{M{-}NH_3}$ equatorial bonds [22,25]. It is not clear whether this difference in the lowest energy excited states is the crucial feature. However, excited state distortion in d^6 complexes would tend to make their photophysical behavior less a function of LFSE than one might expect for the (^2E)Cr(III) excited states (see Figs. 9–11). It is more common to ascribe the photochemical variability to differences in the behavior of coordinately unsaturated intermediates formed by bond breaking in the excited state [14–19]. Amongst such differences in the behavior of intermediates one expects the trigonal bipyramidal geometry to be less stable for a low spin d^6 than for a d^3 metal, based on the greater population of π-antibonding orbitals; simple AOM arguments do not predict much of a difference in energy for the respective square pyramidal structures. At present the significance of such an effect is not clear, and any direct observations of the photochemical intermediates would be useful.

The evidence for dissociative excited state pathways in d^6 systems seems to be growing relatively strong. AOM arguments have been used to rationalize the preference for excited state bond breaking and for intermediate isomerization [15,17,19,264]. There is some uncertainty about the parameters appropriate to rhodium(III) complexes [264], and the photochemical behavior of Co(III) complexes and of $\mathrm{Ir(bpy)}_3^{3+}$ are also not easily rationalized by this approach. The generation of intermediates in electronic excited states is a key component of most AOM approaches, but this assumption is very difficult to justify.

(iii) Metals with other d*-electron configurations*

A small amount of work on ruthenium(III) ammine complexes has shown them to be relatively photoinert, and it is difficult in many instances to discriminate between the chemistry induced by population of charge-transfer-to-metal (CTTM) and ligand field excited states. CTTM photochemistry tends to dominate the studies of iron(III) complexes. No ligand field emission has been reported for such d^5-complexes.

The d^8-systems are a little more interesting. The square planar, low spin d^8 complexes are commonly thought to undergo thermal substitution via an associative pathway. The photochemical reactions may also utilize such a reaction coordinate. However, *cis–trans* photoisomerization of Pt(II) and Pd(II) complexes may well utilize a pathway in which the vibrationally equilibrated, lowest energy excited state is essentially tetrahedral and crosses readily to the transtion state on the ground state surface [265]. The substitutional photochemistry of Pt(II) and Pd(II) has been reviewed and discussed extensively elsewhere [47].

Complexes of nickel(II) represent an informative range of possibilities. Both high spin (4-coordinate tetrahedral, or 5-coordinate square pyramidal, or 6-coordinate octahedral) and low spin (4-coordinate planar) complexes are known and their stereochemistry has been characterized. In these complexes the coordination geometry is dictated by a combination of metal–ligand bonding and ligand stereochemistry. The energy differences between alternate configurations tend to be small. If one considers a planar complex with a singlet ground state, the lowest excited states are undoubtedly of triplet spin multiplicity. In planar $Ni^{II}L_4$ one of the lowest energy triplet excited states becomes the ground state electronic configuration of the complexes with square pyramidal or octahedral coordination geometries. Thus one would expect second coordination sphere species to "collapse" into the coordination sphere of electronically excited, planar $Ni^{II}L_4$, forming a metastable intermediate chemical species. Similarly, photodissociation of a square pyramidal $Ni^{II}L_5$ species should lead to some metastable (singlet) planar $Ni^{II}L_4$ intermediates. These intermediates would be metastable largely because substantial displacements of coordinated ligands are required for spin relaxation to the ground electronic state to occur. In a nice series of papers, McGarvey and co-workers [266–269], have utilized the large color differences between the high spin and low spin forms of Ni(II) to detect these intermediates as transients in flash photolysis studies. These studies amount to photochemical displacements of coordination equilibria, with the large structural changes resulting in reasonably long relaxation times (10^{-8}–10^{-5} s). The detailed correlation between substrate electronic states and possible product species in these Ni(II) systems has recently been published [270]. Presumably owing to the larger spacings between energy states, analogous behavior has not been reported for Pt(II) complexes.

C. SUMMARY AND CONCLUSIONS

Visible light absorption by transition metal complexes occurs at energies which are in excess of the activation energy required for most heterolytic processes in fluid solution. If all the energy contained in the Franck–Condon state generated by light absorption could be transformed into thermal energy localized in the appropriate ground state reaction channel, the corresponding substitutional process would occur. Thus, the thermal-reaction activation energy is the minimum energy requirement for photoreaction. Thermally induced substitutional processes are not selective in the sense that the process observed is always the one (or more) with the lowest activation energy requirements. In thermal reactions these energy requirements are mostly functions of changes in bond lengths, angles, etc., and so are fundamentally Franck–Condon in origin.

Any stereoselectivity of an excited state reaction, for which the excited state meets the basic activation energy requirements of several ground state reaction channels, implies strong selection rules and therefore electronic as well as Franck–Condon contributions to reactivity. The fundamental issue in the photosubstitutional chemistry of transition metal complexes is the identification of the appropriate selection rules for product formation. The usual approach to these problems is to assume separability of electronic and nuclear motion so that the electronic states of the system can be described in terms of inter-nuclear potential energy surfaces and the selection rules can be discussed in terms of surface crossings to product states, retardation factors, etc. In practice, the most important limitation to this approach amongst the systems considered here, seems to arise when the lowest energy electronic excited state would possess a vibrationally equilibrated energy comparable to or less than the transition state energy for the important thermal reaction channels. Thus, in cobalt(III) systems, reaction seems to occur in competition with thermal relaxation, resulting in very small, strongly wavelength dependent product yields. Hollebone et al. [6] have argued that, in such "prompt" reaction systems, product formation is very likely to be governed by strong selection rules. An alternative hypothesis is that the rapidly relaxing system will possess some probability of sampling every product state for which the minimum energy requirements are met; the total product yield would involve a weighted summation over all the vibronic states with energy less than the Franck–Condon state, where the selection rules or symmetry constraints determine the statistical weights. The necessary condition for well defined selection rules, in a system where the reaction competes with vibrational relaxation, is that the relaxing system follows a trajectory in which only a few vibrational modes are activated. In fact, interaction between the distortion coordinate and the principle modes excited on light absorption would be expected to contribute to the spread of excitation energy over most of the vibrational modes in the rapidly relaxing molecule. At the present time neither theoretical considerations nor experimental observations permit a definitive statement on the question of the role or strength of selection rules in the cobalt(III) systems.

It is also likely that prompt processes occur during the course of relaxation of the quartet excited states of chromium(III), and these processes appear to be reasonably selective (e.g., a net *trans* → *cis* isomerization seems to prevail). This implies that reasonably strong selection rules operate for the chemical processes. The dominant pathway for escape from the quartet excited states is often by means of the doublet manifold, and the reactions from the vibrationally equilibrating quartet may occur by *Type IA* reaction behavior with the relaxing system "sampling" reaction channels which have some mixture of doublet state character. Alternatively, one could postulate strong coupling of the excited quartet state potential energy surface to the potential energy surface of a specific chemical intermediate.

Systems in which the minimum energy requirements are met and in which excited state reactions have been demonstrated to proceed from thermally equilibrated lowest energy states ("slow" reaction systems) must necessarily have reaction probabilities which are to some degree determined by electronic factors. A basic concern is whether the formation of photoproducts in such systems is best treated as: (a) a traditional, thermally activated reaction channel leading to intermediate product species which are also electronically excited; or (b) surface crossing to some lower energy transition state for ground state substitutional processes. The latter possibility has no precedent in thermal chemistry. The former is often difficult to justify on energetic grounds.

The best defined examples of such "slow" reaction processes are found in the doublet state behavior of chromium(III) and in the triplet state behavior of rhodium(III) complexes. It often appears that the pathways most consistent with the available information involve surface crossing to the ground electronic state of some substitutional intermediates. In this approach, the "selection rules" are a combination of electronic and Franck–Condon factors; i.e., they reflect the relative shape and the disposition in configuration space of excited state and intermediate potential energy surfaces and the probabilities for crossings between these surfaces. Such surface crossings will tend to be strongly allowed only when the equilibrium configuration coordinates are very different for the upper and the lower potential energy surfaces. The surface crossing postulated in these photochemical systems involves a reaction coordinate for ligand substitution. Electronically correlated (or fully allowed) crossings are possible for (^3X)Rh(III) complexes to certain trigonal bipyramidal (D_{3h}) intermediates and for (^2E)Cr(III) complexes to certain pentagonal bipyramidal (D_{5h}) intermediates, but the potential energy surfaces of these intermediates may not be energetically accessible from the vibrationally equilibrated excited states. Even if these electronically correlated "product states" are at too high an energy to be populated from the reacting excited states, they would be expected to influence the reaction trajectory through configurational mixing in the region of the crossing between the excited states and the potential energy surfaces of lower energy intermediate species. The nuclear distortions induced by the interaction with (or, in the limit, crossing to) the potential energy surfaces of such intermediate species is likely to be important in determining the product distribution and stereochemistry.

While the absolute mechanistic interpretation of the pressure dependence of substitution reactions remains controversial [271–273], it is significant that the volumes of activation are considerably more negative for Cr(III) than for Rh(III) photoproducts (Table 5). This implies that the excited state to products (or intermediates) surface crossing is more associative for Cr(III) than for Rh(III). Unfortunately, the activation volume data for Cr(III) complexes contains an undetermined contribution from quartet state (or "prompt") reactions, and in any case the actual numerical values inferred as transition state properties depend on the specific model assumed.

Entry into a decay channel through a strongly coupled surface crossing will initially result in vibrationally excited intermediate species. The vibrational modes excited will be dictated by the differences in the nuclear coordinates of the excited state and the vibrationally relaxed intermediate species. These vibrational modes will determine the relaxation trajectory across the intermediate surface and whether there is a partitioning between net reaction and relaxation to the original ground state. If the surface crossing occurs at a point displaced along a coordinate which is orthogonal to the reaction coordinate for which the photochemical "intermediate" can be regarded as a "transition state" in a ground state reaction, then relaxation may occur along this orthogonal coordinate faster than progress along the ground state reaction coordinate and the primary photoproduct may appear to be a genuine reaction intermediate.

In any event, there is growing evidence that certain selective aspects of photoinduced reactions of transition metal compounds (their photoisomerization) originates from thermal reactions of intermediate chemical species, and is not directly attributable to the behavior of excited electronic configurations. This is certainly an important theme in the theoretical studies of Vanquickenborne and Ceulemans [14–19] and the role of chemical intermediates has been directly demonstrated in the photochemistry of Ni(II). However, no direct evidence for such intermediates is yet available in the much studied chromium(III) or heavy metal d^6 systems. In this regard, it is important to bear in mind that the chemical intermediates proposed to contribute to the photoproducts of 6-coordinate metal complexes are high energy species: precedents or analogs are rare. The potential for generating such species remains a unique feature of high energy electronic excited states. Particularly owing to the lack of precedents, the detection and characterization of such intermediates is an important chemical challenge.

It must also be recognized that the much discussed photoselectivities are matters of degree and not often of an overwhelming magnitude. For example, yields ratios of isomerically related products rarely exceed 10 : 1, and the implied energy differences for the respective competitive excited state reaction channels rarely exceed 4 kJ mol^{-1}.

In this article we have emphasized those models for transition metal excited state dynamic behavior which most directly incorporate detailed information about molecular structure. Not all of the alternatives have been treated in equal detail. For further information about these alternatives, the reader is referred to the various reviews cited in the text. As is the case in most areas of chemical dynamics, a complete model for the time evolution of transition metal excited states will contain both electronic and nuclear contributions. Similarly, in order to evaluate the contributions of either kind of factor properly, it is necessary to allow for both. We hope that the ideas presented in this review will contribute to the evolution of a more balanced treatment of the excited state dynamics in these systems.

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