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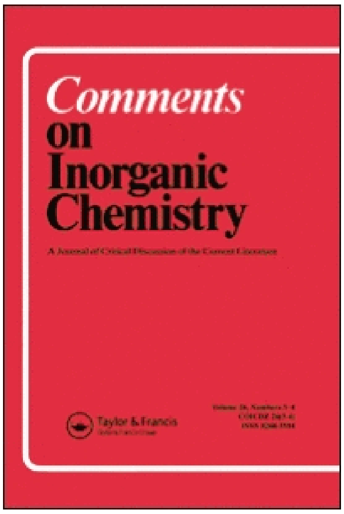

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Concerning Models for Substitution Reactions of Vibrationally Equilibrated Transition Metal Excited States

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Concerning Models for Substitution Reactions of Vibrationally Equilibrated Transition Metal Excited States

Models that have been proposed for the substitution reactions of transition metal excited states generally involve high energy electronic configurations of intermediate species and such pathways may not be viable for vibrationally equilibrated excited states. Nevertheless, simple angular overlap considerations indicate that several dissociative and associative intermediate species are likely to have energies comparable to, or less than these vibrationally equilibrated ligand field excited states. A model is proposed for estimating the intrinsic nuclear barriers to formation of trigonal bipyramidal Cr(III) intermediates and there does seem to be some basis for stereoselectivity. Among possible seven-coordinate intermediates, the capped trigonal prismatic geometry seems most likely to be consistent with observed chromium photosubstitution chemistry.

INTRODUCTION

During the past decade or so, several theoretical models have been proposed to account for the principal stereospecific features of the photosubstitution patterns exhibited by transition metal complexes.[1-9] Of these models, those proposed by Vanquickenborne and Ceulemans[5-9] (VC) have been found to be especially useful by many investigators. This Comment explores the problems and possibilities encountered when certain of the models are used to describe the chemical behavior of vibrationally equilibrated excited states of transition metal compounds.

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Some features which are common to the theoretical approaches of Zink and of VC are: (1) all calculations are based on ground state structural parameters and the energies of ground state absorption maxima, and (2) all photoreactions are considered to be dissociative, with reaction patterns based on inferred weakening of different bonds in the electronic excited state. Such approaches are only rigorously applicable to molecules at the moment of light absorption and it is not obvious how they can be applicable to vibrationally relaxed electronic excited states. Yet in the majority of chromium(III) and rhodium(III) complexes, there is compelling evidence that most of the phochemistry proceeds from the lowest energy vibrationally equilibrated excited states.[10,11] There is also compelling evidence that these lowest energy electronically excited species have molecular structures that differ significantly from those of the ground state.[12-14] It seems surprising that ground state bonding parameters could have any relevance to such distorted excited state species. There may be ways of accommodating such changes in structure and bonding, and some approaches are developed below. In the interest of brevity, only chromium(III) systems are considered. Extension of the approaches described below to systems with different electronic configurations should be straightforward.

VIBRATIONALLY EQUILIBRATED, DISTORTED EXCITED STATES: THE LOWEST ENERGY, EXCITED QUARTET STATE OF CHROMIUM(III)

Wilson and Solomon[12] have shown that the lowest energy vibrationally equilibrated quartet state of $Cr(NH_3)_6^{3+}$, ${}^4T_{2g}^{\circ}$, has an instantaneous D_{4h} microsymmetry, with appreciably lengthened (by 12 pm) equatorial Cr–N bonds and somewhat compressed axial bonds. The equilibrated excited state lies about 2.5×10^3 cm^{-1} lower in energy than the energy of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ absorption maximum. The Jahn–Teller distortion in the ${}^4T_{2g}^{\circ}$ species can be viewed as rotating over all three Cartesian axes. The energy difference, $\Delta E(\text{rep}) = E({}^4T_{2g}^{\text{max}}) - E({}^4T_{2g}^{\circ})$, is the result of a decrease in electron repulsion energy which accompanies the expansion of bond lengths in the "antibonding" excited state. This decrease in energy of the excited state occurs over a single potential energy surface, so it is not associated with a change in bonding parameters (i.e., a single bond dissociation energy for each ligand is usually used to characterize a single surface), and as a consequence ΔE(rep) is not explicitly incorporated into a simple angular overlap argument. That ΔE(rep) is appreciable, $\sim 2.5 \times 10^3$ cm^{-1} for Cr(III) complexes, demonstrates that angular overlap model (AOM) parameters, fitted to the ground state absorption maximum cannot be simply interpreted as bonding parameters. Thus, any coordination sphere expansion, including bond breaking, must decrease repulsions, and the AOM energies of species differing in bond length, coordination geometry, or coordination number must have uncertainties of several thousand cm^{-1}. These uncertainties have been taken into account in what follows: relative energies of electronic states for a given geometry have been based on AOM parameters,[7,8,15,16] but the energy scales have been adjusted to take account of whatever experimental information seems pertinent.

The $^4E^{\circ}$ excited state of $Cr(NH_3)_5Cl^{2+}$ will be taken as a paradigmatic example of application of the approach to complexes of lower symmetry. The plane of the Jahn–Teller expansion of bond lengths will include the NH_3–Cr–Cl axis and will rotate over the NH_3–Cr–NH_3 axes as qualitatively illustrated in Figure 1. On the average, the bonding interactions along the NH_3–Cr–Cl axis will remain relatively long and weak, consistent with bond breaking along this axis.

The activation energy for ground state substitution can be used to establish an experimental lower limit on the energy of the lowest energy five-coordinate intermediates. Since ground state substitution in Cr(III) tends to be stereoretentive, the lowest energy trigonal bipyramidal (TBPY) intermediates are presumed to be slightly higher in energy than the lowest energy square pyramidal (SPY) analogs, qualitatively consistent with the AOM calculations. Only bond breaking along the NH_3–Cr–Cl axis has been considered.

Symmetry constraints have been considered by VC to play a major role in product formation from transition metal excited states. If the vibrationally equilibrated excited states are treated as chemical species undergoing simple chemical reactions, then one must examine the systems for the possibilities of adiabatic crossings from reactant to product potential energy surfaces. The symmetry constraint applicable for these adiabatic crossings is that the product of the representation of the initial state, the representation of the nuclear motion

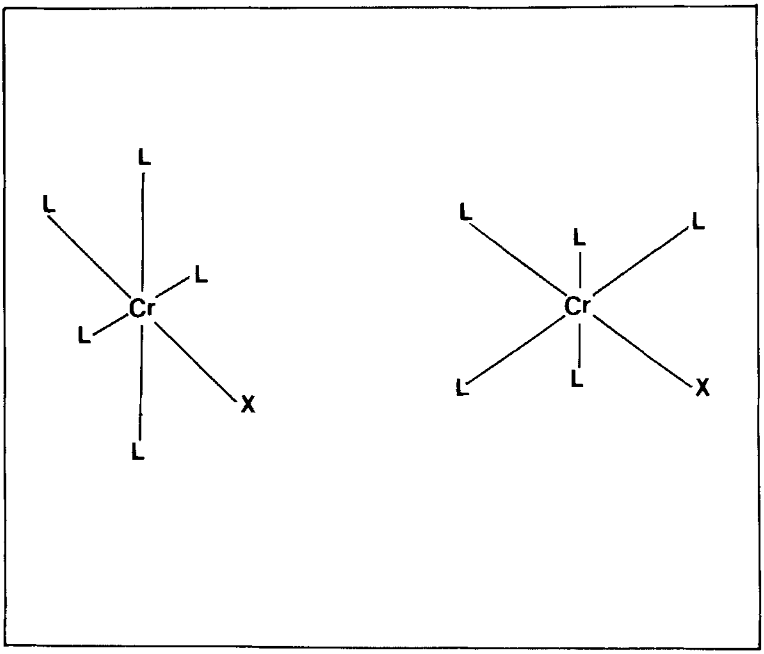

FIGURE 1 Limiting structures for the degenerate distortions of $(^4E^\circ)\mathrm{Cr(NH_3)_5Cl^{2+}}$.

involved in the reactions, and the representation of the final state should contain the totally symmetric representation[17]; e.g., for $\mathrm{Cr(NH_3)_5Cl^{2+}}$, $\Gamma(^4E^\circ) \times \Gamma(\text{nuclear}) \times \Gamma(\text{final}) \supset A_1$. The nuclear motions required to generate any five-coordinate intermediate are complex, but can be represented as sums of normal vibrational modes.

Symmetry analysis of $(^4E^\circ)\mathrm{Cr(NH_3)_5Cl^{2+}}$ is complicated by the Jahn–Teller distortion. Initially we consider only the formation of square pyramidal (SPY) intermediates. The potential SPY intermediates are $(^4E)\mathrm{Cr(NH_3)_4X}$ (also subject to Jahn–Teller distortion) and $(^4\mathrm{B}_1)\mathrm{Cr(NH_3)_4X}$ (for X = $\mathrm{Cl^-}$ or $\mathrm{NH_3}$). It is necessary to consider limiting molecular geometries for the Jahn–Teller distorted species: the geometries corresponding to minima of the degenerate vibrations (i.e., expansions in the *XY* or the *XZ* planes), and the average geometry corresponding to the intersection of surfaces for the degenerate vibrations. The respective symmetries are $^4\mathrm{B}_1$ and $^4\mathrm{B}_2$ (in the C_{2v} point group of the geometries corresponding to the minima of the surfaces) and ^4E (in the C_{4V} point group of the average geometry at the intersection). The $(^4E)Cr^{III}(NH_3)_5Cl \rightleftarrows (^4E)Cr^{III}(NH_3)_4X$ crossings are allowed by a nuclear motion which transforms as A_1 along a reaction coordinate of C_{4V} symmetry. The $(^4B_1)Cr^{III}(NH_3)_5Cl \rightleftarrows (^4B_2)Cr^{III}(NH_3)_4X$, and the $(^4B_n)Cr^{III}(NH_3)_5Cl \rightleftarrows (^4B_n)Cr^{III})(NH_3)_4X$ (n = 1 or 2) adiabatic crossings are allowed by nuclear motions which transform as A_2 and A_1, respectively, in C_{2V}. Simple nuclear motions with these transformation properties are possible, as illustrated in Figure 2. Thus there are no significant symmetry constraints to adiabatic crossings to any of the lowest energy SPY intermediates from $(^4E)Cr(NH_3)_5Cl^{2+}$.

The transformation of the parent six-coordinate complex into a trigonal bipyramidal (TBPY) intermediate can occur along reaction coordinates of either C_{2V} or C_S symmetry. Motions along the C_S coordinates are necessarily totally symmetric in this point group, and this leads to problems of forbidden crossings as discussed by VC.[7,8] While configuration mixing could relax this constraint on surface crossings, there is no obvious advantage to the C_S coordinate and these transformations will not be considered further here. The motions required to transform $(^4E^\circ)Cr(NH_3)_5Cl^{2+}$ into the $(^4E)Cr(NH_3)_5^{3+}$, $(^4B_1)Cr(NH_3)_4Cl^{2+}$ and $(^4A_1)Cr(NH_3)_4Cl^{2+}$ TBPY species are A_1 (in C_{4V}), A_1 (in C_{2V}) and B_1 (in C_{2V}), respectively. These motions do not differ significantly from those discussed above for SPY examples; e.g., they correspond to the replacement of components of a skeletal "buckle" motion (t_{1u} in O_h) by components of a skeletal twist motion (t_{2u} in O_h). This vibronic coupling would permit an adiabatic crossing to any of the proposed low energy TBPY intermediates. As noted in Figure 3, these TBPY intermediates are expected to be much lower in energy than the ^4E SPY species which VC consider to be the initial product of bond breaking. There seems to be no basis for requiring the reacting system to pass through this high energy SPY intermediate. In fact the $(^4E)Cr(NH_3)_4X$ SPY species are not likely to be energetically accessible from $(^4E^\circ)Cr(NH_3)_5Cl^{2+}$.

It should be noted that the recombination reactions also involve nuclear motions, and that one expects some intrinsic (Franck–Condon) barriers to these processes. As a consequence, these coordinatively unsaturated species might be regarded as legitimate chemical intermediates. The complexity of the nuclear motions required for bond breaking (Figure 2) would tend to support this view. These

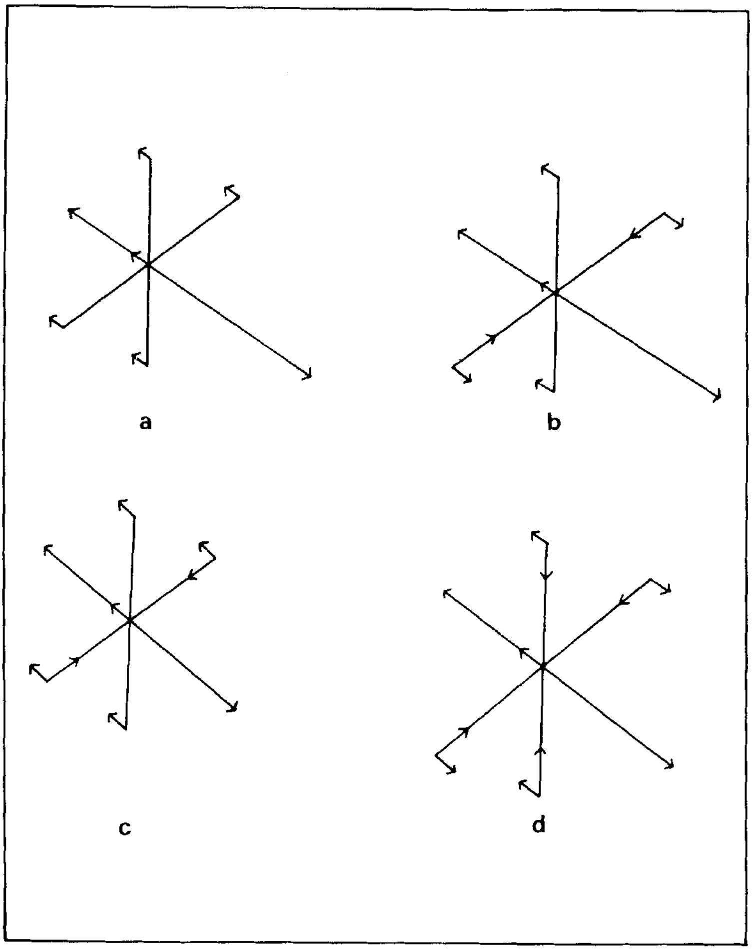

FIGURE 2 Examples of simple nuclear motions which could be represented by normal vibrational modes and would lead to bond cleavage to form proposed five-coordinate intermediates; square pyramidal products result from (a) and (c); trigonal bipyramidal products from (b) and (d). The net motions transform: (a), a_2 in C_{2v} or e in C_{4v}; (b), b_1 or b_2 in C_{2v}; (c), b_1 or b_2 in C_{2v}; (d), a_1 in C_{2v}.

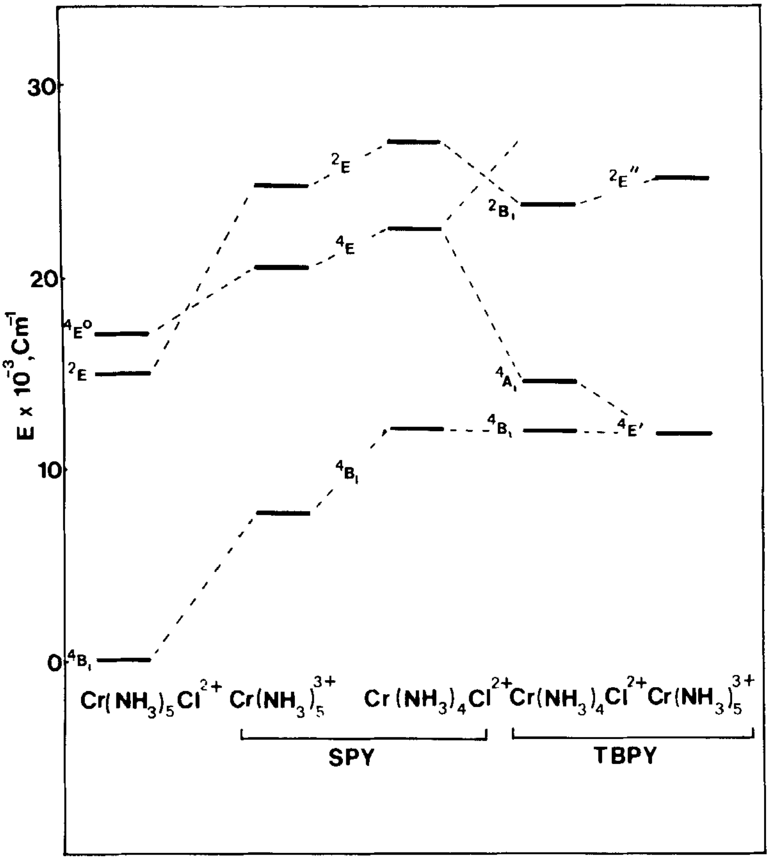

FIGURE 3 Relationships between the electronic state energies observed for $Cr(NH_3)_5Cl^{2+}$ and those estimated for various five-coordinate intermediates. Relative energies of the states of any CrL_4X species are based on AOM considerations, allowing $\sim 3 \times 10^3$ cm^{-1} for decreased electronic repulsions in Jahn-Teller distorted species. The lowest energy SPY intermediates have been identified with the transition states of thermal hydrolysis and their energies taken as equal to estimated thermal activation energies. The lowest energy TBPY intermediates are taken to have slightly higher energies. The dashed lines indicate correlations between states.

nuclear motions will result in activation barriers to the adiabatic crossings from $(^4E^{\circ})\mathrm{Cr(NH_3)_5Cl^{2+}}$ to the various intermediates, and variations in these barriers must be considered in discussions of the selectivity of chemical reactions of the vibrationally equilibrated excited states. The nuclear barriers involved in the various adiabatic crossings are similar in kind to those found to control the rates of thermal spin relaxation processes.[18,19]

A CRUDE MODEL FOR NUCLEAR REORGANIZATIONAL BARRIERS FOR DISSOCIATIVE PATHWAYS

A very approximate estimate can be made of the barriers to adiabatic crossings for dissociative pathways. If the $(^4B_1)\mathrm{Cr(NH_3)_5Cl^{2+}}$ (ground state) and the $(^4E)\mathrm{Cr(NH_3)_5Cl^{2+}}$ (excited state) substitution reactions are dissociative, the energy difference between the equilibrated six-coordinate species and the dissociation limit is probably enough to make the effective reorganizational barriers very small for the recombination reactions from $(^4B_1)\mathrm{Cr(NH_3)_4X}$ and X, and from $(^4E)\mathrm{Cr(NH_3)_4X}$ and X ($X = NH_3$ or Cl), respectively (see Figure 4). As a consequence, the dissociation energies can be used to estimate the "intrinsic reorganizational energy" associated with bond breaking in each of the states. This inference can be discussed more easily by first defining the degenerate ligand-exchange reactions,

$$\mathrm{CrL_6 + L' \rightleftarrows CrL_5L' + L}$$

and,

$$\mathrm{CrL_5 + L' \rightleftarrows CrL_4L' + L},$$

where $\mathrm{CrL_6}$ and $\mathrm{CrL_5}$ are orbitally correlated species and the first exchange is primarily *dissociative* while the second exchange is primarily *associative.* The rates of these exchange reactions can be used to define the respective "intrinsic" nuclear reorganizational parameters, λ(HEX) and λ(SPY) (i.e., $\Delta G^{\neq} = \lambda_i/4$). Then the activation energy for the net dissociation process,

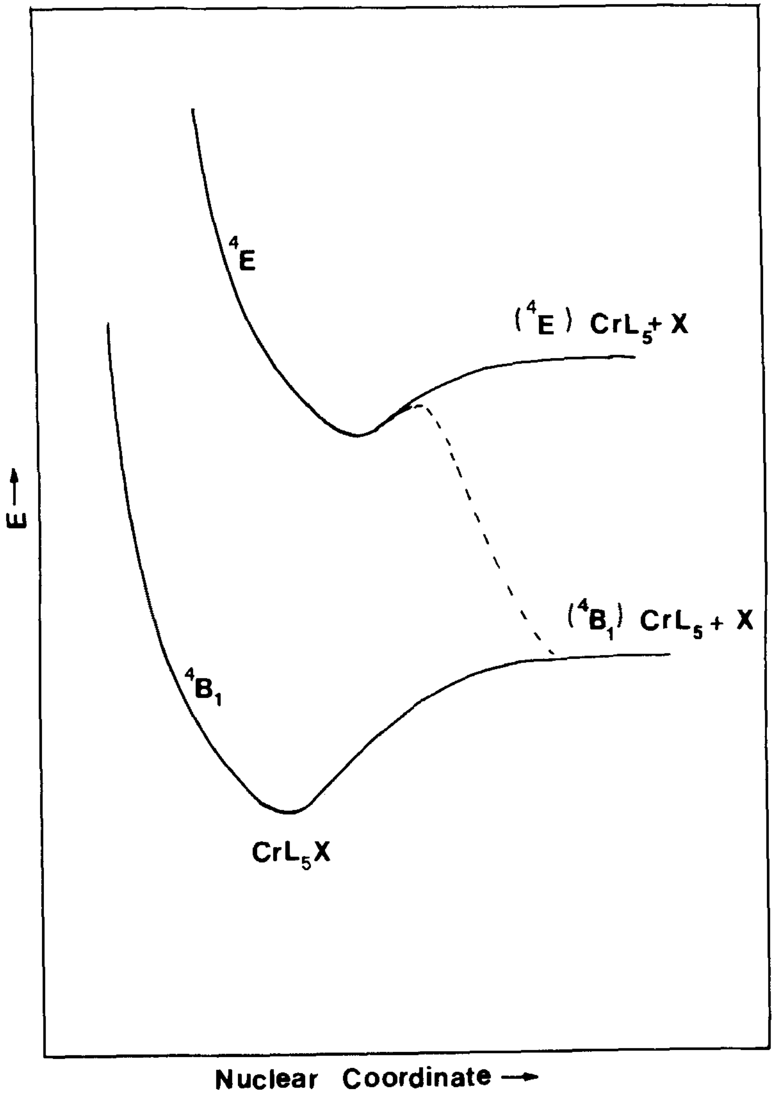

FIGURE 4 Qualitative potential energy curves for the heterolytic dissociation of the ground state ($^4B_1$) and the vibrationally equilibrated quartet excited state ($^4E°$) of $Cr(NH_3)_5Cl^{2+}$. An adiabatic surface crossing is indicated by the dashed curve. This particular surface crossing may have a small probability owing to unfavorable electronic factors.

$$\mathrm{CrL_6} \rightarrow \mathrm{CrL_5} + \mathrm{L},$$

can be described using the usual limiting, classical expression,[18-22] $E_a = (\lambda/4)(1 - \Delta E/\lambda)^2$, where $\lambda \simeq [\lambda(\mathrm{HEX}) + \lambda(\mathrm{SPY})]/2$ and ΔE is the initial state–final state energy gap (negative for an endothermic dissociation). This method of approximating λ leads to a small overestimate of E_a.

For limiting dissociative substitutional behavior of $\mathrm{CrL_6}$ (i.e., when $\lambda(\mathrm{SPY})$ is very small), $\lambda(\mathrm{HEX})/4$ is equal to the heterolytic bond dissociation energy of $\mathrm{CrL_6}$. Using this approach it is possible to estimate E_a for the adiabatic $(^4E^\circ)\mathrm{Cr(NH_3)_5Cl} \rightarrow (^4\mathrm{B_1})\mathrm{Cr(NH_3)_4X}$ crossing. However, in doing so we must take account of the larger bond lengths in the Jahn–Teller distorted, electronically excited $^4E^\circ$ species. This factor will contribute to λ an amount, λ_c, equal to one half the ground state-excited state Stokes shift. Thus, taking $\lambda(\mathrm{SPY}) \sim \lambda_c = 3 \times 10^3\ \mathrm{cm^{-1}}$, $E_a \sim 0 \times 10^3\ \mathrm{cm^{-1}}$ for $\mathrm{X} = \mathrm{Cl^-}$ and $1.4 \times 10^3\ \mathrm{cm^{-1}}$ for $\mathrm{X} = \mathrm{NH_3}$ (setting $\lambda/4 = \{[E(^4E^\circ;\ \mathrm{CrL_5}) - E(^4E^\circ;\ \mathrm{CrL_5X})]/2 + (0.75 \times 10^3)\}\ \mathrm{cm^{-1}}$; where similar Stokes shifts have been assumed for the $(^4\mathrm{B_1})\mathrm{CrL_5X} \rightarrow (^4E)\mathrm{CrL_5X}$ and the $(^4\mathrm{B_1})\mathrm{CrL_5} \rightarrow (^4E)\mathrm{CrL_5}$ transitions. It appears that this reaction channel would favor Cr–Cl bond breaking, in contrast to observation.[10] However, the $(^4E^\circ)\mathrm{Cr(NH_3)_5Cl^{2+}} \rightarrow (^4\mathrm{B_1})\mathrm{Cr(NH_3)_4X}$ surface crossings correspond to a forbidden electronic transition and it is likely that a small value of the electronic matrix element would select against these crossings in competition with the electronically allowed processes discussed below.

The electronically allowed low energy dissociative pathways involve formation of trigonal bipyramidal (TBPY) intermediates. To estimate the reorganizational parameters, λ, for this reaction channel we can consider the following postulates:

1. $\lambda \simeq [\lambda(\mathrm{HEX}) + \lambda(\mathrm{TBPY})]$
2. $[\lambda(\mathrm{HEX})]/4 \sim E(^4E;\mathrm{CrL_4X}) - E(^4E^\circ;\mathrm{CrL_5X})$
3. $[\lambda(\mathrm{TBPY})]/4 \sim E(^4E;\mathrm{CrL_4X}) - E(\mathrm{TBPY}) + \lambda_c/4$

The second of these postulates is based on reasoning similar to that of the preceding paragraphs, where ground state bond lengths are assumed in the TBPY intermediates and λ_c' accounts for bond length differences between the SPY and Jahn–Teller distorted species. The last of these postulates is equivalent to assuming 50% leaving group bond breaking, 50% entering group bond making in the symmetrical intermediate for equatorical ligand–external ligand exchange in the TBPY intermediate. For Figure 3 and the estimates of E_a it has been assumed that $\lambda_c' - \lambda_c \sim 2 \times 10^3\ \text{cm}^{-1}$. Based on these postulates and energies as in Figure 3, $E_a \sim 5 \times 10^3\ \text{cm}^{-1}$, $3 \times 10^3\ \text{cm}^{-1}$, and $4 \times 10^3\ \text{cm}^{-1}$, respectively for formation of $(^4E')\text{Cr(NH}_3)_5^{3+}$, $(^4\text{A}_1)\text{Cr(NH}_3)_4\text{Cl}^{2+}$, and $(^4\text{B}_1)\text{Cr(NH}_3)_4\text{Cl}^{2+}$ from $^4E^\circ$. Apparently the smallest activation barrier occurs along a reaction channel forming the $(^4\text{A}_1)$ TBPY intermediate. This should lead to product stoichiometries and stereochemistries as described by VC.

In summary, the reaction channels available to the equilibrated quartet excited states of Cr(III) must involve only the lowest energy intermediate species. Since the $^4E^\circ$-intermediate energy gaps are small, these reaction channels will involve significant activation barriers and the distribution of products is expected to be largely determined by kinetic factors (i.e., E_a) rather than thermodynamic factors (i.e., state energies).

POSSIBLE REACTION CHANNELS OF THE LOWEST ENERGY DOUBLET STATE

Dissociative reaction pathways are not expected to lead to low energy intermediates of doublet spin multiplicity (see Figure 3). As a consequence any dissociative reaction pathway of the ^2E state must involve intersystem crossing. Such an intersystem crossing process would be promoted by spin orbit coupling with $^4E^\circ$, but the change in spin multiplicity along a dissociative reaction coordinate is more correctly described as a spin relaxation process than as a "back intersystem crossing" process.

The approach discussed above for $^4E^\circ$ results in estimated values of $E_a \sim 1.1 \times 10^3\ \text{cm}^{-1}$ and $4.6 \times 10^3\ \text{cm}^{-1}$ for the direct relaxation of ^2E to the $(^4\text{B}_1)\text{Cr(NH}_3)_5^{3+}$ and $(^4\text{B}_1)\text{Cr(NH}_3)_4\text{Cl}^{2+}$ SPY intermediates, respectively. In these estimates we have assumed similar dissociation energies for $(^4\text{B}_1)\text{Cr(NH}_3)_5\text{Cl}^{2+}$ and for $(^2E)\text{Cr(NH}_3)_5\text{Cl}^{2+}$. This will also be an electronically forbidden pathway for the ^2E species.

Extension of the same arguments to the formation of TBPY intermediates results in activation energies of 8×10^3 cm^{-1}, 8×10^3 cm^{-1}, and 9×10^3 cm^{-1} for the $(^4E')Cr(NH_3)_5^{3+}$, $(^4A_1)Cr(NH_3)_4Cl^{2+}$, and $(^4B_1)Cr(NH_3)_4Cl^{2+}$ intermediates, respectively. It seems likely that the $^4E^{\circ}$ and ^2E TBPY reaction channels will mix sufficiently that the lowest energy pathway would form $(^4A_1)Cr(NH_3)_4Cl^{2+}$ with $E_a \leq 4.5 \times 10^3$ cm^{-1}.

The dissociative pathways do not provide a simple means for describing substitution reactions directly in the ^2E excited state of Cr(III). Rather they require spin relaxation accompanying the substitution process. In view of the small difference in energy between $(^4E^{\circ})Cr(NH_3)_5Cl^{2+}$ and $(^2E)Cr(NH_3)_5Cl^{2+}$, such spin relaxation is probably not distinguishable from "back intersystem crossing" for this complex. Since all the surface crossings are complex, there is no obvious reason to exclude competitive SPY and TBPY pathways, although entry into the SPY (ground state) channel early along the distortion coordinate could amount to an excited state quenching rather than a reaction pathway.

It is to be observed that the inferred activation energies are relatively large for the electronically allowed $^4E^{\circ}$ and for all of the ^2E reaction channels. This is consistent with the complex vibrational motions and the large amplitude distortions that are required. Nevertheless, the numerical values of E_a obtained must be regarded as indicative rather than definitive.

THE ASSOCIATIVE PATHWAYS: ADDUCT OR "EXCIPLEX" FORMATION

Associative pathways have been often suggested for the substitution reactions of Cr(III) excited states.[10,23,24] Unfortunately, there is no established experimental or theoretical basis for estimating either the relative energies of different associative intermediates, or the activation barriers for adiabatic crossings to these intermediates.

An interesting feature of the associative pathway is that one anticipates (based on crude AOM considerations) that some of the lowest energy seven-coordinate quartet and doublet species (i.e., those resulting from edge attack) will be close in energy. Thus the (^2E)Cr(III) species might be able to react by means of an associative pathway without the need for surface crossings that are complicated by spin multiplicity changes. Some aspects of Cr(III) ground state substitution chemistry suggest that the lowest energy associative and dissociative channels do not differ much in energy.[25,26]

There are two limiting pathways, for seventh ligand association with an octahedral substrate. These pathways yield intermediates with the entering ligand bonded at a face (face-capped octahedron) or an edge (pentagonal bipyramid, PBPY) of a distorted octahedral substrate (product symmetries of C_{3v} and C_{2v}, respectively, for an initial $CrL_6(O_h)$ complex). These intermediates are related through simple skeletal vibrational motions, and adiabatic crossings from the various CrL_6 electronic species to the low energy CrL_6S intermediates are vibronically allowed. Based an AOM energies, there appears to be little thermodynamic discrimination between attack between Cl and NH_3 or between adjacent ammonia ligands (the latter may be very slightly favored in $^4E^{\circ}$).

The symmetry of the limiting PBPY and capped octahedral intermediates suggests that these intermediates will not readily lead to stereospecific products: i.e., two or more of the potential leaving groups are equivalent in each of the limiting geometries.

A third seven-coordinate geometry, the face-capped trigonal prism, could contribute to a photoreaction pathway involving stereoisomerism. A low frequency twisting motion (t_{2u} in O_h) coupled with solvent attack on either $^4E^{\circ}$ or ^2E, results in solvent in the capping position and two of the original ligands in a weakly bonded position. This combination of motions would tend to scramble the orbital symmetries, making most crossings adiabatically allowed. An approximate correlation diagram, based on AOM parameters and water addition to $Cr(NH_3)_5Cl^{2+}$, is presented in Figure 5. Some important features of Figure 5 are: (1) the doublet state energies of $Cr(NH_3)_5(OH_2)Cl^{2+}$ are again relatively high and $(^2E)Cr(NH_3)_5Cl^{2+}$ to quartet $Cr(NH_3)_5(OH_2)Cl^{2+}$ crossings would have to occur along any low energy reaction coordinate; (2) the lowest energy quartet $Cr(NH_3)_5Cl^{2+}$ species are probably appreciably lower in energy than the lowest energy excited states of $Cr(NH_3)_5Cl^{2+}$; and (3) the electronically excited quartet states of $Cr(NH_3)_5(OH_2)Cl^{2+}$ appear to have a slight preference ($\sim$ 400 cm^{-1} based on AOM parameters) for water attack adjacent to chloride. The role of nuclear reorganizational barriers is difficult to assess. Based only on the apparent energy differences between states in Figure 5, reaction from the dis-

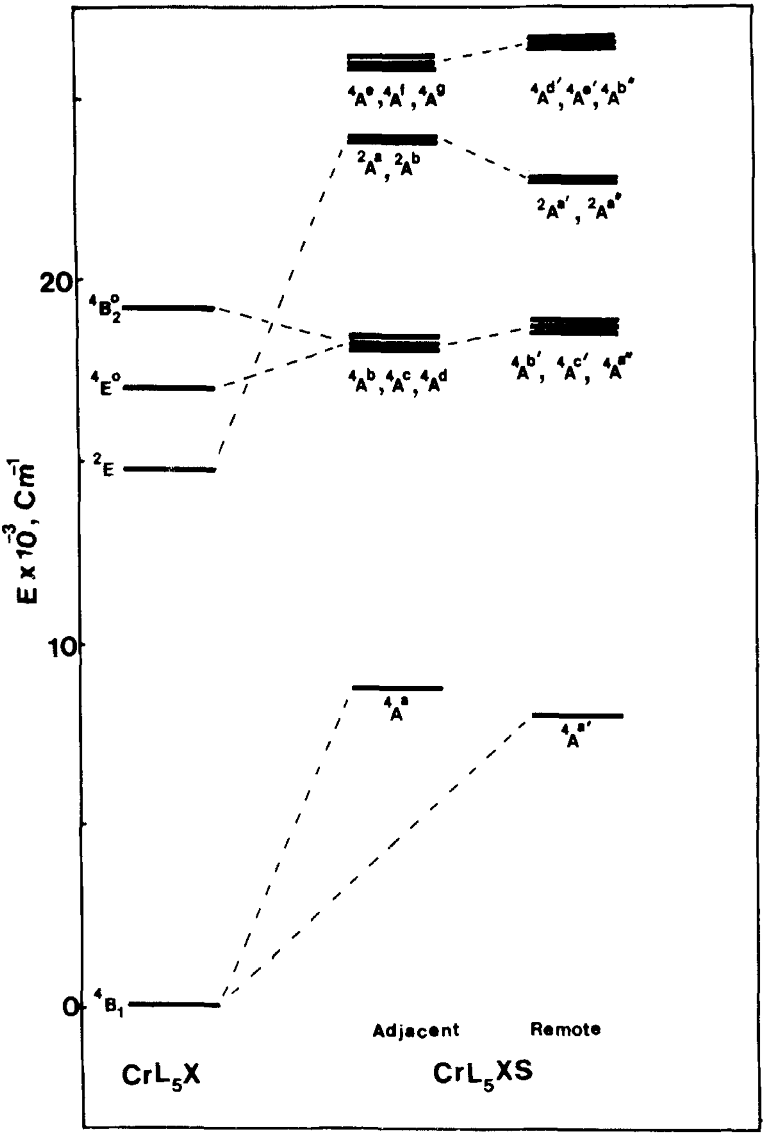

FIGURE 5 Relationships between the lowest energy electronic states of Cr(NH$_3$)$_5$Cl^{2+} and the estimated energies of the electronic states in face-capped trigonal prismatic seven-coordinate intermediates. Energies of the seven-coordinate intermediates are based on AOM parameters and water as the capping ligand. Calculations are based on a Cartesian coordinate system with the *z* axis passing through the capping ligand; the ligands remote from the capping ligand have been placed equidistant from the adjacent octahedral vertices.

torted ${}^4E^\circ$ species would tend to favor loss of ammonia *trans* to chloride, at least if the associative pathway is treated as a relaxation coordinate along which the seven-coordinate "intermediates" are too short-lived to reach vibrational equilibrium. Degeneracy of potential leaving group positions in the equilibrated $Cr(NH_3)_5(OH_2)Cl^{2+}$ species would tend to make loss of a *cis* or *trans* ligand equally likely from electronically excited $Cr(NH_3)_5Cl^{2+}$. It is interesting that the concerted twisting distortion of the substrate and addition of water to form a capped trigonal prismatic intermediate from *trans*-$Cr(N_4)X_2$ would be expected to involve a prohibitive amount of strain energy when N_4 is a macrocyclic ligand, but would be a viable pathway for *cis*-$Cr(N_4)X_2$. This is qualitatively in accord with observations.[27,28]

SUMMARY

The dissociative photosubstitution pathways proposed for transition metal complexes by Vanquickenborne and Ceulemans are in part plausible for vibrationally equilibrated excited states, but the similarity in energy of the equilibrated excited states and the proposed five-coordinate intermediates requires that the reaction pathways involve adiabatic crossings between these excited states and the reactive trigonal bipyramidal intermediates. Any selectivity in bond breaking must arise from the differing magnitudes of the nuclear reorganizational barriers for these crossings. Very approximate estimates of these barriers for $Cr(NH_3)_5Cl^{2+}$, based on adjusted AOM energies of pertinent species, are in accord with this view. Since there are no low energy, five-coordinate doublet species, any dissociative reactions of the lowest energy doublet state of Cr(III) must involve spin-orbit mixing with higher energy quartet excited states and a merging of quartet and doublet reaction trajectories along the distortion coordinate leading from $({}^2E)$–$Cr^{III}L_6$ to $({}^4X)Cr^{III}L_5$.

Both experimental and AOM considerations suggest that there are seven-coordinate intermediate species energetically accessible from the lowest energy electronic excited states of Cr(III). Of the three likely metastable geometries expected for seven-coordinate species, the capped trigonal prismatic geometry is most likely to lead to the observed product stereochemistries.

There appear to be a variety of intermediate species with energies comparable to or lower than those of the vibrationally equilibrated excited states of Cr(III). Discrimination between possible excited state reaction pathways involving these different intermediates must depend largely on the nuclear reorganizational barriers involved in their formation. Two possible reaction pathways, one dissociative and one associative, have been discussed in this report. Some of the potential intermediates may be involved along competitive relaxation pathways which do not involve net reaction. Some pathways could easily involve both reactive and nonreactive relaxation: e.g., formation of a capped trigonal prism may reverse before a metastable seven-coordinate configuration is reached, but after passing the energy maximum along the relaxation coordinate. One hopes that considerations of the sort attempted in this Comment will aid in the design of experimental approaches to resolve the ambiguities.

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