

Relationes

Bond Models for the Photochemical Reactivity of Transition Metal Complexes*

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Received January 28, 1974

Weakening of σ bonds along the labilized axis in the lowest excited quartet state of Cr(III) complexes as estimated through σ -bond orders in a simple MO-LF model, is consistent with substitution of the stronger ligand via a mechanism initiated by a predissociative step.

Key words: Transition metal complexes – Cr(III) complexes – Photochemical reactivity

Several attempts have been presented recently [1–4] to rationalize photochemical reaction modes of transition metal complexes by means of suitable bond models. Experimentally observed trends, particularly the occurrence of photochemical substitution modes different from the thermal ones, are well represented by Adamson's empirical rules [6], whose validity is now generally accepted, provided no stereospecific significance is attached to them [3–5, 7, 8]. Proposed reactivity models [3, 4] agree in explaining the labilization of the weakest octahedral axis (Adamson's first rule [6]) because of population of a σ^* antibonding orbital localized along the same axis in the lowest excited quartet of Cr(III) complexes, as expected from any ligand field model and experimentally confirmed by single crystal spectra. Less defined theoretical arguments have been presented as to which ligand is actually removed from the labilized axis, probably also because when following such models, apparent more commitment to the hypothesis of a dissociative rate-determining step, and a definition of the otherwise vague concept of "strength" of ligands, are required in order to support Adamson's second rule [6], which predicts the stronger ligand on the labilized axis to be actually released, and which is generally recognized to represent correctly experimental facts [3–5, 7, 8]. Until now, it has been pointed out [3, 4] that an obvious implication of any covalent bond model is that the lowest quartet transition ${}^4A_{2g} \rightarrow {}^4T_{2g}(O_h)$ of Cr(III) complexes is essentially a strong-field $\pi \rightarrow \sigma^*$ excitation: if, as usual, the spectrochemically weaker ligand on the labilized axis (e.g. X^-) is a better π -donor than the stronger ligand (e.g. NH_2R), then the excitation implies decrease of the π^* -antibonding effect of X^- , thus stabilizing X^- relatively to Y in the excited state. Adamson's second rule can be therefore accounted for, in cases where an amine ligand is labilized trans to a halide or similar π -donor ligand, provided determining importance is attached to π -bonding only [3, 4]. However, σ -bonding effects should be also considered, and are probably even more important, but have not yet received sufficient attention, since apart from general and not much detailed considerations [1, 2, 5], only an attempt was

* Dedicated to Professor H. Hartmann on the occasion of his 60th birthday.

presented in [3], unfortunately however affected by the choice of a wrong basis for σ molecular orbitals along the labilized axis [3]. I will present here a logical development of a simple covalent bond model, similar to those of Refs. [3, 4], which covers an explanation of Adamson's second rule [6] on the ground of σ^* effects.

Let us consider a molecular point group for a pseudo-octahedral Cr(III) complex allowing factorization of σ -bond orbitals along the labilized z -axis, e.g. D_{4h} for *trans*-CrA₄X₂ (or C_{4v} for *trans*-CrA₄XY). The minimum basis set for a covalent description of σ -bonds along z -axis consists of four (not three as in Ref. [3]) atomic functions, leading to the following MO's:

$$\begin{aligned} \psi_{\sigma z1} &\simeq \alpha(3d_{z^2}) + \beta(\psi_{\sigma x1} + \psi_{\sigma x2}) & (A_{1g} \text{ in } D_{4h} \text{ } (A_1 \text{ in } C_{4v})) \\ \psi_{\sigma z2} &\simeq \gamma(4p_z) + \delta(\psi_{\sigma x1} - \psi_{\sigma x2}) & (A_{2u}(A_1)) \\ \psi_{\sigma^* z1} &\simeq \beta(3d_{z^2}) - \alpha(\psi_{\sigma x1} + \psi_{\sigma x2}) & (A_{1g}(A_1)) \\ \psi_{\sigma^* z2} &\simeq \delta(4p_z) - \gamma(\psi_{\sigma x1} - \psi_{\sigma x2}) & (A_{2u}(A_1)). \end{aligned} \quad (1)$$

$\psi_{\sigma^* z1}$ being the singly occupied orbital in the optical transition to the lowest quartet state in D_{4h} . In C_{4v} symmetry, both A_{1g} and $A_{2u}(D_{4h})$ become A_1 , so p_z can mix with $3d_{z^2}$, and all four basis orbitals in [1] take part into each of the four MO's; although the eigenvectors of the MO's are still expected to be close to those in [1], the condition of strict equality of the squared coefficients to $\psi_{\sigma^* x1}$ and $\psi_{\sigma x2}$ (now $\psi_{\sigma x}$ and $\psi_{\sigma y}$) is released, hence charge densities and bond orders are no longer as a rule equal on Cr-X and Cr-Y bonds when $\psi_{\sigma^* z1}$ is singly occupied, and on the ground of such inequality we can attempt a discussion of differential labilization along these bonds.

In first place, the eigenvectors of the antibonding MO's reflect the degree of ionic character of the involved bonds, which may differ considerably between X, Y and equatorial ligands. In the ionic extreme, it may be easily argued that the populated excited orbitals will be those pointing towards neutral rather than charged ligands, and towards bulky rather than small ligands, leading to selective labilization in the same order. This suggests i.a. that the observed F^- labilization in *trans* [Cr(en)₂F₂]⁺ [1] is to be related at least in part to the ionic character of the F^- ligand.

If, on the other side, attention is focused on covalent effects, the determining factor can be identified in the σ^* -antibonding orders Cr-X and Cr-Y, which are determined by $|\alpha\beta_1|$, $|\alpha\beta_2|$, hence in turn by all factors which enhance covalent mixing between metal d - and ligand σ -orbitals. Labilization should then affect preferentially the ligand (X or Y) for which the σ^* -antibonding order in the lowest excited quartet is higher, i.e. for the ligand whose σ -orbitals have the stronger overlap with $3d_{z^2}$ at equal $H_{\sigma L}$, or smaller $|H_M - H_{\sigma L}|$ at equal overlap. Adamson's second rule is therefore justified provided the "strength" of the ligands is intended as above; this criterion defines amine N as a stronger ligand than halides X^- , in accordance with experimental evidence from Cr(III) photosubstitutions [9-12]. It would however be interesting to check experimentally over a wider range of complexes whether such predictions are confirmed for other pairs of ligands X, Y of varying σ - and π -donor ability.

So far we have discussed relative weakening of bonds as the first step in photosubstitution mechanisms; although undoubtedly important, and obviously precursor of a dissociative event, it is however not necessarily the only rate-determining step. In first place, the above predictions have been made for strictly octahedral geometry of the considered intermediate; this is not warranted, but the implied limitation is probably not too severe, since the same reasoning is also rigorously valid for any distorted geometry preserving factorization of the σ -bonds representation along the X–Cr–Y axis, and even in other cases it loses only gradually the validity as distortions proceed, i.e. it offers a good picture at least of the starting configuration. Secondly, axial bond weakening is probably not sufficient in itself to produce bond fission, but may require to do so a successive concerted geometric distortion and/or incoming ligand association. Actually, simple bond dissociation, implying a square pyramidal intermediate, seems ruled out experimentally by the relative photoinertness of $[\text{Cr}(\text{cyclam})\text{Cl}_2]^+$ [13] showing that equatorial rearrangement is a necessary ingredient of the overall photosubstitution mechanism. Rather, axial bond weakening is to be regarded as the initial step enabling successively either (1) distortion in the course of a molecular vibration towards a trigonal bipyramidal intermediate, which helps pushing out the weakened ligand, or (2) a distortion as in (1), accompanied by insertion of a seventh incoming ligand. Mechanism (1) would be clearly dissociative, and subsequent addition of an incoming L ligand in the equatorial plane of the trigonal bipyramid would produce 100% *cis*-XL complex; this is in agreement with experimental findings [7, 9–12, 14, 15] of *trans*→*cis* isomerization occurring almost constantly in such photosubstitutions. As to mechanism (2), quartet excitation leaves one of the t_{2g} orbitals empty (in the case discussed here, d_{xz} or d_{yz} , since X^- is a stronger π -donor than N, hence d_{xz} and d_{yz} are more destabilized than d_{xy} in the groundstate), and available for binding an incoming seventh ligand; the course of events would be again determined by the labilization of Y favoring in-plane distortions with narrower $\overline{Y}-\text{Cr}-\overline{N}$ and wider $\overline{X}-\text{Cr}-\overline{N}$ angles ("plane" is here *xz* or *yz*, i.e. the equatorial plane of the intermediate bipyramid), eventually leading to removal of Y pushed out by the N ligands coming closer, and entering of the incoming ligand L *cis* to X, still in agreement with experimental formation of *cis* products.

A similar line of thought can also be developed if, instead of basing our predictions on straight implications of the covalent model [3–5] which implies labilization from the lowest quartet and a mechanism initiated by a predissociative (in broad sense) event, we alternatively consider the lowest excited doublets of Cr(III) to be the photochemically active states, in accordance with earlier proposals [16], and in consideration of their high energy and relatively long lifetime [16]. Doublet excitation in Cr(III) complexes allows coupling of two electrons in a t_{2g} orbital, thus making one of the three t_{2g} orbitals easily free to σ -bind a seventh incoming ligand; initially the strength of previous σ -bonds would not be altered, and an associative substitution mechanism would ensue. In other words, doublet excited Cr(III) complexes should be labile in a comparable way to V(III), provided doublet lifetime is long enough to give time to associative events to occur. In the case of a *trans*-Cr(am)₄XY complex as discussed above, the available orbital would again be d_{xz} or d_{yz} , and the resulting pentagonal bipyramid would have

xz or yz as its equatorial plane. This would still confirm Adamson's first rule, since both X and Y would be comprised in the 5-coordinate plane, and not be necessarily in contrast with the second rule, but it becomes now hard to predict whether X or Y or N is actually released, and whether the entering ligand L comes *cis* to X or to Y. Speculations to this regard would be necessarily vague, and based on the relative σ (and π) bond strength of X, Y, *am* and L in the actual geometry of the 7-coordinate intermediate, and one might easily predict less pronounced stereospecificity than expected for substitution mechanisms initiated by selective σ -bond weakening, as in quartet excitation. An approach based on doublet excitation appears therefore less promising, but it would nevertheless be interesting to see whether in cases where the doublet has been experimentally shown, e.g. by sensitization experiments, to be photochemically active, selective rules are still obeyed, or different and less stereospecific substitution modes take place. It appears however easier at present to explain correctly the observed experimental behaviour, and Adamson's rules as far as they conform to it, on the ground of a covalent bond model implying quartet activity and a substitution mechanism initiated by a "predissociative" event.

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