the previous considerations, it follows that one always predicts axial ligand release when $\overline{Dq}_{ax} < \overline{Dq}_{eq}$, *except* when the ground-state bond strengths $M-L_{ax}$ and $M-L_{eq}$ are too different. This does not mean that equatorial ligand release is completely impossible in all other cases. Two amendatory remarks are in place here.

(1) All predictions considered so far relate to excitation of the lowest excited $^4E(^4T_{2g})$ state. Direct excitation of the higher lying $^4B_2$ state gives rise—as can be expected—to equatorial labilization and ligand release. This is effectively proven to hold in wavelength-dependent studies of *trans*-$Cr(en)_2(NCS)Cl^+$,[20] *trans*-$Cr(en)_2(NH_3)F^{2+}$,[6] and *trans*-$Cr(en)_2(NH_3)Cl^{2+}$.[21] However, the equatorial release is always accompanied by reaction modes characteristic of direct ^4E excitation, very likely due to photophysical communication between the two states.

(2) Ligand field models cannot be expected to offer more than a prediction of the *dominant* reaction mode. The $^4E(^4T_{2g})$ photoactive state has also a certain fraction of $x^2 - y^2$ character, labilizing the equatorial plane. This, together with the (small) antibonding properties of z^2 in the xy plane, might be responsible for a minor amount of equatorial ligand release.

More generally, it should be stressed that the validity of the present treatment is subject to two main limitations.

(1) It is assumed throughout that the photochemistry is related to the excited quartet states only. This does not mean that, in actual fact, the doublet states are photoinert; indeed, recent work[22] seems to indicate the simultaneous existence of a specific doublet reactivity; we do not attempt to account for these observations.

(2) The influence of an associative reaction mechanism is not considered. It is very possible that a purely dissociative reaction path is an oversimplification. However, in our opinion, the present status of the theory does not allow a satisfactory treatment of solvation effects. Moreover, any successful model that rationalizes Adamson's rules pays major attention to excited-state bond strength and bond labilization. This suggests very strongly that the dissociation of the leaving ligand is a capital factor in the photomechanism.

Registry No. $Cr(NH_3)_5F^{2+}$, 19443-25-5; *trans*-$Cr(en)_2(NH_3)F^{2+}$, 58410-71-2; *trans*-$Cr(en)_2F_2^+$, 24407-74-7.

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Department of Chemistry
University of Leuven
3030 Heverlee, Belgium

L. G. Vanquickenborne*
A. Ceulemans

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McConnell's Model vs. the $HPO_4 \rightarrow CO_3$ Model for Carbonate Apatite

Sir:

McConnell and Foreman[1] have raised some objections on our model for carbonate apatite.[2] Actually, these objections can be regarded as a defense for the McConnell model[3,4] rather than as a true criticism to our model. In fact, while most of ref 1 is devoted to supporting McConnell's proposal, only inappropriate arguments are dedicated to question the foundations for $HPO_4 \rightarrow CO_3$.

The McConnell and Foreman proposal that $3PO_4 \rightarrow 4CO_3$ "to preserve the oxygen lattice essentially intact" is unnecessary. For example, no OH or H_2O librational bands are present in the infrared spectrum of carbonate apatite. These librational bands actually result from the equivalence between the three oxygens surrounding one OH or one water molecule in the lattice[5] and would have to appear if the McConnell model should hold.

The internal hydrogen motion in nonstoichiometric hydroxylapatite is shown as a stabilizing mechanism allowing the existence of these compounds. If the geometrical or electronic characteristics of the unit cell should not permit such a mechanism to act, nonstoichiometric hydroxylapatite could not exist. This is the case for Sr, Ba, and Pb apatites[6] which never contain HPO_4 ions whatever the initial conditions for their syntheses are. These compounds, when synthesized under conditions other than required by the apatitic stoichiometry, take atmospheric CO_2 to form the stoichiometric carbonate apatite of the corresponding cation. The only possible explanation for this phenomenon is that CO_3 replaces the HPO_4 formed because of the initial conditions of synthesis. Since the crystallographic structure of Sr, Ba, and Pb apatite is close to that of Ca apatite, it seems reasonable that the mechanism of CO_3 inclusion into the Ca apatite is also through $HPO_4 \rightarrow CO_3$. Moreover, when nearly HPO_4-free carbonate apatite is heated at around 800 °C, it converts into stoichiometric hydroxylapatite plus a certain amount of more or less hydrated calcium oxide. It does not seem at all clear how the McConnell model could justify this transformation. Nevertheless, it is readily shown that, from formula **4** or **5** of our paper,[2] the products of calcination of nearly HPO_4-free carbonate apatite are completely justified. One would get

$$((4 - x)/4)Ca_{10}(PO_4)_6(OH)_2 + (3x/2)CaO$$

in agreement with that observed.

The strongest criticism made by McConnell and Foreman of our model is of the interpretation of the infrared data. Since they state that our interpretations are "highly speculative", we are obliged to present our interpretations in a more detailed form. CO_3 ions, which belong to the D_{3h} point group as free ions, possess lower symmetries when included into the apatitic lattice. The ν_2 mode is assigned to the species A_2, to which T_z belongs, and therefore gives rise to one active infrared band when one CO_3 ion is placed on a single site. The possibility of factor-group splitting for the CO_3 bands at ca. 870 cm^{-1} seems unreasonable because, if it holds for phosphate in apatites, it would also hold for fluorinated carbonate apatite where only one ν_2 band appears. Moreover, when hydroxylapatite is heated at high temperature in a strong current of dry CO_2, one obtains a carbonate apatite (A) having only one ν_2 band at 880 cm^{-1}. Since no substitution of any kind of phosphate by carbonate might occur in this process, we suggest that the presence of two ν_2 bands at 880 and 872 cm^{-1} in the infrared spectrum of carbonate apatite are due to the fact that CO_3 occupies two essentially different sites within the apatitic lattice. The infrared spectra of completely fluorinated and chlorinated carbonate apatite show only one ν_2 band at 862 cm^{-1} therefore suggesting only one site for the CO_3. Since F and Cl occupy sites mainly within the hexagonhelicoidal apatitic channels, replacing OH, it is natural to conclude that one of the sites that CO_3 occupies in the apatitic lattice is replacing two OH's along the channels (site A) and the other replacing HPO_4 outside the channels (site B).

It can be stated that the McConnell model is, in spite of its difficulties, equivalent in some way to the one given by us. In fact, if we consider two apatitic unit cells (along the *c* axis) and set $x = 1$, we have

$$\mathrm{Ca_{18}(PO_4)_{10}(HPO_4)_2(OH)_2{\cdot}2H_2O}$$

Then, according to our model, the two HPO_4 ions will be replaced by two CO_3's, while the two OH's cannot be substituted for by one CO_3 because the two OH's are spacially separated by one water molecule. However, if the hydrogen migration takes place from H_2O to PO_4, a new $HPO_4 \rightarrow CO_3$ will occur:

$$\mathrm{Ca_{18}(PO_4)_9(CO_3)_3(OH)_3{\cdot}H_2O}$$

Now, two of the three resulting OH groups are necessarily adjacent and, therefore, can be replaced by one CO_3. The final result should be that three HPO_4's and two OH's are replaced by four CO_3's. If we suppose the initial sample be stoichiometric (which is implicitly assumed in the McConnell model), the above substitution mechanism may be assimilated to (i) the substitution $3PO_4 \rightarrow 4CO_3$, (ii) two vacancies of Ca, and (iii) H_2O replacing OH, which follow the McConnell assumptions.

Finally, we must agree with the last objection by McConnell and Foreman. The difficulty arose from a trivial operational error in formula **6**[2] that does not introduce further modifications in the results and interpretations of our paper. Formula **6** in our paper would read

$$\mathrm{Ca_{10-\mathit{x}}(PO_4)_{6-7\mathit{x}/4}(CO_3)_{3\mathit{x}/2}(HPO_4)_{\mathit{x}/4}(OH)_{2-\mathit{x}/4}{\cdot}(\mathit{x}/4)H_2O}$$

Registry No. Carbonate apatite, 12286-89-4.

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Instituto de Optica "Daza de Valdés"
C.S.I.C., Serrano, 121
Madrid-6, Spain

P. F. González-Díaz*
M. Santos

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Electron Transfer. 43. Relative Rates as Criteria for Mechanism. A Caveat

Sir:

In 1963 Marcus[1] pointed out that when a series of oxidants is reduced by two different reagents via adiabatic[2-4] outer-sphere electron-transfer processes, the ratio of the two rate constants should be very nearly the same for all members of the series.[5,6] Since then, this principle has been useful in diagnosing substantial inner-sphere contributions to electron-transfer reactions. If the ratio of specific rates for the reaction of a single oxidant with two reductants differs greatly from that observed in bona fide outer-sphere cases, it may be inferred that the reductant enjoying the greater enhancement is utilizing an additional (i.e., an inner-sphere) path.[7] No such conclusion is possible for the second reductant.

The present communication cautions against use of this principle in its inverse form. In cases involving two reductants, each of which may, in principle, react by either an outer- or inner-sphere route with a common oxidant, it cannot be assumed that a ratio of specific rates corresponding to that found in outer-sphere systems implies that these reductants are reacting mainly by an outer-sphere path.[8]

Figure 1 is a log–log plot of the specific rates (25 °C, $\mu = 1.0$)[7a,9] for reductions of a number of organic $(\mathrm{NH_3})_5\mathrm{Co^{III}}$ complexes, using both Cr^{2+} (k_{Cr} values) and Eu^{2+} (k_{Eu} values). Oxidants represented by squares feature structures dictating outer-sphere reduction, whereas those designated by circles are carboxylato derivates, for which strong evidence supporting inner-sphere reaction with both reductants has been presented.[7a,10] Both sets of points fall close to the regression line shown, which corresponds to the relationship $\log k_{Eu} = 0.93 \log k_{Cr} + 0.97$. Moreover, the slope is very nearly unity, the value predicted by Marcus[1] for such log–log comparisons in outer-sphere systems. Rates for the carboxylato oxidants are, as a group, greater than those for the outer-sphere oxidants, but in those cases shown, rate enhancements resulting from intervention of the bridged path are comparable for the two reductants. This is not invariably so, for inner-sphere rates are known to be influenced by conjugative effects, chelation, and nonbonded interactions which may operate selectively on different reductants.[9,11] Nevertheless, partial superposition of kinetic patterns may occur, and these become more likely when such patterns are diffuse (reflecting the generally approximate nature of extrathermodynamic relationships). The carboxylato complexes (circles) in Figure 1 fall in the region where otherwise distinct inner- and outer-sphere Cr(II)–Eu(II) patterns[9] overlap, a sizable area where mechanistic ambiguity would exist were it not for the availability of other criteria.

In Figure 2, specific rates for reduction by U^{3+} (k_U values, 25 °C, $\mu = 0.20$)[11] are compared to those for reduction by Eu^{2+} ($\mu = 1.0$). Included in this log–log plot are seven Co(III) complexes (squares) for which outer-sphere reduction paths are mandatory, six carboxylato complexes (circles) which are reduced mainly via bridged paths,[11] and four cobalt-free heterocyclic species (triangles) reduced by both reagents to pyridine-related radicals.[12,13] One member of the latter quartet, methyl viologen (point 25), is devoid of lead-in donor substituents and therefore utilizes only an outer-sphere path, whereas reductions of 3- and 4-pyridinecarboxamides (points 23 and 24) and isonicotinic acid (point 26) appear to be mainly inner sphere.[13,14] Note also that the thermodynamic driving force for reductions of the heterocycles, for which formal reduction potentials lie between −0.51 and −1.01 V,[12b] is much weaker than that for reduction of the Co(III) complexes, the potentials for which are highly positive. Despite these differences, points for all 17 oxidants in Figure 2 are seen to cluster about a line having nearly unit slope.[15] Here again,