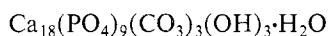


of factor-group splitting for the CO_3 bands at ca. 870 cm^{-1} seems unreasonable because, if it holds for phosphate in apatites, it would also hold for fluorinated carbonate apatite where only one ν_2 band appears. Moreover, when hydroxyl-apatite is heated at high temperature in a strong current of 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 hexagonal 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

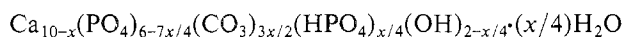


Then, according to our model, the two HPO_4 ions will be replaced by two CO_3 's, while the two OH's cannot be substituted for by one CO_3 because the two OH's are spatially separated by one water molecule. However, if the hydrogen migration takes place from H_2O to PO_4 , a new $\text{HPO}_4 \rightarrow \text{CO}_3$ will occur:



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 $3\text{PO}_4 \rightarrow 4\text{CO}_3$, (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 6² that does not introduce further modifications in the results and interpretations of our paper. Formula 6 in our paper would read



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

References and Notes

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

Sir:

In 1963 Marcus¹ pointed out that when a series of oxidants is reduced by two different reagents via adiabatic²⁻⁴ 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 ($25\text{ }^\circ\text{C}$, $\mu = 1.0$)^{7a,9} for reductions of a number of organic $(\text{NH}_3)_5\text{Co}^{\text{III}}$ 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 derivatives, 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 $\log k_{\text{Eu}} = 0.93 \log k_{\text{Cr}} + 0.97$. Moreover, the slope is very nearly unity, the value predicted by Marcus¹ 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 $\text{Cr}(\text{II})$ - $\text{Eu}(\text{II})$ patterns⁹ 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, $25\text{ }^\circ\text{C}$, $\mu = 0.20$)¹¹ are compared to those for reduction by Eu^{2+} ($\mu = 1.0$). Included in this log-log plot are seven $\text{Co}(\text{III})$ 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 $\text{Co}(\text{III})$ 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,

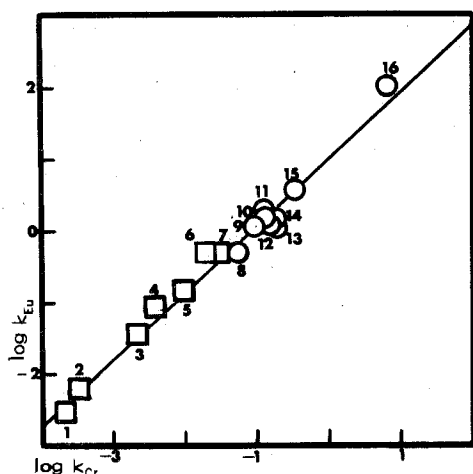


Figure 1. log-log plot comparing the specific rates for reductions of various cobalt(III) complexes by Cr^{2+} and Eu^{2+} (25 °C, $\mu = 1.0$). Squares designate complexes reacting via outer-sphere paths, whereas circles represent carboxylato complexes, for which reductions are mainly inner sphere.^{7a,10} Individual oxidants are (1) $\text{Co}(\text{NH}_3)_6^{3+}$, (2) $\text{Ro}(\text{imidazole})^{3+}$, (3) $\text{Ro}(\text{pyrazole})^{3+}$, (4) $\text{Ro}(\text{pyridine})^{3+}$, (5) $\text{Ro}(\text{dimethylformamide})^{3+}$, (6) $\text{Ro}(\text{acetonitrile})^{3+}$, (7) $\text{Ro}(N,N\text{-dimethylnicotinamide})^{3+}$, (8) $\text{Ro}(\text{diphenylacetato})^{2+}$, (9) $\text{Ro}(N\text{-methyl-2-pyridinecarboxylato})^{3+}$, (10) $\text{Ro}(3\text{-pyridinecarboxylato})^{2+}$, (11) $\text{Ro}(\text{difluoroacetato})^{2+}$, (12) $\text{Ro}(\text{propionato})^{2+}$, (13) $\text{Ro}(\text{cyclopropanecarboxylato})^{2+}$, (14) $\text{Ro}(\text{acetoxycetato})^{2+}$, (15) $\text{Ro}(\text{furoato})^{2+}$, and (16) $\text{Ro}(\text{lactato})^{2+}$ ($\text{Ro} = \text{“roseo”} = (\text{NH}_3)_5\text{Co}^{\text{III}}$). The least-squares line shown corresponds to the equation $\log k_{\text{Eu}} = 0.93 \log k_{\text{Cr}} + 0.97$.

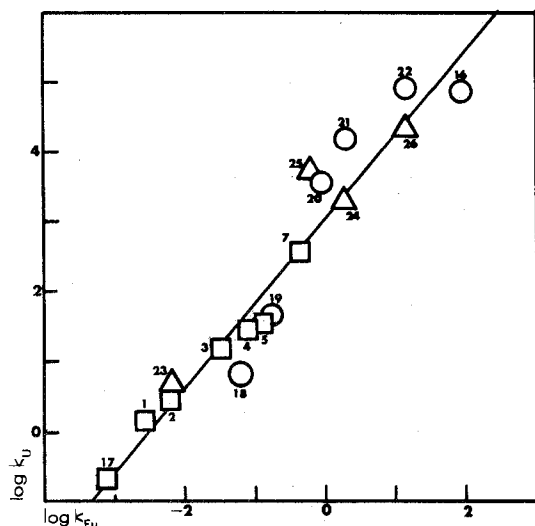


Figure 2. log-log plot comparing specific rates for reductions by U^{3+} (25 °C, $\mu = 0.20$) and Eu^{2+} (25 °C, $\mu = 1.0$). Squares designate $\text{Co}(\text{III})$ complexes reacting via outer-sphere paths, circles (carboxylato)cobalt(III) complexes, and triangles cobalt-free heterocyclic species. Individual points 1–5, 7, and 16 refer to oxidants listed in Figure 1. Other oxidants are (17) $\text{Co}(\text{en})_3^{3+}$, (18) $\text{Ro}(\text{triethylacetato})^{2+}$, (19) $\text{Ro}(\text{trimethylacetato})^{2+}$, (20) $\text{Ro}(\text{cyclopentanecarboxylato})^{2+}$, (21) $\text{Ro}(\text{acetato})^{2+}$ (limiting rate at low acidity), (22) $\text{Ro}(\text{formato})^{2+}$, (23) 3-pyridinecarboxamide (conjugate acid), (24) 4-pyridinecarboxamide (conjugate acid), (25) methyl viologen, (26) 4-pyridinecarboxylic acid (conjugate acid) ($\text{Ro} = \text{“roseo”} = (\text{NH}_3)_5\text{Co}^{\text{III}}$). The least-squares line shown corresponds to the equation $\log k_{\text{U}} = 1.23 \log k_{\text{Cr}} + 3.05$.

patterns overlap, and relative rates have become noninformative as to mechanism.

The warning here does not apply to comparisons in which the structure of one of the reductants requires that it react via an outer-sphere path (e.g., $\text{Ru}(\text{NH}_3)_6^{2+}$). Moreover, un-

certainly may be diminished by showing not only that observed ratios correspond to outer-sphere values but also that they differ substantially from ratios found for bona fide inner-sphere series in the appropriate reactivity range. Because of the vagaries to which inner-sphere systems are subject, however, arguments of the latter type must be considered indicative rather than conclusive.

Acknowledgment. The author thanks Professors William G. Movius and Fredrick G. Walz, Jr., for valuable discussions.

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Severe Distortions of a Polyhedral Metallocarborane Structure

Sir:

The readiness with which large polyhedral systems undergo distortions and rearrangements to isomeric species allows them to seek localized bonding patterns which may be related to smaller geometrically related species. Of the five structures