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Carbon–Carbon Bond Formation in the Reaction of Calcium Atoms with Ethers

Sir:

Although reactions of metal atoms with organic compounds have received considerable attention,[1] studies with the group 2 metals have been restricted largely to magnesium.[2] We report here some unusual reactions which occur when calcium atoms are codeposited with a large excess (~100:1) of an ether at −196 °C.

The codeposition of calcium atoms[3] with dimethyl ether at −196 °C resulted in the formation of a highly reactive orange-brown solid. Hydrolysis of this material leads primarily to a mixture of hydrocarbons, which were identified by GC–mass spectroscopy as methane, acetylene, ethylene, ethane, propyne, propene, propane, 1-butene, and 2-butene (cis and trans).[4] Some higher C_6 (C_6H_{10}, C_6H_{12}) and C_8 (C_8H_{14}) hydrocarbons and butanol were also detected.

When the organocalcium compound was hydrolyzed in D_2O, the same mixture of products was produced, although in slightly different yields. The mass spectra of the products obtained from this reaction showed extensive incorporation of deuterium. These data are shown in Table I.

If one assumes that D_2O labels each metal–carbon bond present in the organometallic, then it follows that extensive carbon–calcium bond formation has occurred during the cocondensation process. The activation of inert bonds in hydrocarbons with metal atoms has also been observed very recently by others. Davis and Klabunde[5] observed the low temperature cleavage of alkanes by small clusters of nickel atoms. Hydrolysis of the product yielded a mixture of alkanes, although no products with molecular weights higher than the starting alkanes were observed. Skell and his co-workers[6] have also observed the cleavage of carbon–hydrogen and carbon–carbon bonds in isoalkanes with zirconium and titanium atoms.

Table I. Hydrolysis of the Codeposition Product of Calcium Atoms and Dimethyl Ether in D_2O

product	composition, %[a]	yield, %[b]
CH_3D, CH_2D_2	<1	trace
C_2D_2, C_2HD	17	0.044
C_2H_3D	21	0.054
C_2H_5D, $C_2H_4D_2$	2	0.012
C_3H_3D	<1	trace
C_3H_5D, $C_3H_4D_2$, $C_3H_3D_3$	1	0.001
C_4H_7D, $C_4H_6D_1$ (1-butene)	12	0.032
C_4H_7D, $C_4H_6D_2$ (2-butene)	21	0.054
C_6H_9D, $C_6H_8D_2$	4	0.009
$C_6H_{11}D$, $C_6H_{10}D_2$	15	0.042
$C_8H_{12}D_2$	3	0.007

[a] Obtained from GC analyses. [b] Mole of product per mole of calcium vaporized.

The codeposition of calcium atoms with several other ethers was also investigated. For example, hydrolysis of the product obtained from diethyl ether yielded the same mixture of alkanes, alkenes, and alkynes obtained from dimethyl ether; however, the mixture was much richer in acetylene and propyne.

Bromination of the organocalcium compound obtained from dimethyl ether leads to a complex mixture of bromides. Four of these were identified readily as methyl bromide, methylene bromide, bromoform, and tetrabromoethylene. Other products with empirical formulas $C_2H_4Br_2$, $C_2H_3Br_3$, $C_2H_2Br_4$, C_2HBr_3, and $C_4H_7Br_3$ were detected by GC–mass spectroscopy. These compounds are thought to arise from bromolysis of carbon–calcium bonds as well as addition of bromine to the unsaturation present in the organometallic or the liberated alkene or alkyne.

An X-ray powder diffraction pattern of the cocondensation product of calcium and dimethyl ether showed the presence of $Ca(OH)_2$, but neither CaO nor calcium carbide was detected. The use of X-ray powder patterns to detect products is not conclusive, however, since it is known that experiments of this type rarely give crystalline solids.

Since calcium atoms do not react with alkanes and perfluoroalkanes, it is likely that the oxygen group of the ether serves as an activating point. Oxidative insertion of calcium atoms into carbon–oxygen bonds yielding CH_3OCaCH_3 or $CH_3CaOCaCH_3$ probably follows. It is quite obvious, however, that extensive insertion of calcium atoms into either carbon–hydrogen or carbon–carbon bonds must also be invoked to account for the products obtained from the hydrolyses experiments. Matrix isolation experiments to delineate these steps are in progress.[7]

Acknowledgment. We gratefully acknowledge The Robert A. Welch Foundation (Grants C-490 and C-109) for support of this work.

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Laser-Induced Metal Ion Luminescence: Interlanthanide Ion Energy Transfer Distance Measurements in the Calcium-Binding Proteins, Parvalbumin and Thermolysin. Metalloprotein Models Address a Photophysical Problem

Sir:

Förster-type nonradiative energy transfer has found considerable utility in the estimation of distances between organic moieties bound to proteins.[1,2] Recently the potential for distance measurements in proteins has been demonstrated for terbium(III) as a luminescent donor with transition metal acceptor ions.[3–5] In these cases a Förster-type dipole–dipole mechanism[6,7] satisfactorily accounts for the results. We have shown that the measurement of the reciprocal excited-state lifetimes, τ^{-1}, of bound Eu(III) and Tb(III) in both H_2O and D_2O solution using direct pulsed dye laser excitation of the metal ion levels provides a measure of the number of water molecules coordinated to the lanthanide ion, Ln(III).[8,9] Furthermore we have developed a laser excitation spectroscopic technique involving the $^5D_0 \leftarrow {}^7F_0$ transition of Eu(III) which allows a detailed characterization of individual metal ion binding sites in macromolecules.[10] We report here the first observation, using our laser techniques, of inter-Ln(III) ion energy transfer for protein-bound Ln(III) ions. The utility of experiments of this type in the measurement of distances between Ca(II) binding sites in proteins which bind more than one of these ions is assessed. It is well established that Ln(III) ions provide valid substitutional probes for Ca(II)[11–13] and, in the cases of the proteins thermolysin (E.C. 3.4.24.4)[14] and parvalbumin (carp-3, pI 4.25),[15,16] the subjects of the present study, Ln(III) ion binding has been studied by X-ray crystallographic techniques.

There exists a considerable body of experimental work concerning inter-Ln(III) ion energy transfer in doped glasses and crystalline materials.[17–19] Much of this work was sought to establish the multipolar nature of the transfer mechanism; e.g., whether it is dipole–dipole, dipole–quadrupole, or quadrupole–quadrupole in nature. It is significant, however, that two independent theoretical investigations[20,21] have shown that it is impossible to determine the multipolarity of the mechanism from experiments wherein the concentration of the acceptor ion is varied. The present work involves proteins of known structure[14–16,22,23] which, in effect, provide model systems in which an isolated pair of donor and acceptor ions are held at a known distance from one another. This is, of course, exactly the case for which Förster derived his equations.[6,7]

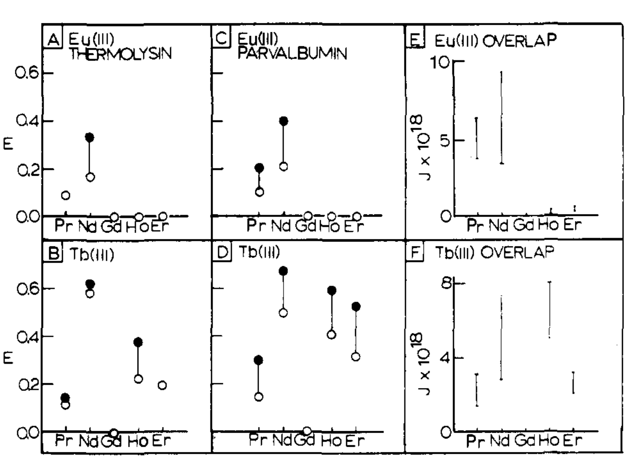

Figure 1. Panels A–D: energy transfer efficiencies, *E* (see eq 1), are indicated for the various acceptor ions for both Eu(III) and Tb(III) donors in thermolysin and parvalbumin; results in H_2O are given as open circles, those in D_2O as closed circles. Panels E and F: range of spectral overlap integrals, *J* ($cm^6\ mol^{-1}$), computed between corrected emission spectra of Eu(III) and Tb(III) bound to the two proteins and the absorption spectra of various model complexes (mostly aminopolycarboxylate polydentate chelate complexes) of the indicated energy acceptor ions.

As a working hypothesis we assume that the dipole–dipole mechanism, which holds for interorganic and Tb(III) → transition metal ion energy transfer, is operative. In this case the efficiency of energy transfer, *E*, is given by

$$E = [1 - \tau/\tau_0] = [(r/R_0)^6 + 1]^{-1} \tag{1}$$

where τ and τ_0 are the excited-state lifetimes in the presence and absence of energy transfer, respectively. r is the actual donor–acceptor distance and R_0, the critical distance for 50% energy transfer, is given by

$$R_0{}^6 = 8.78 \times 10^{-25} \kappa^2 n^{-4} \phi J \text{cm}^6 \tag{2}$$

where 8.78×10^{-25} is the product of fundamental constants. κ^2, the orientation factor, has been taken as $2/3$ because of the near isotropic nature of the absorptions and emissions of Ln(III) ions owing to the degeneracies or near degeneracies of their levels. n is the refractive index of the medium between the interacting metal ions,[24] ϕ is the quantum yield of the donor in the absence of an acceptor, and J is the spectral overlap integral given by

$$J = \frac{\int F(\nu)\epsilon(\nu)\nu^{-4}\mathrm{d}\nu}{\int F(\nu)\mathrm{d}\nu} \tag{3}$$

where $F(\nu)$ is the luminescence intensity of the donor at frequency ν (cm^{-1}) and $\epsilon(\nu)$ is the molar extinction coefficient ($M^{-1}\ cm^{-1}$) of the acceptor.

The quantity J is, in principle, an experimentally determinable quantity. However, since the absorption spectra of protein-bound Ln(III) ions are, for the most part, unobtainable owing to their low molar extinction coefficients, these quantities were estimated from the overlap of the corrected emission spectra of Eu(III) and Tb(III) bound to the proteins in question with absorption spectra of a number of model complexes. The ranges of the J values so determined are indicated graphically in Figure 1.

Parvalbumin contains two Ca(II) binding sites separated by 11.8 Å[22] which are spontaneously and simultaneously substituted for by Ln(III) ions when the latter are added to solution. An additional site or sites become occupied during the course of a titration with Ln(III) ions, but this complication can be eliminated by carrying out the experiments at pH values in the range 3.5–4.0.[25,26] Donor–acceptor ion pairs are ob-

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