

- (4) The results of a typical experiment are as follows:<sup>5</sup> methane (0.001); methanol (trace); acetylene (0.043); ethylene (0.052); ethane (0.006); propylene (0.002); propene (0.004); propane (trace); 1-butene (0.031), 2-butenes (0.052); butanols (0.033); C<sub>8</sub>H<sub>10</sub> (0.009); C<sub>8</sub>H<sub>12</sub> (0.042); C<sub>8</sub>H<sub>14</sub> (0.007).
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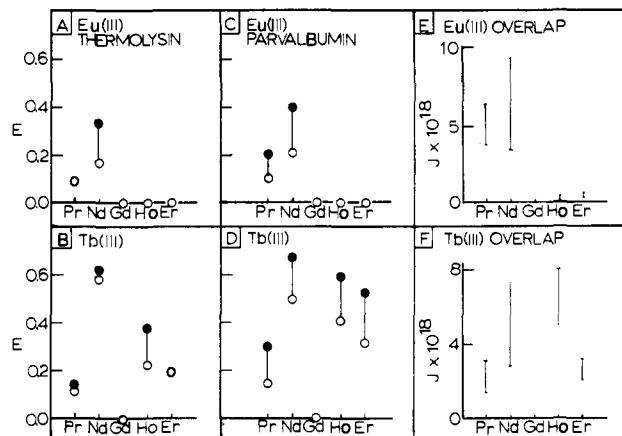
Received September 14, 1979

**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.<sup>1,2</sup> Recently the potential for distance measurements in proteins has been demonstrated for terbium(III) as a luminescent donor with transition metal acceptor ions.<sup>3–5</sup> In these cases a Förster-type dipole-dipole mechanism<sup>6,7</sup> satisfactorily accounts for the results. We have shown that the measurement of the reciprocal excited-state lifetimes,  $\tau^{-1}$ , of bound Eu(III) and Tb(III) in both H<sub>2</sub>O and D<sub>2</sub>O 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).<sup>8,9</sup> Furthermore we have developed a laser excitation spectroscopic technique involving the <sup>5</sup>D<sub>0</sub> ← <sup>7</sup>F<sub>0</sub> transition of Eu(III) which allows a detailed characterization of individual metal ion binding sites in macromolecules.<sup>10</sup> 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)<sup>11–13</sup> and, in the cases of the proteins thermolysin (E.C. 3.4.24.4)<sup>14</sup> and parvalbumin (carp-3, pl 4.25),<sup>15,16</sup> 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.<sup>17–19</sup> 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<sup>20,21</sup> 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<sup>14–16,22,23</sup> 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



**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<sub>2</sub>O are given as open circles, those in D<sub>2</sub>O as closed circles. Panels E and F: range of spectral overlap integrals,  $J$  (cm<sup>6</sup> mol<sup>-1</sup>), 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.

course, exactly the case for which Förster derived his equations.<sup>6,7</sup>

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

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

where  $\tau$  and  $\tau_0$  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

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

where  $8.78 \times 10^{-25}$  is the product of fundamental constants.  $\kappa^2$ , 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,<sup>24</sup>  $\phi$  is the quantum yield of the donor in the absence of an acceptor, and  $J$  is the spectral overlap integral given by

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

where  $F(\nu)$  is the luminescence intensity of the donor at frequency  $\nu$  (cm<sup>-1</sup>) and  $\epsilon(\nu)$  is the molar extinction coefficient (M<sup>-1</sup> cm<sup>-1</sup>) 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<sup>22</sup> 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.<sup>25,26</sup> Donor-acceptor ion pairs are ob-

**Table I.** Nonradiative Energy Transfer Efficiencies ( $E$ ), Estimated Interionic Distances ( $r$ ), and Other Parameters for Lanthanide Ions Bound to Parvalbumin and Thermolysin in H<sub>2</sub>O

donor ion	acceptor ion	parvalbumin <sup>a</sup>				thermolysin <sup>b</sup>			
		$R_0, \text{\AA}^{c,d}$	$\tau^{-1}, \text{ms}^{-1}$	$E$	$r, \text{\AA}$	$R_0, \text{\AA}^{e,f}$	$\tau^{-1}, \text{ms}^{-1}$	$E$	$r, \text{\AA}$
Eu(III)	Pr(III)	8.5	2.19	0.11	12.1	8.5	1.96	0.10	12.4
Eu(III)	Nd(III)	9.2	2.48	0.21	11.4	8.9	2.15	0.17	11.5
Eu(III)	La(III)	7.7	1.03	0.15	10.3	8.1	0.78	0.12	11.3
	Gd(III)								
	Yb(III)								
Tb(III)	Pr(III)	7.7	1.03	0.15	10.3	8.1	0.78	0.12	11.3
Tb(III)	Nd(III)	9.3	1.73	0.49	9.3	9.5	1.68	0.59	8.9
Tb(III)	Ho(III)	9.4	1.48	0.41	10.0	9.7	0.89	0.22	11.9
Tb(III)	Er(III)	8.1	1.28	0.32	9.2	8.4	0.85	0.20	10.6
	La(III)								
	Gd(III)								
	Yb(III)								
Tb(III)	La(III)	0.88	0.88	0.00			0.70	0.00	
	Gd(III)								
	Yb(III)								

<sup>a</sup> 0.01 M piperazine, pH 6.5. <sup>b</sup> 0.05 M Tris, 5 M NaBr,  $10^{-4}$  M Ln(III), pH 6.0. <sup>c</sup> Estimated using the following  $J$  values for Tb to Pr, Nd, Ho, and Er— $J = 0.24, 0.75, 0.85,$  and  $0.30 \times 10^{-17} \text{ cm}^6 \text{ mol}^{-1}$ , respectively—and Eu to Pr and Nd— $J = 0.69$  and  $1.08 \times 10^{-17} \text{ cm}^6 \text{ mol}^{-1}$ , respectively. <sup>d</sup> Estimated using  $\phi^{\text{Eu}} = 0.28$  and  $\phi^{\text{Tb}} = 0.49$ . <sup>e</sup> Estimated using the following  $J$  values for Tb to Pr, Nd, Ho, and Er— $J = 0.27, 0.70, 0.80,$  and  $0.34 \times 10^{-17} \text{ cm}^6 \text{ mol}^{-1}$ , respectively—and Eu to Pr and Nd— $J = 0.65$  and  $0.83 \times 10^{-17} \text{ cm}^6 \text{ mol}^{-1}$ , respectively. <sup>f</sup> Estimated using  $\phi^{\text{Eu}} = 0.34$  and  $\phi^{\text{Tb}} = 0.59$ .

tained by performing experiments on parvalbumin to which 0.4 equiv of donor [Eu(III) or Tb(III)] and 1.6 equiv of acceptor ion [other Ln(III) ion] have been added. Under these conditions <4% of the molecules possess luminescent donor ions at both sites. Energy transfer was monitored via the luminescent lifetimes of Eu(III) ( $\lambda_{\text{ex}} \approx 580 \text{ nm}$ ) and Tb(III) ( $\lambda_{\text{ex}} \approx 488 \text{ nm}$ ) excited by pulsed dye laser radiation using an apparatus and technique described elsewhere.<sup>9,10</sup> The energy transfer results are given in Figure 1 and Table I.

Thermolysin contains four Ca(II) binding sites. The Ca(II) ion at site 1 is readily substituted by Ln(III) ions when these are added to solution even in the presence of 1 mM Ca(II).<sup>3,14</sup> Soaking thermolysin crystals in the presence of Ln(III) ions results in the substitution of these ions for Ca(II) at sites 1, 3, and 4 [with the concomitant expulsion of Ca(II) at site 2];<sup>14</sup> however if site 1 has previously been occupied by a Ln(III) ion, then this procedure mainly affects only sites 3 and 4.<sup>27</sup> It is thus possible to make hybrid species with a Eu(III) or Tb(III) donor ion at site 1 and various acceptor ions at sites 3 and 4. Since site 1 is separated from sites 3 and 4 by 29.7 and 11.7 Å, respectively, Ln(III) ions at sites 1 and 4 represent, in effect, an isolated pair since the  $r^{-6}$  dependence of energy transfer will cause the site 1 → site 3 energy transfer to be only 0.4% of that between sites 1 and 4. The energy transfer results obtained for thermolysin with Eu(III) and Tb(III) energy donors in site 1 and various Ln(III) ions at the other sites are given in Figure 1 and Table I.

Although the  $J$  integrals evaluated for model systems span a considerable range, particularly for the Tb(III)–Nd(III) pair, there is, excluding this pair, a reasonable correlation (Figure 1) for both Eu(III) and Tb(III) donor ions between the energy transfer efficiencies and the  $J$  integrals computed for a dipole-dipole energy transfer mechanism. The  $J$  values calculated for the Tb–Nd systems are extremely sensitive to small changes in both the emission and absorption spectra with virtually the entire overlap involving the “hypersensitive”<sup>28</sup>  $^4G_{5/2} \leftarrow ^4I_{9/2}$  transition in the Nd(III) acceptor. It is possible that this may account in some measure for the fact that the calculated  $J$  values are somewhat lower than those necessary to account for all of the energy transfer. For both donor ions, acceptor ions which have zero or negligibly small  $J$  integrals, e.g., La(III), Gd(III), Yb(III), Lu(III), exhibit zero transfer efficiencies as expected. Likewise no energy transfer is observed for Eu(III) as a donor with either Ho(III) or Er(III) present as a potential acceptor, a fact consistent with the very small  $J$  values calculated for these two pairs (Figure 1). The increased transfer efficiency on going from H<sub>2</sub>O to D<sub>2</sub>O solution

comes in via the quantum yield factor in eq 2 and is borne out by experiment in most cases (Figure 1).  $R_0$  values for the various donor–acceptor pairs for the two proteins were estimated (Table I) using  $J$  integrals at the upper end of the range determined experimentally on model complexes. Taking these  $R_0$  values, in conjunction with the experimentally measured efficiencies, values of the donor–acceptor separation,  $r$ , indicated in Table I were obtained. With the exceptions of the Tb–Nd systems, the results are in reasonably good agreement with the fortuitously identical 11.7–11.8-Å distances between binding sites found in these proteins by X-ray diffraction.

Our results, obtained using metalloproteins to isolate pairs of ions, demonstrate that energy transfer from Eu(III) and Tb(III) to various Ln(III) acceptor ions can be accounted for quantitatively by a Förster-type dipole-dipole mechanism. Furthermore we have established a new class of interionic distance probe effective over distances in the 6–15-Å range, depending on the choice of donor–acceptor pair. Inter-Ln(III) ion energy transfer has potential utility for the study of the many known calcium-binding proteins possessing multiple metal ion binding sites<sup>29,30</sup> and for nucleic acids wherein Ln(III) ions are substituted for bound Mg(II).<sup>31–33</sup>

**Acknowledgments.** This work was supported by the National Institutes of Health through Grant GM23599. Matching funds for the Departmental Laser Facility at Penn State were granted by the National Science Foundation through their major equipment grant program. We thank V. K. Arkle, W. E. Collier, and J. L. Morse for experimental assistance.

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Received January 21, 1980

## Approaches to Homogeneous Reduction of Carbon Monoxide. 2. Reactions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$ with Metal Carbonyls: Selective Reduction of CO to Ethane

Sir:

A potential route to homogeneous CO reduction involves initial C-H bond formation by attack of a nucleophilic transition metal hydride on an electrophilic metal carbonyl.<sup>1</sup> We have previously reported that the reaction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$  (I) with  $\text{Fe}(\text{CO})_5$  yields an intermediate with a new C-H bond,<sup>2</sup> although the final product,  $(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Nb}(\mu\text{-H})\text{Fe}(\text{CO})_4$  (II),<sup>4</sup> does not contain reduced CO.<sup>5</sup> We have extended this study to include other metal carbonyls and find that, in certain cases, product-selective alkane formation can be observed under very mild conditions.

I reacts with several first-row binary metal carbonyls under Ar in benzene solution to give organometallic products accompanied by hydrogen evolution. The rate depends significantly on the identity of the metal carbonyl, exhibiting an interesting correlation with position in the periodic table. The approximate times for complete reaction<sup>6</sup> and organometallic products for each carbonyl follow:  $\text{Cr}(\text{CO})_6$ , 2 h, 45 °C,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}(\text{CO})$  (III);  $\text{Mn}_2(\text{CO})_{10}$ , 30 min, 40 °C, III;  $\text{Fe}(\text{CO})_5$ , 20 min, 25 °C, II;  $\text{Co}_2(\text{CO})_8$ , instantaneous, 25 °C,  $(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Nb}(\mu\text{-CO})\text{Co}(\text{CO})_3$  (IV).<sup>7</sup> The significance of the trend in reactivity is not clear; IR stretching frequencies for these carbonyls<sup>8</sup> do not indicate any substantial changes in CO electrophilicity (such as in going from III to  $\text{Fe}(\text{CO})_5$ , for example<sup>2</sup>) which would be expected to affect reactivity.<sup>9</sup> No organic products can be detected in solution or in the gaseous phase.

When the reaction of I with  $\text{Cr}(\text{CO})_6$  is carried out under an atmosphere of  $\text{H}_2$  instead of Ar, disappearance of I proceeds at roughly the same rate. However, large amounts of dark precipitates form (only traces are observed under Ar) and the yield of III is lowered considerably. The solids are soluble only in mineral acids and thus appear to consist of metal oxide species. The gas phase, sampled after 3 h or longer, contained ethane in ~10% yield (based on Nb). Only traces ( $\leq 1\%$  yields) of methane, ethylene (but see below), and propane could be detected.<sup>10</sup> The reactions of I with  $\text{Cr}(\text{CO})_{6-x}(\text{C}^{13}\text{CO})_x$  leads to  $\text{C}^{13}$ -labeled ethane.<sup>11</sup> For all the other metal carbonyls listed

above, no difference in reactivity or products was found for reactions under  $\text{H}_2$  compared with under Ar.

The selective formation of a  $\text{C}_2$  hydrocarbon is highly significant; with few exceptions, hydrocarbon formation from CO is generally selective for methane or else not very selective at all. It is notable that the reaction of  $\text{AlH}_3$  with group 6 metal carbonyls is selective for  $\text{C}_2$ , but the major product is ethylene ( $\text{C}_2\text{H}_4:\text{C}_2\text{H}_6 \sim 95:5$ ). A mechanism involving a carbenoid intermediate was proposed.<sup>13</sup> The observation here of a  $\text{C}_2$  product with a group 6 metal suggests possible mechanistic similarity: i.e., that  $\text{C}_2\text{H}_4$  is the initial product (either free or complexed) which is efficiently hydrogenated by the system involving I but *not* by  $\text{AlH}_3$ . In fact, when the gas phase is monitored during the course of the reaction,<sup>14</sup> ethylene comprises a substantial fraction of the  $\text{C}_2$  product during early stages. (In a typical run, the ratio of  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$  was 0.23 after 1 h, 0.09 after 2 h, 0.006 after 5 h.) Similarly, if 1 equiv of  $\text{C}_2\text{H}_4$  is added to the original reaction atmosphere, it is gradually hydrogenated during the reaction. The fact that hydrogenation continues after all starting material is consumed indicates that the reaction byproducts are responsible for catalytic hydrogenation.<sup>15</sup> Furthermore, when I and  $\text{Cr}(\text{CO})_6$  are reacted under  $\text{D}_2$  the ethane contains zero, one or two deuterium atoms per molecule;<sup>10</sup> this would be consistent with a mechanism where in  $\text{C}_2\text{H}_4$  is formed initially using only hydrogen derived from I, while hydride derived from atmospheric  $\text{D}_2$  becomes involved only in the subsequent hydrogenation.<sup>17</sup>

Reaction of I with  $\text{Cr}(\text{CO})_6$  under a mixed  $\text{H}_2\text{-CO}$  atmosphere does not lead to any catalysis; instead (as with  $\text{H}_2\text{-C}_2\text{H}_4$ )<sup>15</sup> formation of ethane and insoluble metal oxides are both suppressed, and III is formed nearly quantitatively.<sup>17</sup> I reacts with  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  in similar fashion (comparable rates and precipitate formation), but with notable differences: the gaseous products (in trace amounts only) are methane for Mo and a mixture of methane and ethane for W; the soluble organometallic product in each case is clearly not III but appears to be a bimetallic species.<sup>20</sup>

Catalytic CO reduction does not appear to be possible with this combination of reagents, because of both the tendency to form unreactive III and the formation of metal oxides rather than free  $\text{H}_2\text{O}$  from the O atom. However, the selective formation of ethane under conditions where the metal hydride species is potentially stable to CO reduction products<sup>1</sup> offers encouragement for further studies along these lines.

**Acknowledgment.** We thank the National Science Foundation for support through Grant CHE 77-01585, Mr. Don Schifferl for instrumental assistance, and Dr. Don Darensbourg for communicating results prior to publication.

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