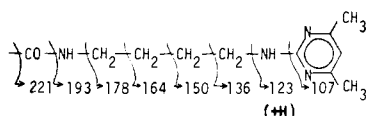


In agreement with the cyclopropene structure is the appearance of one of the  $=\text{CH}$  carbons and the  $\alpha$ - $\text{C}-\text{H}$ - carbon at abnormally high fields, 102.8 and 28.9 ppm, respectively.<sup>10</sup>

Structure **1a** also agrees with its selective uptake of 3 mol of hydrogen, noted above, which would give an alkylcyclopropanecarboxamide (**5a**). The dimethylpyrimidyl derivative (**6a**) of **5a** was synthesized from 1-decene by the route shown in Chart I. The cis and trans isomers of **6a** were separated and analyzed by GC-mass spectrometry; the more abundant (presumably the trans isomer)<sup>11</sup> cochromatographed with **6a** and gave the same mass spectrum as **6a** prepared from the natural product.

The structure of the minor homologue, polyandrocarpine II, was assigned as **1b** (Chart I) by its molecular formula ( $\text{C}_{17}\text{H}_{28}\text{N}_4\text{O}$ )<sup>7a</sup> and those of its derivatives (**3b**, **5b**, **6b**),<sup>7a,b</sup> all with formulas  $\text{CH}_2$  less than their polyandrocarpine I analogues. The GC-mass spectral fragmentation pattern of **2b** locates the missing  $-\text{CH}_2-$  group in the guanidinoalkylamine group, since **2b** gives peaks from  $m/e$  107 through 221, as shown.



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## References and Notes

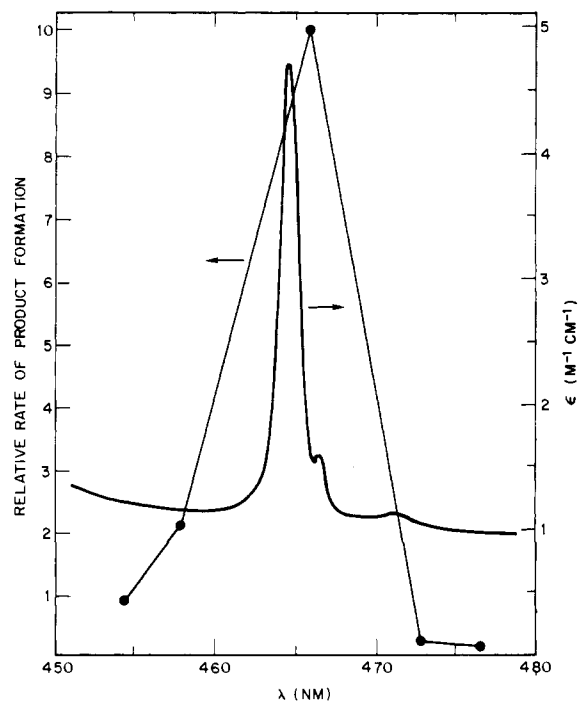
- (1) Presented in part at the Second International Symposium on Marine Natural Products (IUPAC-Societa Chimica Italiana), Sorrento, Italy, Sept 12-15, 1978.
- (2) *New York Times*, July 19, 1976, p 1.
- (3) The tunicate (ITBE 2-VI-76-1-1) was identified, from a sample preserved in ethanol, by Dr. D. P. Abbott (Hopkins Marine Station, Pacific Grove, Calif.), who indicated that this was the same tunicate reported earlier (R. J. Andersen and D. J. Faulkner, *Proc. Food-Drugs Sea*, 1972, 111-115 (1973)) to have activity against *Staphylococcus aureus*.
- (4) Biological activity data were provided by (a) Dr. L. H. Li and Ms. S. L. Kuentzel, The Upjohn Co.; (b) Dr. L. P. Hager and Mr. J. Nemanich, University of Illinois; (c) Dr. J. J. Vavra and Mr. G. E. Zurenko, The Upjohn Co.; and (d) Dr. R. G. Hughes, Roswell Park Memorial Institute.
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## Lanthanide Photochemistry Initiated in f-f Transitions

Sir:

There have been few studies concerning photochemical reactions of the lanthanides (Ln) and all have involved photo-

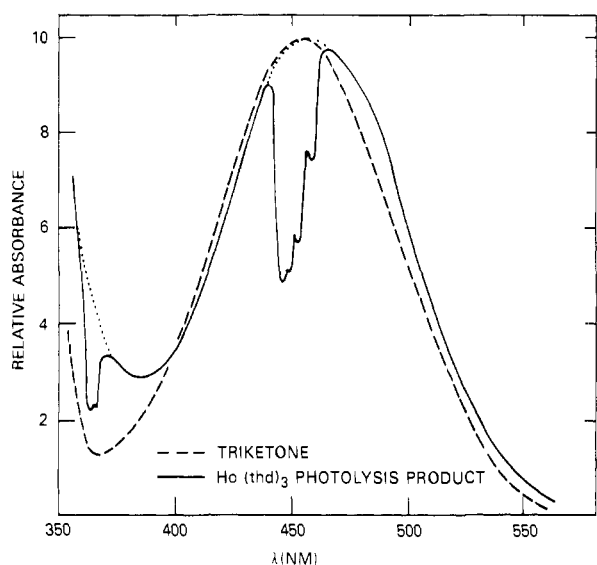


**Figure 1.** A portion of the absorption spectrum for  $\text{Eu}(\text{thd})_3$  in acetone (right-hand scale). The large feature is due to the  ${}^7F_0 \rightarrow {}^5D_2$  transition and is split owing to its hypersensitivity. The slight hump at 472 nm is due to  ${}^7F_1 \rightarrow {}^5D_2$  thermally excited-state absorption. The photochemical rate of appearance of product, monitored spectrophotometrically, and normalized by total incident energy, is given on the left-hand scale. Error bands at each wavelength are  $\pm 20\%$  of the rate at that wavelength.

redox processes in charge transfer or f-d bands in  $\text{Ce}(\text{III,IV})$ <sup>1,2</sup> and  $\text{Eu}(\text{III,II})$ .<sup>3,4</sup> The line-like intrashell f-f absorption features<sup>5</sup> found in the lanthanides (Figure 1) occur throughout the ultraviolet to near-infrared spectral regions and have been ignored with respect to photochemical reactivity, since the 4f electrons are presumably effectively shielded from interactions with the chemical environment.<sup>6</sup> However, it is well known that energy can be efficiently exchanged between electronic states of complexing ligands and excited Ln 4f levels.<sup>7,8</sup> Under the appropriate conditions, such energy-transfer processes could result in photochemistry. This communication reports the first demonstration that energy absorbed in an f-f transition can result in a photochemical change, photosubstitution.

Since complexes of lanthanides are much less stable than those of most transition metals, strongly chelating ligands are required in any study of photosubstitution reactions, in order to reduce thermal reactions.<sup>9</sup> In the experiments presented here, the bidentate  $\beta$ -diketonate, 2,2,6,6-tetramethyl-3,5-heptanedionate (thd), was used. Complexes<sup>10</sup> of either  $\text{Pr}(\text{III})$ ,  $\text{Eu}(\text{III})$ , or  $\text{Ho}(\text{III})$  were dissolved in an appropriate solvent to give solutions 0.01 M in Ln(III) for most experiments. The samples, 0.5-1.0 mL, were irradiated and spectrophotometrically analyzed in stoppered 1-cm fused silica spectrophotometer cells. The photolytic source was an argon ion laser, line tunable over ten transitions in the blue to green region of the spectrum. The 100-200 mW laser beam was passed through the cells without focussing, using a 1.5-mm-diameter spot size.

Irradiation results in the formation of a broad absorption peak (see Figure 2) and the rate of formation is observed to be linear in both laser power and irradiation time, hence linear in incident energy. This effect is observed with all three Ln(thd)<sub>3</sub>, but only in coordinating solvents, such as pyridine, ethanol and acetone.<sup>11</sup> No effect is observed in poorly coordinating  $\text{CCl}_4$  or hexane. Furthermore, little effect is seen when solutions are deaerated before photolysis by bubbling with argon gas. The spectra of the products also includes structure

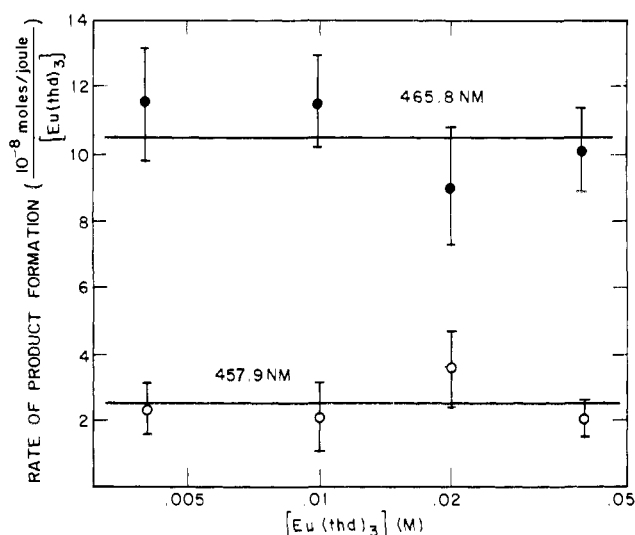


**Figure 2.** Comparison of absorption spectra for the photolysis product in acetone (difference spectrum using an unphotolyzed sample as a reference) with that observed for 2,2,6,6-tetramethyl-3,4,5-heptanetrione in dichloromethane.<sup>17</sup> The negative absorption features superimposed upon the product peak are due to the presence of photosubstituted Ho(III) species whose hypersensitive transitions at 450 nm ( $^5I_8 \rightarrow ^5G_6$ ) and 357 nm ( $^5I_8 \rightarrow ^3H_6$ ) have smaller extinction coefficients than those found in Ho(thd)<sub>3</sub>.

which can be assigned to changes in the intensity of the hypersensitive<sup>12-14</sup> lanthanide 4f transitions, as indicated by the solid line in Figure 2. Finally, the rate of increase of the broad absorption band is observed to be a strong function of photolysis wavelength.

A chemical mechanism which accounts for the above observations is photosubstitution of thd<sup>-</sup> ligand by the solvent. It is clear that the solvent must display coordinating properties or else solvent replacement of the β-diketonate is thermodynamically unfavorable.<sup>9</sup> Following its substitution, the free thd<sup>-</sup>, apparently in an excited state,<sup>15</sup> reacts with oxygen in solution, forming a peroxide<sup>16</sup> which then decomposes, yielding a 3,4,5 triketone and OH<sup>-</sup>. The evidence for a vicinal triketone as the observed product is clear. The spectrum closely resembles that published for the appropriate triketone, 2,2,6,6-tetramethyl-3,4,5-heptanetrione,<sup>17</sup> shown in Figure 2. Molecular oxygen must be present for a photochemical reaction to be observed. Finally, the changes in intensity and shape of the lanthanide hypersensitive transitions indicate a change in coordination number or symmetry about the Ln ion.<sup>13,14,18</sup> The simplest explanation is that photosubstitution by the solvent has occurred.

Figure 1 indicates that production of the triketone is greatly enhanced by absorption within the f-f transition. This effect is most prominent in Eu(III) complexes, but similar wavelength dependences, showing peaking (that is, spectral selectivity), are observed for Pr(III) and Ho(III) as well. Furthermore, a small amount of photochemical production of triketone is observed outside the f-f bands. These observations can be accounted for by considering the energy levels of the complexing ligands. The energies and assignments of some of the electronic transitions for a few β-diketonates have been determined, and they all display singlet absorption below 330 nm.<sup>8,19</sup> In addition, there is a lower lying triplet at 400–500 nm, depending upon the chelate and the metal ion to which it is bound.<sup>8,19</sup> Some absorption to the spin-forbidden triplet level ( $\epsilon \sim 0.03 \text{ M}^{-1} \text{ cm}^{-1}$  for Fe(hfa)<sub>3</sub>)<sup>20</sup> is expected which evidently results in low rates of triketone formation. However, energy absorbed in the far more intense f-f transitions is apparently transferred to the triplet level, resulting in photodissociation of the complex with subsequent substitution.



**Figure 3.** Rate of product formation vs reagent concentration in acetone. The samples are optically thin at the wavelengths and concentrations employed; thus the rate is sensibly independent of concentration. The rate constants are derived assuming  $\epsilon = 33 \text{ M}^{-1} \text{ cm}^{-1}$  for the product at 460 nm.<sup>17</sup> The error bars give single standard deviation limits (averages of four-eight runs) and horizontal lines are the averages of all data at a single wavelength.

Some of the transitions employed in experiments involving Eu(III) and Ho(III) (at 465 and 450 nm, respectively) are hypersensitive.<sup>13,14</sup> It has been suggested that hypersensitivity in f-f transitions involves metal-ligand covalency via charge-transfer levels.<sup>14</sup> Since Eu(III) has the lowest energy charge-transfer band of the lanthanides<sup>21</sup> (thus allowing the greatest mixing of hypersensitive and charge-transfer levels), this suggestion could account for the fact that the wavelength dependence shows the greatest peaking for Eu(III) complexes. On the other hand, both Ho(III) and Pr(III) display a much greater density of electronic transitions in the photolysis spectral region used,<sup>5,22</sup> so that the wavelength dependent rate may merely reflect the large number of states available for absorption of energy, resulting in less spectral selectivity.<sup>23</sup>

It is apparent that the production of triketone is due to photochemical and not thermal processes since the rate of formation of products is a linear function of laser power, while solutions sitting for weeks at room temperature do not give any evidence of this type of decomposition. Furthermore, in the case of optically thin solutions of Eu(thd)<sub>3</sub>, the rate of triketone formation is linear in reagent concentration (Figure 3), indicating that there are no significant effects due to local laser heating. From the data in Figures 1 and 3, using  $33 \text{ M}^{-1} \text{ cm}^{-1}$  as the molar extinction coefficient for the triketone at the peak,<sup>17</sup> the quantum yield at 465.8 nm is calculated to be  $\sim 0.01$ . This number is only approximate since no compensation was made for product absorption. However, at the small extents of photolysis used for quantum yield estimations (<5%), product absorption was less than reagent (Eu(thd)<sub>3</sub>) absorption. Furthermore, the product appeared to be photochemically stable at the photolysis wavelengths employed.

It can be seen that the wavelength of the laser line closest to the  $^7F_0 \rightarrow ^5D_2$  transition of Eu(III) falls only on the shoulder of the absorption band (Figure 1). Far greater rates than those observed here can be expected when a tunable source is employed to allow photolysis at the peak of the transition. Experiments using a tunable dye laser as a source will begin shortly.

Whether or not the mechanism presented is correct in every detail, evidence for photochemistry in f-f transitions is unequivocal. It remains to be demonstrated whether such processes can be made selective to a particular lanthanide in a mixture. Conditions must be chosen carefully, to reach a

compromise between ligand lability (thermal processes) and photochemical processes. Quantum yields and selectivity may improve with the choice of chelates and solvents. It is hoped that, if elemental selectivity is achieved, then such processes as those described here can be employed in photochemical separation processes<sup>4,24</sup> for those lanthanides and actinides with only one stable oxidation state in solution.

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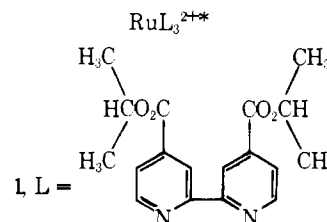
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## Applications of Photoinduced Electron-Transfer Reactions: Visible Light Mediated Redox Reactions of Substrates Using Transition Metal Complexes as Catalysts

Sir:

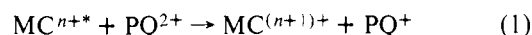
Electron-transfer quenching of excited states has become a well-established phenomenon through numerous investigations.<sup>1-5</sup> These reactions can produce potentially powerful oxidants and reductants; however, the usual consequence is no permanent chemistry since the products rapidly react with each

other in a subsequent electron-transfer step. Recently, it was demonstrated that both quenching and back-electron-transfer processes could be retarded for metal complexes by the incorporation of bulky hydrophobic groups around the periphery of the complex,<sup>6</sup> for reductive quenching of complexes such as  $\text{RuL}_3^{2+}$  by certain amines the coupling of reduced back-electron-transfer rates with a rapid reaction of one of the products permits the isolation of the high energy reduced product  $\text{RuL}_3^+$ .<sup>6</sup> In the present paper we report studies in



which oxidative quenching of excited states of metal complexes such as **1**,  $\text{Ru}(\text{bpy})_3^{2+}$  (**2**), and metalloporphyrins can be used to accomplish permanent chemical changes. In this case the key to avoiding nonproductive back-reaction is the secondary reaction of a highly reactive oxidized substrate with solvent in a hydrogen-atom transfer generating neutral free radicals which are not highly oxidizing. The cases reported here indicate that both "reagents" generated in the quenching process can be used in carrying out selective reactions with visible light as a reagent and metal complexes in nonaqueous media as catalysts.

It has previously been demonstrated through luminescence quenching experiments and flash photolysis studies that paraquat ( $\text{PQ}^{2+}$ ) (*N,N'*-dimethyl-4,4'-bipyridine) quenches excited states of **1**, **2**, and palladium octaethylporphyrin (**3**) in acetonitrile or butyronitrile by electron transfer as shown:<sup>2,6</sup>



Back-electron transfer



rapidly regenerates the starting materials with rate constants  $k = 1.8, 8.1, \text{ and } 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for **1**, **2**, and **3**, respectively. Thus the systems of  $\text{PQ}^{2+}$  and **1**, **2**, or **3** in dry acetonitrile have a net photostability. In rather striking contrast we find that addition of small to moderate amounts of several organic materials to solutions containing metal complexes and  $\text{PQ}^{2+}$  results in net photochemical change. The photoreaction can be conveniently monitored by ESR or by changes in the absorption spectrum as shown in Figure 1 for **1** and  $\text{PQ}^{2+}$ . In the ESR experiments, irradiation of several samples, carefully dried and degassed with argon, leads to the same results: no paramagnetic species are detectable prior to irradiation, but upon photolysis with visible ( $\lambda > 420 \text{ nm}$ ) light a rapid generation of a single paramagnetic species is observed. Both the envelope and hyperfine splitting pattern are consistent with the identification of this species as the paraquat radical cation,  $\text{PQ}^+$ .<sup>7,8</sup> Changes observed in the UV-visible spectra of degassed irradiated solutions (Figure 1) are completely consistent with the ESR results. A rapid formation of  $\text{PQ}^+$  ( $\lambda_{\text{max}}$  at 605 and 395 nm) is observed, but no net decomposition of **1** occurs. The results appear best described by a sequence in which electron-transfer quenching (eq 1) is followed by oxidation of the added substrate to regenerate **1**



in competition with back electron transfer (eq 2). Substrates which have been found thus far to react under irradiation of **1** leading to a build up of  $\text{PQ}^+$  include pyridine, 2,6-lutidine, *N,N*-dimethylformamide, triethylamine, and water.<sup>9</sup> Since