

to explain the various reactions of chlorine(I) through the common intermediate  $\text{H}_2\text{OCl}_2$ .

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knowledged.

**Registry No.**  $(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$ , 42901-32-6;  $(\text{en})_2\text{Co}(\text{SCH}_2\text{COO})^+$ , 42901-31-5;  $(\text{en})_2\text{Cr}(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$ , 48131-66-4;  $(\text{en})_2\text{Co}(\text{SeCH}_2\text{CH}_2\text{NH}_2)^{2+}$ , 58866-01-6;  $\text{CH}_3\text{I}$ , 74-88-4;  $\text{H}_2\text{O}_2$ , 7722-84-1;  $(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)$ , 68645-75-0.

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## Reaction Kinetics of the Intermediate Produced in the Laser Pulse Photolysis of Tungsten Hexacarbonyl in Fluid Solution

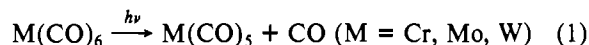
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Laser pulse photolysis at 353 nm of tungsten hexacarbonyl in room-temperature methylcyclohexane produces an intermediate, proposed to be  $\text{W}(\text{CO})_5\text{S}$ , S denoting solvent, with an absorption maximum at 425 nm and  $\epsilon_{\text{max}} 7.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ . In the presence of added L = 4-acetylpyridine, the intermediate reacts completely to form  $\text{W}(\text{CO})_5\text{L}$  as the final product. The rate of disappearance of the intermediate is pseudo first order, with  $k_{\text{app}}$  linear in L at low concentration but approaching a limiting value at higher concentrations. The proposed mechanism is one of reversible dissociation of  $\text{W}(\text{CO})_5\text{S}$  to  $\text{W}(\text{CO})_5$  and S with rate constants  $k_1$  and  $k_{-1}$ , followed by scavenging of the  $\text{W}(\text{CO})_5$  by L, with rate constant  $k_2$ . At 20 °C  $k_1 = 1.9 \times 10^6 \text{ s}^{-1}$  and  $k_2/k_{-1} \approx 270$ ; the corresponding activation quantities are  $E_1^* = 3.9 \text{ kcal mol}^{-1}$  and  $E_{-1}^* - E_2^* = 2.6 \text{ kcal mol}^{-1}$ . The nature of the primary photolysis step is discussed.

### Introduction

The photochemical behavior of organometallic complexes is of importance to the production of catalytically active compounds and to the advancement of synthetic organometallic chemistry.<sup>1</sup> In particular, intermediates produced in the photolysis of group 6 hexacarbonyls have been the subject of an increasing number of investigations. The primary photoreaction appears to be one of efficient CO dissociation:<sup>2-4</sup>



In the presence of coordinating ligand L, the substitution product  $\text{M}(\text{CO})_5\text{L}$  is formed with near unitary quantum efficiency.<sup>2</sup> It is the structure, the solvation, and the reaction kinetics of the  $\text{M}(\text{CO})_5$  species that has been of much interest.

In a classical study, Stolz, Dobson, and Sheline<sup>5,6</sup> found the infrared absorption spectrum of  $\text{M}(\text{CO})_5$  produced in isopentane/methylcyclohexane glasses at 77 K to be consistent with a  $C_{4v}$  square-pyramidal structure but with isomerization to a  $D_{3h}$  trigonal-bipyramidal structure on thawing of the glass. Extensive investigations by Turner and co-workers<sup>7-9</sup> further supported the presence of a  $C_{4v}$  intermediate in low-temperature matrices and one able to undergo thermal reaction with the photoproduct or added CO. A suggestion<sup>10</sup> that  $\text{M}(\text{CO})_5$  could be weakly coordinating to even poor donors was substantiated by evidence for  $\text{M}(\text{CO})_5\text{N}_2$  in  $\text{N}_2$  or  $\text{Ar}/\text{N}_2$  matrices

at 20 K<sup>8</sup> and, more specifically, for weak bonding between  $\text{Cr}(\text{CO})_5$  and rare gas or hydrocarbon in the corresponding matrices.<sup>9,11</sup>

$\text{M}(\text{CO})_5$  intermediates have also been examined in room-temperature fluid solution by means of conventional flash photolysis and pulse-radiolysis techniques.<sup>12-17</sup> Kelly et al.<sup>14</sup> reported that on flash photolysis of  $\text{Cr}(\text{CO})_6$  in cyclohexane, an intermediate was produced with an absorption maximum at 503 nm, thought to be  $\text{Cr}(\text{CO})_5$ , and highly reactive toward solvent impurities. However, more recent work suggests that the intermediate may have been  $\text{Cr}(\text{CO})_5\text{S}$ , S denoting solvent. The intermediate produced in perfluorocarbon solvents was found to combine with CO,  $\text{N}_2$ , and cyclohexane with rate constants at about the diffusion limit,<sup>16</sup> so that in cyclohexane as solvent the immediately produced species should be the solvent coordinated one. There is thus some gathering of evidence that the first observed intermediate both in fluid solution and in low-temperature matrices is not  $\text{M}(\text{CO})_5$  but  $\text{M}(\text{CO})_5\text{S}$ , although the M-S bond may be a weak one.

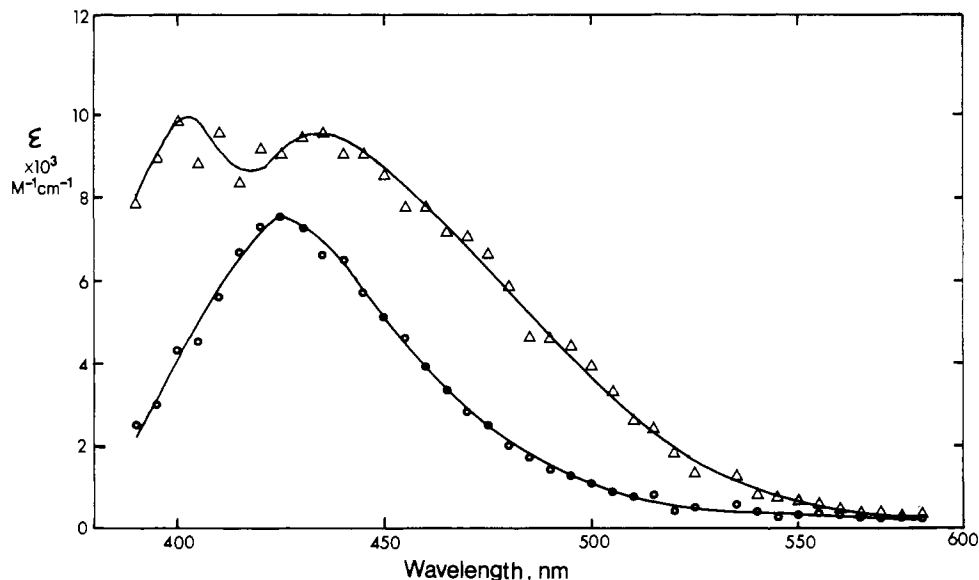
We report in this paper the observation of an intermediate following photolysis of  $\text{W}(\text{CO})_6$  in methylcyclohexane solvent at room temperature and on the kinetics of its subsequent reaction with 4-acetylpyridine. The experiment is one of monitoring absorbance changes, following pulsed-laser photolyses.

### Experimental Section

**Materials.** Tungsten hexacarbonyl (Strem Chemicals) was purified by sublimation. The ligand 4-acetylpyridine (Aldrich) was used without further purification. Solvents used were obtained from MCB Manufacturing Chemists and were OmniSolv grade. The methyl-

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**Figure 1.** Absorption spectra recorded following laser pulse photolysis of  $5 \times 10^{-4}$  M  $W(CO)_6$  and  $5 \times 10^{-3}$  M 4-acetylpyridine in methylcyclohexane at 20 °C: O, transient absorption spectrum recorded immediately followed laser pulse;  $\Delta$ , product absorption spectrum recorded after decay of transient.

cyclohexane, however, was further purified by several distillations so as to remove emitting impurities.

**$W(CO)_5(4\text{-acetylpyridine})$ .** The compound was prepared by reacting photogenerated  $W(CO)_5(\text{tetrahydrofuran})$  with 4-acetylpyridine, according to a literature procedure,<sup>4,18</sup> in tetrahydrofuran (THF) solvent. The THF was removed by rotary evaporation, and the solid product was dissolved in isooctane and purified by chromatography on alumina (MCB Manufacturing Chemists). Elution was first with isooctane until the UV absorption features of  $W(CO)_6$  could no longer be detected in the eluant, followed by elution of the product complex with benzene. The product was recovered by rotary evaporation. The infrared and UV-visible absorption spectra agreed well with those published.<sup>18</sup> Anal. Calcd: C, 32.4; H, 1.6; N, 3.1. Found: C, 32.9; H, 1.8; N, 3.3.

**Equipment and Procedures.** Details of the laser photolysis and monitoring equipment are described elsewhere.<sup>19,20</sup> Excitation was at 353 nm, with 20-ns, frequency-tripled pulses from the Nd glass laser. The pulse energy was measured by means of the photodiode pulse produced by a portion of the beam and recorded as one of the oscilloscope traces so that correction could be made for the  $\pm 10\%$  variation in laser pulse energy. Absolute pulse energies were checked by means of a Korad Model 108 ballistic thermopile and were in the 90–140-mJ range, depending on the laser power settings. The 1-cm diameter laser beam was shaped by means of a cylindrical lens to give an irradiated area of  $2 \times 9$  mm on the front window of a four clear-sided quartz cell. The temperature of the solution in the cell was controlled to 0.1 °C by circulating thermostated water.

The transmitted monitoring beam was reduced down onto the slit of a Jarrell-Ash Mark 10 monochromator and exited onto a five-stage RCA 4840 photomultiplier. Typical entrance and exit slits were 1 mm. Saturation effects were avoided by employing a mechanical shutter.<sup>20</sup> Solutions were deaerated by argon purging for 20 min, as a precautionary measure although lack of such purging had no measurable effect. Conventional absorption spectra were obtained by means of a Cary 14R recording spectrophotometer.

## Results

A typical experiment consisted of excitation of a methylcyclohexane solution which was  $5 \times 10^{-5}$  M in  $W(CO)_6$  and around 0.02 M in 4-acetylpyridine. The transmitted intensity of the monitoring beam showed an instantaneous decrease from  $V_0$  to  $V_{in}$ , that is, a decrease which followed the 20-ns laser pulse half-time. A measurably slow further change then oc-

curred, in which  $V_t$ , the intensity at time  $t$  after the pulse, dropped to a final value  $V_{\infty}$ . Here,  $V$  denotes voltage of the oscilloscope signal from the photomultiplier. Since  $W(CO)_6$  does not absorb in the 400–600-nm region,  $\log(V_0/V_{\infty})$  gives the optical density of the final product,  $D_{\infty}$ , and is thus proportional to its extinction coefficient. The variation of  $D_{\infty}$  with wavelength corresponded closely to the absorption spectrum of  $W(CO)_5(4\text{-acetylpyridine})$ , with maxima at 404 and 442 nm. This is shown in Figure 1, with the  $D_{\infty}$  values scaled to be the known molar extinction coefficients. The actual degree of photolysis by a single laser pulse was about 50%, that is, the observed  $D_{\infty}$ 's were about half of those calculated for complete reaction.

Next,  $\log(V_{\infty}/V_{in})$  gave  $D_{in} - D_{\infty}$ , the difference in optical densities of unreacted transient and final product, so that  $D_{in}$  values could be calculated. This intermediate will be identified as a pentacarbonyl and almost certainly was fully converted to final product in view of the great excess of 4-acetylpyridine over the small amount of competitor CO produced in the photolysis. On this basis,  $D_{in}/D_{\infty}$  is also the ratio of the respective extinction coefficients, and it was thus possible to obtain *absolute* molar extinction coefficient values for the transient. The plot of these is included in Figure 1. The value of  $\epsilon_{max}$  is  $7.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 425 nm, and the position of the maximum is within the range of wavelengths reported for tungsten pentacarbonyl species generated in low-temperature matrices [ $SF_6$  (461 nm), Ar (437 nm), Xe (417 nm), and  $CH_4$  (413 nm)]<sup>9</sup> as well as in the pulsed-radiolysis study in cyclohexane (415 nm).<sup>17</sup> The same transient absorption spectrum as reported here is found on pulse photolysis of  $W(CO)_5L$  complexes in methylcyclohexane, with L = 4-cyanopyridine, 4-acetylpyridine, and 4-benzoylpyridine.<sup>21</sup>

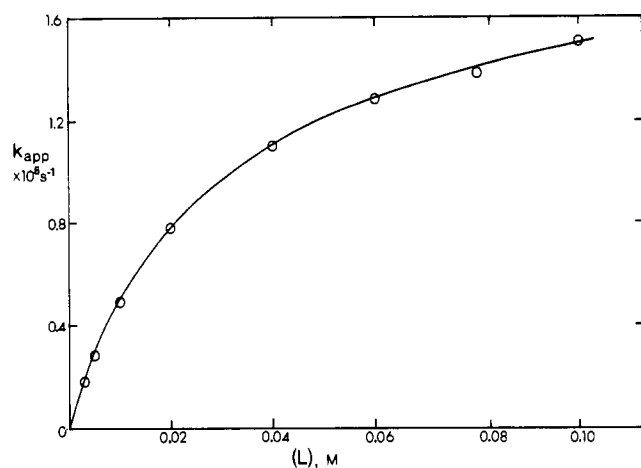
The growth  $D_{in}$  to  $D_{\infty}$  was exponential, that is,  $\ln(D_t - D_{\infty})$  varied linearly with time over the full run of the oscilloscope traces. Data were usually taken at 480 nm, but it was checked that the  $k_{app}$  values obtained from the slope of such plots did not vary with monitoring wavelength over the range 400–500 nm. These  $k_{app}$  values were linear in 4-acetylpyridine concentration (L) at low concentrations but showed saturation at higher ones, as illustrated in Figure 2.

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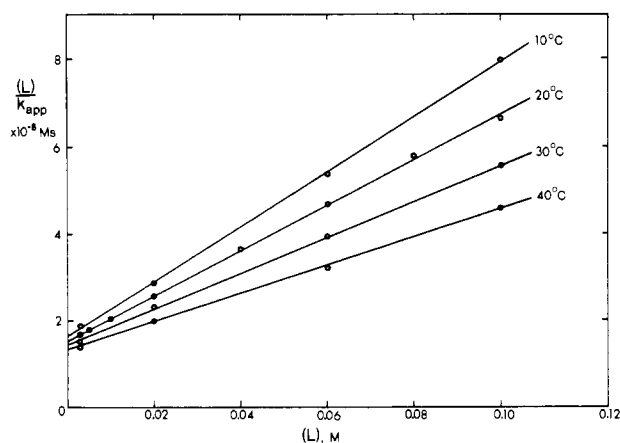
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(21) Unpublished work in this laboratory, following the emission studies previously reported.<sup>22</sup> The primary photochemical step for  $W(CO)_5L$  complexes at this irradiation wavelength is considered to be loss of  $L^{1-4,23-25}$  so that a pentacarbonyl transient is indeed expected.



**Figure 2.** Dependence of the observed first-order rate constant,  $k_{app}$  in  $s^{-1}$ , for decay of the intermediate species on concentration of 4-acetylpyridine in a  $5 \times 10^{-4}$  M  $W(CO)_6$ -methylcyclohexane solution.

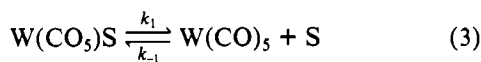
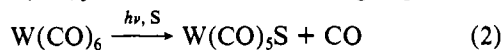


**Figure 3.** Least-squares lines of  $[L]/k_{app}$  vs.  $[L]$  at 10, 20, 30, and 40 °C.  $[L]$  is the concentration of 4-acetylpyridine, in a  $5 \times 10^{-4}$  M  $W(CO)_6$ -methylcyclohexane solution, and  $k_{app}$  is the observed rate constant in  $s^{-1}$ , for decay of the intermediate species.

Photoexcited emission from  $W(CO)_6$  may have been marginally present, but, if so, it followed the laser pulse. In contrast, then, to the above  $W(CO)_5L$  complexes,<sup>22</sup> emitting species, if present, were less than 5 ns in lifetime (for these experiments, the laser pulse was gated down to 5-ns half-time).

### Discussion

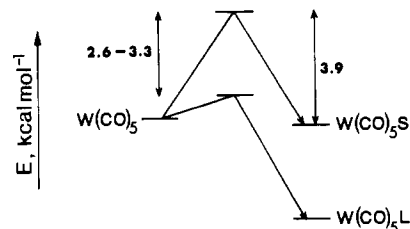
The simplest explanation of our kinetic results appears to be the following. We take the observable product, our transient, to be  $W(CO)_5S$ , and write the following sequence:



Steady-state analysis gives

$$d[W(CO)_5S]/dt = k_{app}[W(CO)_5S] \quad (5)$$

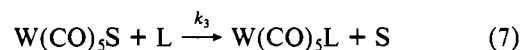
$$k_{app} = \frac{k_2 K_1 [L]}{1 + k_2 [L]/k'_{-1}} \quad k'_{-1} = k_{-1}(S), K_1 = k_1/k_{-1} \quad (6)$$



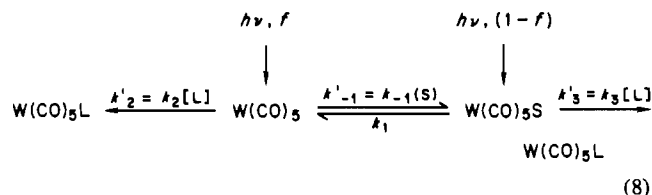
**Figure 4.** Energy diagram for  $W(CO)_5L$ ,  $W(CO)_5S$ , and  $W(CO)_5$ .

According to eq 6, a plot of  $[L]/k_{app}$  vs.  $[L]$  should be linear with intercept  $k'_{-1}/k_1 k_2$  and slope  $1/k_1$ . This behavior was indeed followed, as shown in Figure 3, for several temperatures.

Before proceeding further, alternative mechanisms should be considered. First, direct bimolecular reaction between  $L$  and  $W(CO)_5S$  (eq 7) can be ruled out;  $k_{app} = k_3$  does not



saturate in this mechanism. Another possibility is that  $W(CO)_5$  is the initial transient species, with ensuing reaction either with  $L$  or reversibly with  $S$ . The complete kinetic picture becomes that of eq 8. In this general case,  $D_{in}$  might cor-



respond to fraction  $f$  of  $W(CO)_5$  and  $1-f$  of  $W(CO)_5S$ . The solution of this set of coupled reactions is known (see ref 26 and 27), and it was possible to search for a set of rate constant and  $f$  values that would fit our observations. The general solution contains two exponentials,  $e^{-\lambda_1 t}$  and  $e^{-\lambda_2 t}$ , where  $\lambda_{1,2}$  are solutions to a quadratic equation in the rate constants; the rate law is thus biphasic in the appearance of  $W(CO)_5L$ . One constraint is that the relative rate constant values be such that  $\lambda_1 > \lambda_2$  so that we could observe single exponential behavior in our time regime. Another is that the resulting  $k_{app}$  show saturation with increasing  $[L]$ . Briefly, no suitable regime of rate constants would be found to satisfy both constraints except for the limiting case of  $f = 0$  and  $k_3 = 0$ , corresponding to eq 2-4, and then only if  $k'_{-1} > k_1$ .

We can therefore return to the proposed mechanism. It indeed seems physically reasonable that  $W(CO)_5S$  be the intermediate, that is, our transient species. The various matrix-isolation experiments show the absorption spectrum to be medium dependent, so solvent is in some manner implicated. Equation 6 now gives meaning to the slopes and intercepts of Figure 3. At 20 °C we find  $k_1 = 1.9 \times 10^6 s^{-1}$  and  $k_2/k'_{-1} = 34 M^{-1}$ . On correcting for solvent concentration, the preference ratio  $k_2/k_{-1}$  becomes about 270, a number corresponding to an activation energy difference between reactions 3 and 4 of 3.3 kcal mol<sup>-1</sup>.

The temperature-dependence data of Figure 3 yield good Arrhenius plots from which we find  $E_1^* = 3.9$  kcal mol<sup>-1</sup> (hence  $\Delta S_1^{\ddagger} = -16.5$  cal K<sup>-1</sup> mol<sup>-1</sup>) and  $E_{-1}^* - E_2^* = 2.6$  kcal mol<sup>-1</sup>, the subscripts denoting the corresponding rate constants; the least-squares uncertainty in the above values is about 1 kcal mol<sup>-1</sup>. The relevant energy diagram is shown in Figure 4, where the range 2.6-3.3 kcal mol<sup>-1</sup> for  $E_{-1}^* - E_2^*$

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includes the estimate from the value of the scavenging ratio. An average of 3.0 kcal mol<sup>-1</sup> would lie within both experimental error limits. We now, of course, have a kinetic estimate of the W-S bond energy as  $\leq 3.9$  kcal mol<sup>-1</sup>.

We turn finally to the detailed nature of the primary photostep (2). This could consist of reaction 1 followed by rapid solvent coordination, but, if so, the M(CO)<sub>5</sub> species of reaction 1 cannot be the same as that of reaction 3, in view of the analysis around eq 8. A defensible possibility is that the former species is C<sub>4v</sub> while the latter one is D<sub>3h</sub>. Alternatively and perhaps indistinguishably, reaction 1 could be concerted. Yet another possibility, suggested by ligand field analysis of the d<sup>6</sup> case by Vanquickenborne and Ceulemans<sup>28</sup> (see also ref 29), is that the immediate product of reaction 1 is an excited-state

C<sub>4v</sub> species, which relaxes to ground-state C<sub>4v</sub> and coordinates solvent. Our intermediate of reaction 3 would again be the D<sub>3h</sub> species. The lifetime of an excited-state C<sub>4v</sub> complex must be short, however, since we see no indication of its presence either in emission or in transient absorption. It seems more reasonable to expect the relatively long-lived intermediate to be D<sub>3h</sub> rather than C<sub>4v</sub> though one could interchange the C<sub>4v</sub> and D<sub>3h</sub> designations in the above discussion (see ref 30 and 31).

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**Registry No.** W(CO)<sub>6</sub>, 14040-11-0; 4-acetylpyridine, 1122-54-9; methylcyclohexane, 108-87-2.

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## Energy Transfer between Uranyl(VI) and Europium(III) in Aqueous Perchlorate Solution

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Fluorescence measurements on aqueous solutions containing uranyl(VI) and europium(III) perchlorates have shown that energy transfer from uranyl to europium is pH dependent. The uranyl species involved is not the UO<sub>2</sub><sup>2+</sup> ion itself but one or more of the hydrolytic species. Emission spectra of the europium ion in the presence of uranyl indicate the formation of a complex between the lanthanide ion and the hydrolyzed uranyl species. The relative intensities of the europium emission lines, the energy-transfer efficiency, and the dependence of energy transfer on concentrations are all consistent with a mechanism which involves this complex.

### Introduction

Fluorescence spectra and lifetime measurements are finding increasing use in probing the environment of lanthanide ions.<sup>1-3</sup> The variation in the relative intensities of the various emission lines and the fluorescence lifetimes of europium(III) in aqueous solution have provided information on the interaction between Eu<sup>3+</sup> and ClO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>.<sup>2</sup> An earlier fluorescence study in this laboratory<sup>4</sup> demonstrated that energy transfer between *o*-benzoyl benzoate and Eu<sup>3+</sup> in ethanol/water solution involved the formation of a complex. Relative intensities of europium(III) emission lines and equilibrium constant determinations provided evidence for inner-sphere interaction. These results suggested that energy transfer from other potential donors to Eu(III) in solution may take place by a similar mechanism. The work reported in this paper involves energy transfer between the positively charged species uranyl(VI) and Eu(III).

The U(IV)-Eu(III) system has been studied previously in a variety of media.<sup>5,6</sup> There are, however, several factors which complicate the interpretation of the results. The anions present in solution, nitrate, formate, and acetate, form complexes with both Eu(III) and uranyl.<sup>7-9</sup> Also, the lack of

information on the pH of the solutions leaves in doubt the nature of the uranyl species present. It was generally assumed that the UO<sub>2</sub><sup>2+</sup> ion was the absorbing and donor species, yet in aqueous solution this ion exists in appreciable concentration only under relatively acidic conditions. At higher pH's dimeric and polymeric hydrolysis species are the dominant forms.<sup>10,11</sup> The work described in this paper was carried out in perchlorate solution to reduce complex formation, and the pH of the solutions was carefully measured. So that the fluorescence intensities could be enhanced, D<sub>2</sub>O was used as solvent.<sup>12</sup>

### Experimental Section

**Preparation of Solutions.** Europium perchlorate solutions were prepared by dissolving 99.99% Eu<sub>2</sub>O<sub>3</sub> (Michigan Chemical Co.) in excess perchloric acid. Excess acid was removed by evaporating almost to dryness and then redissolving in distilled H<sub>2</sub>O. The process was repeated several times until the acid concentration was reduced. Finally, Eu(ClO<sub>4</sub>)<sub>3</sub> was dissolved in D<sub>2</sub>O and evaporated almost to dryness before being dissolved in D<sub>2</sub>O and brought up to a known volume. The concentration was checked by passing samples through a cation-exchange column and titrating the liberated acid.

Uranyl perchlorate solutions were prepared by ion exchange of uranyl acetate solutions. An exchange column of Dowex 1 × 10 anion-exchange resin was converted to the perchlorate form by passing

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