

Table I. Magnetic Susceptibilities^{a,b}

Compound	Color	10 ⁶ χ _m , cgs	μ _{eff} (obsd)	Theor ¹³
Yb	Orange	7,800	4.31	4.5
Er	Pink	39,000	9.64	9.6
Gd	Yellow	26,880	7.98	7.94

^a Measured by the Faraday method at 300°K. ^b Estimated error is ±3%; values are corrected for diamagnetism.

dienyl⁵ and cyclooctatetraenyl⁶ ligands. The only well-characterized σ-bonded derivatives presently known are the Yb and Lu tetrakis(2,6-dimethylphenyl) derivatives, isolated as lithium salts.⁷ We wish to report the preparation of a new class of organolanthanide compounds, (η⁵-C₅H₅)₂LnC≡CPh (Ph = phenyl; Ln = Gd, Er, and Yb). The Gd and Er derivatives represent the first examples of compounds containing a σ-bonded organic moiety bound to the respective metals.

These complexes are formed in good yields by the reaction of the particular (η⁵-C₅H₅)₂LnCl⁸ and lithium phenylacetylide⁹ in THF at -20°. The compounds are purified by continuous extraction into benzene.¹⁰ The compounds are destroyed by oxygen (though the Gd compound is stable in air for a few minutes) and both the phenylacetylide and cyclopentadienyl ligands are hydrolyzed by H₂O.

In the infrared spectra, all three compounds exhibit strong sharp C≡C stretches at ~2050 cm⁻¹.¹¹ In addition, strong bands at 692 and 760 cm⁻¹ are characteristic of a monosubstituted phenyl group. The bands at 3100, 1450, 1010, and 775 cm⁻¹ are indicative of a η⁵-bonded cyclopentadienyl moiety.¹²

The magnetic susceptibilities of the compounds are reported in Table I, and are indicative of the metal in the tripositive state.¹³ One would not expect to see much deviation from these values as the 4f orbitals seem to be quite well shielded and should be perturbed only slightly by ligand fields.¹⁴

Visible spectra were taken for all of the complexes. The spectra of the erbium compound is interesting as it differs somewhat from the "free" Er³⁺ ion. The bands are broadened slightly and the values for ε are larger by over a factor of ten.^{15,16} Bukietynska and Choppin¹⁸

(5) For a review, see (a) H. Gysling and M. Tsutsui, *Advan. Organometal. Chem.*, **9**, 361 (1970); (b) R. G. Hayes and J. L. Thomas, *Organometal. Chem. Rev.*, *Sect. A*, **7**, 1 (1971).

(6) K. O. Hodgson, F. Mares, D. F. Starks, and A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **95**, 8650 (1973).

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(8) R. E. Maginn, S. Manastyrskij, and M. Dubeck, *J. Amer. Chem. Soc.*, **85**, 672 (1963).

(9) Prepared from the reaction of *n*-butyllithium and ethynylbenzene in THF.

(10) All compounds gave satisfactory elemental analyses as performed by Schwarzkopf Microanalytical Laboratories. *Anal.* Calcd for C₁₅H₁₅Yb: C, 53.44; H, 3.73. Found: C, 53.10; H, 4.04. Calcd for C₁₅H₁₅Er: C, 54.24; H, 3.79; Er, 41.97. Found: C, 53.97; H, 3.82; Er, 41.60. Calcd for C₁₅H₁₅Gd: Gd, 40.47. Found: Gd, 40.56.

(11) In contrast, the C≡C stretch for ethynylbenzene comes at ~2085 cm⁻¹.

(12) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 7281 (1969).

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(14) H. G. Friedman, Jr., G. P. Choppin, and D. G. Feuerbacher, *J. Chem. Educ.*, **41**, 355 (1964).

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(16) Values are also high compared with conventional coordination compounds; cf. ref 17.

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(18) K. Bukietynska and G. R. Choppin, *J. Chem. Phys.*, **52**, 2875 (1970).

suggested that changes of the intensity and shape of the hypersensitive¹⁹ absorption band are due to the formation of inner-sphere complexes to a limited extent. High values can be related to the predominant existence of species in solution with low symmetries²⁰ and/or some degree of covalency. Since the symmetries in the starting material and products should be essentially identical, the observed enhancement lends support to these complexes being more covalent in nature. Also, a large charge transfer band is present which originates in the uv and extends into the visible region. This indicates that there is at least some interaction, other than strictly ionic, between the ligand and the metal. The origin of the charge transfer is probably ligand to metal.^{6,21} However, this interaction need not be a large one to be observed. Also, it is not clear whether the electron is transferred into a 4f or 5d orbital.

The visible spectra of the Yb complex is uninformative as it is dominated by a large charge transfer band which is present in the (η⁵-C₅H₅)₂YbCl compound.²² The Gd complex (an f⁷ compound) is devoid of all transitions except for the charge transfer band as seen in the Er complex.

Though heretofore unknown for most lanthanides, the formation of metal-carbon σ bonds by our reaction scheme appears to be a general one and should work for other ligands and metals as well.^{23,24} Further studies are in progress to elucidate the nature of the lanthanide-carbon σ bond.

Acknowledgment. We wish to thank the United States Air Force Office of Scientific Research, AFOSR 71-2017, for financial support and Dr. Allen Gebala for helpful discussions.

(19) Hypersensitive transitions are spectral bands which exhibit substantial changes in intensity without a significant wavelength shift for very similar chemical environments.

(20) B. R. Judd, *J. Chem. Phys.*, **44**, 839 (1966).

(21) J. C. Barnes, *J. Chem. Soc.*, 3880 (1964).

(22) This is the only lanthanide whose cyclopentadienide complexes do not correspond closely to the free ion.

(23) Preliminary results in our laboratories indicates this to be so.

(24) F. A. Hart, *et al.*, postulate⁷ that lanthanide-carbon σ bonds are most favored for the heavier elements of this series. Maginn, *et al.*, also note⁸ that they were only able to prepare (η⁵-C₅H₅)₂LnCl for the heavier lanthanides and that this was due to some subtle effect of the lanthanide contraction.

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Transverse Relaxation in Homonuclear Coupled Spin Systems

Sir:

It is often stated that for nonviscous liquids, nuclear spin-spin relaxation times (T_2) are equal to spin-lattice relaxation times (T_1) unless "slow" processes occur. This notion, which is based on an unwarranted extension of the Bloch equations, is incorrect for the general case of molecules with scalar coupling. Data presented here, together with a complete density matrix analysis,¹ show that the presence of homonuclear scalar coupling gives rise to T_2 values which are consid-

(1) R. L. Vold and R. R. Vold, to be submitted for publication.

erably shorter than corresponding T_1 's, even in the absence of slow processes such as chemical exchange and relaxation by scalar coupling to rapidly relaxing quadrupolar nuclei. Similar effects of heteronuclear coupling to other spin $1/2$ nuclei have been described previously.²⁻⁴

Table I shows relaxation times measured for selected

Table I. Proton Relaxation Times and (Rates)^a

	T_1 (R_1)	T_2 (R_2)	\bar{T}_2 (\bar{R}_2) ^b
Isopropyl Iodide			
(CH ₃) ₂ ^c	7.3 (0.137)	7.0 (0.143)	7.8 (0.128)
CH ^d	13.7 (0.073) ^e	7.9 (0.126)	
Isopropyl Acetate			
(CH ₃) ₂ ^c	6.2 (0.161)	6.2 (0.161)	6.7 (0.149)
CH ^d	13.2 (0.076) ^e	7.1 (0.141)	
CH ₃ CO	8.5 (0.118)	7.8 (0.128) ^f	

^a $R_1 = 1/T_1$ and $R_2 = 1/T_2$ sec⁻¹. ^b Weighted average relaxation times calculated from eq 1. ^c Equal values were obtained for both lines of the doublet within experimental error. ^d All components of the septet relaxed at the same rate. Listed values were obtained from the center line. Limited resolution (nonspinning sample, $\Delta\nu_{1/2} \sim 2$ Hz) prevented detection of small differences. ^e A small deviation from single exponential behavior was observed; the reported T_1 was obtained from the initial slope. For a justification of this procedure, see ref 16. ^f At $2\tau = 1.2$ msec, T_2 increased to 8.4 sec. Spin echo spectra (R. L. Vold and R. R. Vold, *J. Magn. Resonance*, **13**, 38 (1974)) show that long range coupling to the acetyl protons is less than 0.05 Hz. The short value of T_2 at $2\tau = 200$ μ sec may be due to a nonzero value for this coupling.

proton lines of neat isopropyl iodide and isopropyl acetate. All measurements were performed at 26° on a 55-MHz spectrometer described elsewhere.^{5,6} The samples were degassed by distillation at $\sim 10^{-5}$ Torr followed by several freeze-pump-thaw cycles. T_1 values were obtained by the usual 180°- τ -90°-FT sequence and T_2 values by a similar Fourier transform version⁷ of the Carr-Purcell-Meiboom-Gill (CPMG) spin echo sequence with a spacing $2\tau = 200$ μ sec between refocusing pulses. Semilogarithmic plots spanning ~ 1.5 decades were linear except where noted, and the values of T_1 and T_2 are considered accurate⁸ within $\sim 3\%$.

At first glance the short T_2 observed for the methine proton in isopropyl iodide might be ascribed to scalar relaxation by coupling to the rapidly relaxing iodine. However, the difference, $1/T_2 - 1/T_1 = 0.053$ sec⁻¹ for this proton is *ca.* eight times larger than that found for methyl iodide,⁴ and a similar large difference, 0.075 sec⁻¹, is observed for the methine proton in isopropyl acetate. Relaxation in isopropyl acetate is certainly dominated by dipole-dipole interactions, and infrared,

microwave, and ultrasonic measurements on esters⁹ have demonstrated that internal rotation rates are much too high to affect T_2 's by chemical exchange.

The differences between T_1 and T_2 values are due to the combined effects of scalar coupling and the rf pulses on the motion of the transverse magnetization vectors during the spin echo decay. Very small pulse intervals were used to avoid modulation of the spin echo decay with consequent phase and amplitude distortion of the spectra,^{10,11} as well as other errors due to field instability and inhomogeneity.^{5,12} In this "spin lock" limit, the magnetizations are refocused before any appreciable differential precession occurs, and the observed transverse decay times may also be designated T_{1p} .^{13,14} In a CPMG spin echo experiment spin locking occurs if the pulse rate $1/2\tau$ is much larger than the frequency spread of the spectrum.

The following heuristic argument explains the short T_2 values observed under spin lock conditions. Chemical shifts are all effectively zero for the duration of the CPMG pulse train, while the scalar coupling is unaltered.¹⁵ Therefore the effective coupling strength is extremely large, and transverse relaxation of any line should be indistinguishable from that of any other line. Thus, if a set of spins, $A_n X_m$ with $J_{AX} = 0$, has transverse relaxation times $T_{2A}^0 = T_{1A}$ and $T_{2X}^0 = T_{1X}$ in the spin lock limit, then all lines in the scalar coupled system ($J_{AX} \neq 0$) will relax with the same transverse relaxation time \bar{T}_2 where

$$1/\bar{T}_2 = (n/T_{2A}^0 + m/T_{2X}^0)/(n + m) \quad (1)$$

If we apply eq 1 to the T_1 values listed in Table I, we obtain calculated values of \bar{T}_2 listed in the third column. Agreement with observed T_2 values is satisfactory considering the simplicity of the argument and demonstrates that scalar relaxation by coupling to iodine is unimportant for isopropyl iodide.

Complete density matrix calculations on AX and AX₂ spin systems¹ confirm the essential features of the argument leading to eq 1. Equation 1 neglects the fact that scalar coupling does not mix states of different symmetry and that different relaxation mechanisms have different symmetry properties. Differences between observed and calculated T_2 's are due to effects of this nature. For sufficiently simple spin systems it is possible to experimentally distinguish contributions of different relaxation mechanisms on this basis.

It is important to note that complexities inherent in the density matrix analysis cannot be avoided by using long pulse intervals, thereby allowing free precession to develop. Under ideal conditions T_2 's observed as $2\tau \rightarrow \infty$ will equal those obtained from line widths in a perfectly homogeneous field. They will normally be less than T_1 due to irreversible dephasing from spin-lattice relaxation combined with scalar coupling.^{6,16}

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(8) Measurements on a test sample of degassed benzene under the same instrumental conditions except for necessary minor adjustments of pulse widths yielded $T_1 = T_2 = 20.9 \pm 0.3$ sec.

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Efficiency of Excited State Carbonyl Production from the Thermolysis of 3,3-Diphenyl-1,2-dioxetane

Sir:

The unique ability of 1,2-dioxetanes to generate electronically excited carbonyl molecules during thermal decomposition has attracted considerable interest recently in these peroxides.¹ Thermochemical calculations suggest that sufficient energy is available from the thermal decomposition of 1,2-dioxetanes to obtain one of the carbonyl products in an excited state^{1a} (efficiency = $\alpha = 1.0$). However, experimental α values range from 0.005 to about 1.0.^{11,i,n,o,s,z,aa,bb} It is of considerable interest to determine what factors are responsible for the efficient conversion of the available thermal energy into electronic energy.

With this longer range goal as our objective, we now report the efficiency of excited state carbonyl production from the thermolysis of 3,3-diphenyl-1,2-dioxetane (DPD). Isomerization of *trans*-stilbene was used to determine the total efficiency of excited state carbonyl formation¹² from DPD, while excited state benzophenone molecules were specifically monitored by cycloaddition with 2-methyl-2-butene.

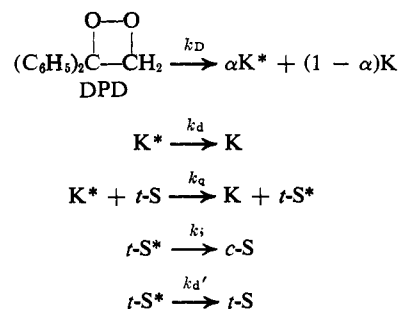
In Scheme I, the pertinent processes are shown for the decomposition of DPD in the presence of *trans*-stilbene (*t*-S) where *cis*-stilbene (*c*-S) is produced. The total excited state carbonyl molecules (benzophenone and formaldehyde) are represented by K^* and the ground state species by K . The apparent quantum yield (Φ_{App}) for isomerization of *t*-S is given by eq 1, where

$$\Phi_{App} = \alpha \Phi_{ET} \Phi_{t \rightarrow c} \quad (1)$$

$\Phi_{t \rightarrow c}$ is the quantum yield for isomerization of *t*-S and

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Scheme I



Φ_{ET} is the quantum yield for energy transfer between K^* and *t*-S (eq 2).

$$\Phi_{ET} = \frac{k_q[t\text{-S}]}{k_q[t\text{-S}] + k_a} \quad (2)$$

DPD was allowed to decompose in degassed benzene solution with *t*-S at 45° through approximately ten half-lives.² The amount of *c*-S was determined by glc (3% SE-30 on Varaport-30, 5 ft \times 1/8 in., 115°, flow 24 ml of N₂/min, FID; *t_r*(min), *c*-S (9.8), *t*-S (19)) and Φ_{App} was calculated as the ratio of millimoles of *c*-S produced/millimoles of DPD decomposed. With $\Phi_{t \rightarrow c} = 0.55^3$ and assuming Φ_{ET} is unity, α is calculated from eq 1. These data are given in Table I, where the con-

Table I. Isomerization of *trans*-Stilbene (*t*-S) from the Thermolysis of 3,3-Diphenyl-1,2-dioxetane (DPD) in Degassed Benzene at 45°

$10^3[\text{DPD}]_0,$ <i>M</i>	$10^2[t\text{-S}],$ <i>M</i>	$10^2\Phi_{App}^a$	$10^2\alpha^b$
1.98	2.00	1.77	3.22
19.8	2.50	1.85	3.36
5.10	2.50	1.72	3.13
5.10	5.00	2.16	3.93
1.98	10.0	1.89	3.44
19.8	20.0	2.01	3.65
		Av 1.90 \pm 0.12	Av 3.46 \pm 0.23

^a Φ_{App} = millimoles of *c*-S produced/millimoles of DPD decomposed. ^b α = total efficiency of excited state carbonyl production from DPD, where $\alpha = \Phi_{App}/0.55$ and $\Phi_{t \rightarrow c} = 0.55$, $\Phi_{ET} = 1.00$.

centrations of both *t*-S and DPD are varied. The calculation of α from eq 1, with the approximation that Φ_{ET} is unity, requires that $k_q[t\text{-S}] \gg k_a$ in eq 2. This approximation appears reasonable for the data in Table I, where k_q is estimated to be $6.9 \times 10^9 M^{-1} \text{sec}^{-1}$ at 45°⁴ and at the lowest *t*-S concentration ($2.00 \times 10^{-2} M$), $k_q[t\text{-S}] = 1.4 \times 10^8 \text{sec}^{-1}$. This value is then sufficiently large, compared to $k_a \cong 10^5 \text{sec}^{-1}$ at 23°⁵ for benzophenone in benzene, to satisfy the approximation. As

(2) The preparation, characterization, products, and kinetics of DPD will be reported elsewhere.

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(4) This is obtained by correcting the reported value of $k_q = 5.0 \times 10^9 M^{-1} \text{sec}^{-1}$ at 25.5°⁶ to 45° with the Debye equation⁶ and with reported viscosities of benzene.⁷

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