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Nitrogen-14 Nuclear Magnetic Resonance Studies of Acetonitrile Exchange from the First Coordination Sphere of Manganese(II)

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The ^{14}N nuclear relaxation times of acetonitrile (CH_3CN) solutions of manganese(II) perchlorate have been studied as a function of temperature. Saturation studies have shown that a scalar coupling mechanism controls the relaxation of the ^{14}N nucleus in the coordination sphere of the Mn(II) ion. A determination of the kinetic parameters for the exchange of CH_3CN from the first coördination sphere of Mn(II) yielded a first-order rate constant, k_1, at 25° of $(1.2 \pm 0.3) \times 10^7$ sec^{-1}, a $\Delta H^{\ddagger}$ for exchange of 7.25 ± 0.25 kcal/mol, and a $\Delta S^{\ddagger}$ for exchange of -1.8 ± 0.8 eu. The value determined for the scalar coupling constant, A/h, was 3.2×10^6 Hz.

Introduction

Since the derivations by Swift and Connick[2] of the equations describing the broadening of the nmr lines of nuclei in dilute solutions of paramagnetic ions where chemical exchange is a factor, many studies on solvent-exchange reactions in nonaqueous solvents have appeared in the literature. However, very few solvent-exchange studies in nonaqueous solvents have appeared with divalent transition metal cations other than Ni(II) and Co(II). This paper presents a study of the ^{14}N relaxation of the Mn(II)–CH_3CN system and a determination of the exchange parameters for the complex.

Theory

In a solution containing paramagnetic metal cations, solvent molecules coordinated to the metal experience a strong fluctuating local magnetic field due to the unpaired electrons on the metal, and, hence, the nuclear spins on the solvent molecules are relaxed faster; *i.e.*, the transverse relaxation time, T_2, becomes shorter. Uncoordinated (bulk) solvent molecules are not so greatly affected. If exchange takes place between the bulk environment and the coordination sphere, the macroscopic effect on the bulk solvent nmr signal is an average T_2 which is shorter than that of the pure solvent (when no paramagnetic ions are present). Hence, the line width, $\Delta\nu$, related to T_2 by eq 1, is increased.

$$\Delta\nu = 1/\pi T_2 \tag{1}$$

The line width as expressed in eq 1 is a measure of the full width of the nmr line at half-height and is expressed in units of hertz. The temperature dependence of the paramagnetic contribution to the line width can be analyzed by the equation of Swift and Connick[2] (eq 2),

$$1/T_{2p} = (P_m/\tau_m)\{1/T_{2m}^2 + 1/T_{2m}\tau_m + \Delta\omega_m^2/(1/T_{2m} + 1/\tau_m)^2 + \Delta\omega_m^2\} \tag{2}$$

where the symbols have their usual meaning. The first-order rate constant for solvent exchange, k_1, is given by

$$k_1 = 1/\tau_m \tag{3}$$

The relaxation caused by the paramagnetic cation may be controlled by one of two mechanisms. Swift and Connick[2] referred to them as the "$\Delta\omega_m$ mechanism" and the "T_{2m} mechanism." As was the case with the Mn(II)–water system,[2] a T_{2m} mechanism governs the Mn(II)–acetonitrile system. When the T_{2m} mechanism is controlling, the relaxation is governed by the rate of relaxation of the nucleus when it is in the coordination sphere of the cation. For this case $(1/T_{2m})^2 >> \Delta\omega_m^2$. Hence, eq 2 reduces to the relatively simple expression

$$P_m T_{2p} = T_{2m} + \tau_m \tag{4}$$

Equation 4 shows that if a sufficiently wide temperature range is studied, two limiting regions in a log $(1/T_{2p})$ *vs.* $1/T$ plot should be observed; one, a τ_m(exchange)-controlled region and the other a T_{2m}(relaxation)-controlled region. If τ_m were controlling, the temperature dependence would be related to the rate constant for chemical exchange, while if T_{2m} were controlling, the interactions between the coordinated nuclei and the paramagnetic cation would govern the relaxation. Two interactions must be considered in the influence of T_{2m}, a scalar coupling interaction[3] and a dipole–dipole interaction.[4] The relative importance of these two interactions can be determined by comparing the values of $1/T_2$ to $1/T_1$ for the same solution. For the frequencies employed in this study, the relatively complex expressions for $1/T_{1m}$ and $1/T_{2m}$ given in ref 3 and 4 may be considerably simplified.[5] Using the simplified equation of Bernheim, *et al.*, for the dipolar interaction, we estimate that the dipolar contribution to the line width of a 3.4×10^{-4} M Mn(II) solution would be 0.25 Hz when the Mn–N distance was assumed to be 2 Å (this distance is no doubt larger) and the correlation time for tumbling was assumed to be 10^{-11} sec. Data will be presented later which verify that the scalar coupling mechanism is important while the dipole–dipole interaction is negligible. If the dipole–dipole

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(1) To whom all correspondence should be addressed.

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term is neglected, the proper expression for $1/T_{2m}$ becomes[2]

$$1/T_{2m} = \{S(S + 1)/3\}(A/\hbar)^2\{1/T_{1e} + 1/\tau_m\}^{-1} \quad (5)$$

where S is the total electron spin, which is equal to $^5/_2$ for Mn(II), A is the scalar coupling constant, $\hbar$ is Planck's constant divided by 2π, and T_{1e} is the longitudinal electron spin relaxation time. Substituting the correct form for T_{2m} now into eq 4 gives[2]

$$P_mT_{2p} = \tau_m + c(1/T_{1e} + 1/\tau_m) \quad (6)$$

where c is a constant defined by

$$c = \{3/S(S + 1)\}(A/\hbar)^{-2} \quad (7)$$

Experimental Section

Reagent grade acetonitrile from Fisher Scientific Co. was distilled before use from P_4O_{10} and a 60–70% cut was taken.

Manganese was purchased in the form of metal chips from Alfa Inorganics, Inc., with a total purity of 99.8% and a purity from other metals of 99.97%. Manganese(II) perchlorate was prepared by adding dropwise diluted Merck reagent grade $HClO_4$ (70%) to the chips until all the metal had reacted. The $Mn(ClO_4)_2 \cdot 6H_2O$ was then recrystallized from water several times until all traces of excess acid were removed.

Solutions for the nmr and esr studies were prepared and sealed in tubes on a vacuum line. The solutions were dried using a modified Soxhlet extractor modeled after that of Arthur, Haynes, and Varga[6] and employing Linde 3A Molecular Sieves as the drying agent. After completion of the studies, the tubes were broken *in vacuo* and analyzed for water on a Varian Associates Model ICR-9 ion cyclotron resonance spectrometer. The solution in the tube was vaporized and a sample of the vapors collected in a bulb. Contents of the bulb were analyzed for water on the ICR-9 by comparing the intensity of the *m/e* 18 (H_2O) peak to the total intensity of the acetonitrile peaks from *m/e* 12 to 42 inclusive. Calibration samples were also prepared *in vacuo* using a double-bulb apparatus for water and acetonitrile vapors and a correction factor was determined. An upper limit to the water concentration of 2×10^{-4} M was found in the solution used for the line-broadening studies.

Concentrations of the Mn(II) in the various solutions were determined by titration with a standard EDTA solution using Calmagite Indicator purchased from Mallinckrodt Chemical Works. The EDTA was standardized with the same indicator against both $CaCO_3$ and Mn chips dissolved in HCl. The two primary standards gave identical results within the error limits of the titrations.

The nmr spectra were obtained on a modified Varian Associates Model V-4200 wide-line spectrometer operated at a fixed radiofrequency of 4.3348 MHz. Spectra were obtained under conditions of slow passage and negligible saturation from samples sealed in 9-mm Pyrex tubes using the side-band technique.[7] All the line widths reported in this paper are averages of at least four separate spectra. The esr experiments were performed on a Japan Electron Optics Laboratory Co. Ltd. Model JES-3BS-X X-band (9.5 GHz) spectrometer operating at 100-kHz field modulation using a 2-mm Pyrex sample tube.

Temperature control was achieved with a Varian Associates Model V-4540 variable-temperature controller. A copper *vs.* constantan thermocouple inserted in a thermocouple well on the nmr tube was used to monitor the temperatures which are thought to be accurate to ±0.5°.

Results and Discussion

The results of the pure acetonitrile studies are presented in Table I. A least-squares treatment of the log $(1/T_2)$ *vs.* $1/T$ data points yielded an activation energy of 1.83 ± 0.07 kcal/mol (all error limits reported herein are 95% confidence limits). The line widths and their temperature dependence are consistent with a quadrupole relaxation mechanism ($I = 1$ for ^{14}N) where the correlation time is that for rotational tumbling, τ_r, of the acetonitrile molecules. This model has been applied by Moniz and Gutowsky[8] and by Bopp[9] to the longitudinal relaxation rates, $1/T_1$'s, of the ^{14}N resonance of acetonitrile. They reported activation energies of 1.9 and 1.7 ± 0.1 kcal/mol, respectively. Bopp also reported an ambient temperature value for $1/T_1$ of 260 ± 30 sec^{-1}. Our least-

TABLE I

EXPERIMENTAL RELAXATION TIMES

$10^3/T$, °K^{-1}	10^3T_1,[a] sec	10^3T_2,[a] sec	10^3T_1,[b] sec	10^3T_2,[c] sec
4.355				1.177
4.281				1.230
4.278		1.451		
4.246		1.708		1.282
4.131		1.708		
4.100				1.413
4.039				1.444
4.038		1.970		
3.897				1.450
3.836		2.351		
3.778				1.492
3.728		2.695		
3.685				1.399
3.631	2.915	3.003		
3.618		2.961		
3.575				1.400
3.512		3.377		
3.501		3.305		
3.479				1.302
3.435	3.140	3.537		
3.420				1.242
3.385		3.697		
3.342	3.611	3.851		
3.331				1.140
3.316			4.169	
3.304		4.097		
3.273				1.088
3.251	4.297	4.307		
3.231			5.163	
3.213				1.052
3.179		4.421		
3.133			4.386	
3.111				1.030
3.072		4.787		
3.058	5.220	5.085		
3.047			5.373	
3.026				1.047
3.011		5.005		
2.959			5.399	
2.943	5.774	5.451		
2.942				1.116
2.929		5.413		
2.879	5.571	5.900		
2.862				1.231
2.834				1.289
2.768				1.430

[a] Pure CH_3CN. [b] 2.22×10^{-4} M Mn(II). [c] 3.39×10^{-4} M Mn(II).

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squares treatment yields a value at 25° for $1/T_2$ of 265 ± 12 sec^{-1}. Therefore, we feel quite confident in our choice of a relaxation mechanism and in the validity of our experimentally determined line widths. Also, as expected for acetonitrile, $T_1 = T_2$ within the error limits reported.

On the basis of eq 2, one would expect the line width to be linearly dependent on the Mn(II) concentration. A plot of the line width *vs.* Mn(II) concentration at 33 ± 1° (not shown) for six solutions in the concentration range (1–6) $\times 10^{-4}$ *M* was linear. As expected, the line extrapolated to the line width of pure acetonitrile at an Mn(II) concentration of zero.

In order to verify the scalar coupling mechanism discussed in the theory section, the longitudinal relaxation times for a Mn(II) solution were determined by the progressive-saturation method described by Reuben, Fiat, and Folman.[10] Table I gives the experimental T_1's for a 2.22×10^{-4} *M* Mn(II) solution in acetonitrile. Although the progressive-saturation method gives rather wide scatter, Table I does show that while Mn(II) solution T_1's do not differ appreciably from the pure acetonitrile T_1's and T_2's, the T_2's for the Mn(II) solutions are much smaller. This is consistent[2] with a scalar coupling relaxation mechanism.

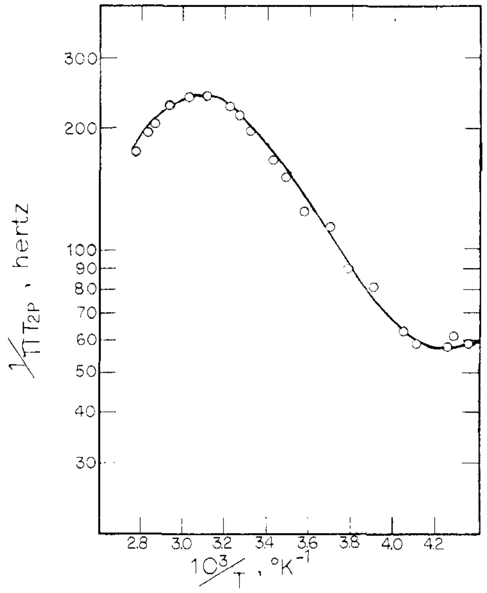

Figure 1.—Variations in the log of the line width of a 3.39×10^{-4} *M* Mn(II) solution with $1/T$ compared to a computer-calculated theoretical line.

Figure 1 shows the temperature variation of log $(1/T_{2p})$ for a solution 3.39×10^{-4} *M* in Mn(II). In order to analyze this temperature dependence by eq 6, it was necessary to obtain values of $1/T_{1e}$ over the temperature range covered in the nmr experiments. The instrumentation necessary for a determination of $1/T_{1e}$'s was not available, but the $1/T_{2e}$'s were determined and the approximation was made that $T_{1e} = T_{2e}$. The solution used in the esr study was the same as for the nmr study. Because of the interaction of the electron spins with the moment of the ^{55}Mn nucleus ($I = ^5/_2$), the esr spectrum consists of six lines of unequal widths and intensities. The narrowest of these lines, the fourth, was used in this study because it is least subject to inhomogeneous broadening due to the hyperfine interactions[11] with the ^{55}Mn nucleus. A least-squares analysis of the esr data shown in Figure 2 yielded an activation energy of 0.58 ± 0.07 kcal/mol.

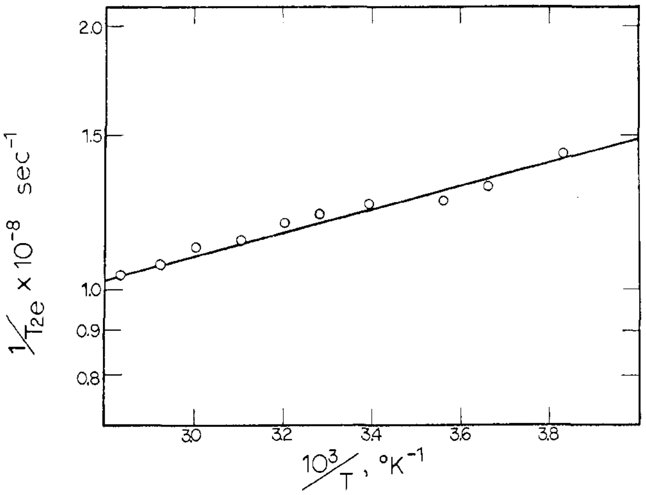

Figure 2.—Variation in the log of the electron spin relaxation rate with $1/T$ for a 3.39×10^{-4} *M* Mn(II) solution.

The bend observed in Figure 1 at low temperatures indicates the presence of another relaxation mechanism not predicted by eq 6. It is believed that at these low temperatures, the manganese complex, $Mn(CH_3CN)_6^{2+}$, is sufficiently long-lived that the second coordination sphere effects become important. The effects of the paramagnetic ion in relaxation processes outside the first coordination sphere are, of course, reduced. Since the dipolar mechanism has a $1/r^6$ dependence and since it was negligible in the first coordination sphere relaxation process, the scalar coupling mechanism should still predominate in the second-sphere relaxation process.[12,13] However, a calculation of the scalar coupling term using a correlation time for rotational tumbling, τ_r, yields a value for A/h much too large. If A/h for the second coordination sphere is assumed equal to that determined for the first coordination sphere, a lower limit to the correlation time of 9×10^{-10} sec at −35° is obtained. A correlation time of this order of magnitude does not seem unreasonable for the diffusion-controlled exchange of the solvent molecules from the second coordination sphere. The electron spin longitudinal relaxation times are, however, of comparable magnitude at these low temperatures. As the temperature increases T_{1e} increases (see Figure 2) while the second coordination sphere mean lifetime certainly decreases. Over most of the temperature range studied, therefore, the correlation time for this proposed second-sphere scalar coupling interaction would be

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dominated by the above-mentioned mean lifetime. Accordingly, the activation energy for the second sphere process was set equal to the 1.83 kcal/mol value found for rotational diffusion of the pure solvent. It should be noted that any reasonable mechanism proposed for the so-called second coordination sphere broadening would have a correlation time corresponding to rotational diffusion. While our calculations were made assuming an activation energy of 1.83 kcal/mol for the second sphere process, a treatment of the second-sphere activation energy as a variable showed that values ranging from 1.5 to 2.5 kcal/mol gave linear rate law plots. The exchange parameters calculated for activation energies within this interval also agreed within experimental error to those reported in Table II. Near the minimum observed in Figure 1, the functional form of the line width is closely approximated by

$$1/T_{2p} = P_m/\tau_m + \text{(second-sphere contribution)} \quad (8)$$

TABLE II

COMPARISON OF WATER AND ACETONITRILE EXCHANGE PARAMETERS

Cation	Exchange parameter	Water results	Acetonitrile results
Mn(II)	k_1,[a] sec^{-1}	3.1×10^7 [b]	$(1.2 \pm 0.3) \times 10^7$ [c]
	$\Delta H^{\ddagger}$, kcal/mol	8.1[b]	7.25 ± 0.25[c]
	$\Delta S^{\ddagger}$, eu	2.9[b]	-1.8 ± 0.8[c]
	A/h, Hz	9.2×10^6 [d]	3.2×10^6 [c]
Co(II)	k_1,[a] sec^{-1}	1.35×10^6 [d] 2.13×10^6 [f]	1.4×10^5 [e]
	$\Delta H^{\ddagger}$, kcal/mol	8.0[b] 10.4[g]	8.1[e]
	$\Delta S^{\ddagger}$, eu	-4.1[b] 5.3[e]	-7.5[e]
Ni(II)	k_1,[a] sec^{-1}	2.7×10^4 [b]	3.9×10^3 [e] $(2.8 \pm 0.5) \times 10^3$ [h]
	$\Delta H^{\ddagger}$, kcal/mol	11.6[b]	10.9 ± 0.5[e] 11.7 ± 1.0[h]
	$\Delta S^{\ddagger}$, eu	0.6[b]	-8.8 ± 2[e] -3.6 ± 1.0[h]

[a] All rate constants at 25°. [b] Reference 2. [c] This work. [d] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **42**, 2553 (1964). [e] N. A. Matwiyoff and S. V. Hooker, *Inorg. Chem.*, **6**, 1127 (1967). [f] Calculated from data in ref *g*. [g] A. M. Chmelnick and D. Fiat, *J. Chem. Phys.*, **42**, 39 (1967). [h] D. K. Ravage, *Inorg. Chem.*, **6**, 1127 (1967).

The minimum in Figure 1 occurs at $10^3/T = 4.246$ deg^{-1} where the observed line width is 56.9 Hz. To calculate the second-sphere contribution, an activation energy for the exchange process is assumed and the relative contributions of the two terms in eq 8 is made. The second-sphere contributions for each of the data points in Figure 1 was then calculated and subtracted from the line widths. The resultant curve showed no anomalous behavior over the temperature range studied.

The small activation energy of the electron spin relaxation process relative to that expected for ligand exchange permits a treatment of eq 6 as a quadratic in τ_m neglecting the temperature dependence of T_{1e}. Two unknowns remain in eq 6, however, τ_m and the constant c. Rearranging eq 6, differentiating with respect to τ_m, and equating to zero, we get

$$d(P_m T_{2p} - c/T_{2e})/d\tau_m = 1 - c/\tau_m^2 = 0 \quad (9)$$

The maximum in the corrected log $(1/T_{2p})$ *vs.* $1/T$ plot should then occur when $\tau_m = \sqrt{c}$. The value of c calculated from the positive root was used in eq 6 to evaluate the τ_m's for each data point. The exchange parameters were calculated from an absolute rate theory expression

$$k_1 = kT/h \exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT) \quad (10)$$

the log (k_1/T) values were analyzed by a least-squares analysis as a function of $1/T$, and the value obtained for the enthalpy of activation for the exchange, $\Delta H^{\ddagger}$, was used to again estimate the second-sphere contribution. This procedure was repeated on an IBM 360 computer until two successive values of $\Delta H^{\ddagger}$ agreed to within 5 cal/mol. Figure 3 shows a plot of log (k_1/T) *vs.* $1/T$ for each of the data points. Also calculated was a theoretical curve using eq 6, the final exchange parameters, and the final second-sphere contributions. This theoretical curve is shown in Figure 1 with the original data points. Table II presents the final kinetic parameters obtained from the computer analysis for the acetonitrile study along with the Mn(II)-water exchange parameters found by Swift and Connick.[2] The scalar coupling constant reported in Table II predicts a chemical shift of ±19 Hz for a 3.39×10^{-4} M solution of Mn(II) at 300°K. An attempt was made to measure this shift and hence verify directly our reported A/h value. However, both the calculated and observed shifts were smaller than the experimental error in the measurements.

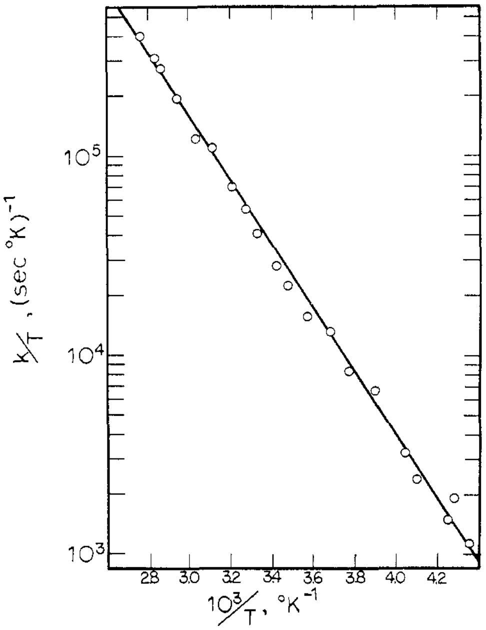

Figure 3.—Variation of log (k_1/T) calculated from each of the data points shown in Figure 1 with $1/T$.

Table II also gives the acetonitrile and water exchange parameters for Ni(II) and Co(II). A plot of log k_1 for water exchange *vs.* log k_1 for acetonitrile exchange (not shown) is roughly linear. This would seem to indicate that a similar exchange mechanism is operative for the three cations. As with water,[2,14] we believe the rate-determining step for acetonitrile exchange is largely dissociative.

We are continuing the study of nonaqueous solvent-exchange reactions at this laboratory. In particular, we are making a study of the Fe(II)–acetonitrile system.

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Photoinduced Reduction of Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)iron(III)

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The absorption and emission spectra of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, HHFA, and its iron(III) chelate, Fe(HFA)$_3$, were recorded from 600 to 200 nm. The photochemistry of the chelate, Fe(HFA)$_3$, was studied as a function of irradiating wavelength, light intensity, and chelate concentration. On this basis, the primary photochemical process was determined to be iron(III) reduction to iron(II). In ethanol, the product isolated is Fe(HFA)$_2$·2C$_2$H$_5$OH. This product has been synthesized independently and studied spectroscopically. The wavelength dependence of the quantum yield of Fe(HFA)$_2$·2C$_2$H$_5$OH indicates that reduction may take place by two mechanisms, depending upon the irradiating wavelength. The first mechanism corresponds to direct excitation of a charge-transfer band at 345 nm. The second mechanism involves excitation of a ligand π–π^* transition followed by a spin-allowed crossing to the charge-transfer state. Reduction then takes place from this charge-transfer state.

The physical and chemical properties of the 1,3-diketonate complexes of the first transition series have been extensively studied.[1] Tentative assignments of the ultraviolet absorption spectra of the iron(III) complexes have been made on the basis of empirical and theoretical treatments.[1–4] The absorptions occurring within the ultraviolet region are of two types: (a) transitions within the ligand π system and (b) ligand-to-metal and metal-to-ligand charge-transfer transitions.

In 1963, Goan,[5] *et al.*, reported the photochemical preparation of 1,3-diketonate complexes of iron(III) by irradiating benzene solutions of Fe(CO)$_5$ and various 1,3-diketones. Several studies dealing with the photochemistry of iron complexes have been reported.[6] However, to our knowledge no photochemical studies have been reported for the 1,3-diketonate complexes of iron. In the present paper we report the results of a photochemical study of tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)iron(III), hereafter abbreviated Fe(HFA)$_3$. Irradiation of alcoholic solutions with ultraviolet light results in a reduction of iron(III) to iron(II), a reaction characteristic of a large number of 1,3-diketonate complexes of the first transition series.[7] We have undertaken a detailed photochemical study of these chelates with two objectives in mind: (a) to use the photochemical data as an aid in assigning charge-transfer absorptions and (b) to study the mechanism of light-induced electron transfer as a function of irradiating wavelength and ligand electronic structure.

Experimental Section

Synthesis.—The 1,1,1,5,5,5-hexafluoro-2,4-pentadione (HHFA) was purchased from Columbia Organic Chemical Co. It was dried according to the method described by Belford, *et al.*[8] Fe(HFA)$_3$ was prepared using standard methods.[9] The product was recrystallized from petroleum ether (bp 37–55°). The bright red crystals melt at 47°. *Anal.* Calcd for Fe(C$_5$HF$_5$O$_2$): C, 26.6; H, 0.45; F, 50.3. Found: C, 26.54; H, 0.73; F, 46.3.

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