change 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.

(14) R. G. Wilkins and M. Eigen, *Advan. Chem. Ser.*, **No. 49**, 58–59 (1965).

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

By H. D. GAFNEY, R. L. LINTVEDT, and I. S. JAWORIWSKY

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)$_2 \cdot 2C_2H_5OH$. This product has been synthesized independently and studied spectroscopically. The wavelength dependence of the quantum yield of Fe(HFA)$_2 \cdot 2C_2H_5OH$ 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 photo-

chemical 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$_6$O$_2$): C, 26.6; H, 0.45; F, 50.3. Found: C, 26.54; H, 0.73; F, 46.3.

(1) J. P. Fackler, *Progr. Inorg. Chem.*, **7**, 361 (1966).

(2) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **22**, 183 (1961).

(3) I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, **50**, 265, 276 (1969).

(4) R. L. Lintvedt and L. K. Kernitsky, *Inorg. Chem.*, **9**, 491 (1970).

(5) J. Goan, G. Huether, and H. Podall, *ibid.*, **2**, 1078 (1963).

(6) For a comprehensive review see A. W. Adamson, W. L. Waltz, E. Zinto, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

(7) (a) R. L. Lintvedt and H. D. Gafney, "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, New York, N. Y., 1968, p 85, and unpublished results from our laboratory; (b) N. Filipescu and H. Way, *Inorg. Chem.*, **8**, 1863 (1969).

(8) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

(9) M. C. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Chem.*, **2**, 411 (1963).

Fe(HFA)₃·2THF.—Twenty-five grams of iron (100 mesh) and 10 g of anhydrous FeCl₃ were added to 100 ml of freshly distilled, dry tetrahydrofuran. Dry excess HHFA (15 ml) was pipetted into the resulting solution of Fe(II). The reaction mixture was stirred for 30 min after which the reddish purple liquid layer was decanted off and evaporated to one-fourth of its original volume. This solution was placed in a freezer at −10° overnight. The red-purple crystals that formed were recrystallized twice from dry petroleum ether (bp 36–55°). The Fe(HFA)₂·2THF melts at 105°. *Anal.* Calcd for Fe(C₅HF₆O₂)₂(C₄H₈O)₂: C, 35.1; H, 3.0; F, 38.2. Found: C, 35.3; H, 3.03; F, 37.6.

Fe(HFA)₂·2C₂H₅OH.—A solution of Fe(II) in THF was prepared as described above. The solution was evaporated to dryness in a nitrogen atmosphere. Then 200 ml of dry ethanol was added to the residue and then evaporated almost to dryness, under N₂. Ethanol addition and evaporation was repeated twice. The final ethanol solution was evaporated to dryness. About 10 g of the grayish white salt was added to 50 ml of freshly distilled ethanol. This suspension was stirred and the dry HFA was added directly to the suspension. The reaction occurs immediately and is very exothermic. The resulting red solution was stirred for 1 hr and then evaporated to half its original volume. All operations must be carried out in an inert atmosphere. The flask was sealed and placed in a freezer at −10° overnight. The red crystals were filtered, but attempts to dry them by suction resulted in decomposition. Therefore, the product was filtered, but not dried. The wet crystals were recrystallized from petroleum ether (bp 37–55°), filtered, and allowed to dry in a desiccator. The product was vacuum sublimed (*ca.* 50° at 10⁻¹ mm). The brick red, needlelike crystals decomposed at 93°. *Anal.* Calcd for Fe(C₅HF₆O₂)₂(C₂H₅OH)₂: C, 30.8; H, 2.56. Found: C, 28.2; H, 2.59. On standing in stoppered vials, the compound slowly decomposes to a yellow-brown solid.

Spectral and Photochemical Measurements.—All solvents used were reagent grade. The methanol was distilled over sodium just prior to use. The ethanol used was freshly distilled over Mg(OC₂H₅)₂. The 95% ethanol was prepared by adding distilled water to freshly distilled absolute ethanol. *n*-Propyl, isopropyl, *n*-butyl, and *t*-butyl alcohols were not purified.

Preliminary experiments were carried out in a reaction vessel equipped with a quartz immersion well. The source was a low-pressure Klockner–Moeller Original Hanau Type PL-368 Hg lamp. The light was filtered using a Hanovia Pyrex sleeve filter (0% *T* at 290 nm). The photolysis vessel was connected to a vacuum line and a trap at 77°K. The trap could be shut off and removed for product analysis. The photolysis cell was thermostated to 0°. A second type of reaction cell contained an opening in which a conductivity cell was mounted. Resistance measurements were made during the photolysis using an Industrial Instruments Model RC16B2 conductivity bridge and a nonaqueous conductivity cell.

Electronic absorption spectra were recorded with a Cary 14 spectrophotometer and a Bausch and Lomb Spectronic 20. Emission spectra were recorded using an Aminco–Bowman spectrophotofluorometer. Phosphorescence spectra were determined at 77°K. Infrared spectra were recorded with a Perkin-Elmer Model 621 spectrophotometer.

The Fe(II) chelate produced in the photolysis was isolated by slow evaporation of the photolysis solution. The product was vacuum sublimed. It yielded two fractions, the most volatile melting at 47° and the least volatile melting at 90°. Melting points and spectral data showed that the component that melts at 47° is Fe(HFA)₃ and the component that melts at 90° is Fe(HFA)₂·2C₂H₅OH.

For quantum yield determinations an optical train was constructed. The source was a Hanovia medium-pressure Hg lamp with a 450-W transformer which was connected to a Raytheon voltage stabilizer with 115-V output at 17.4 A. The lamp was thermostated by mounting it in a quartz immersion well which was placed inside the lamp housing. Although the immersion well reduces the light intensity considerably, it allows us to main-

tain an intensity which varies less than 5% over a 12-hr period. The emerging light was focused with a quartz condensing lens (2-in. focal length) on the entrance slit of a Bausch and Lomb Model 33-86-25-06 grating monochromator (2700 grooves/mm). The reaction cell (10 × 10 × 40 mm rectangular quartz cell) was mounted 1 cm from the exit slit of the monochromator. The beam was perpendicular to the cell. Since the resulting rectangular light image did not homogeneously fill the entire reaction cell, the solutions were stirred with a 5-mm magnetic stirring bar.

The quantum yields were determined by measuring the initial rate of the photochemical reaction. This was done by determining the amount of Fe(II) produced in a known time at a constant light intensity. The absorbed light intensity, in quanta per second, was determined by ferric oxalate actinometry.[10,11] The lamp was allowed to warm up for 2 hr after which the intensity was measured by irradiation of a 0.009 *M* solution of ferric oxalate in water. The amount of Fe(II) produced in the actinomer solution was determined by measuring the absorbance of the 1,10-phenanthroline complex at 510 nm. The values were compared to a Beer's law plot prepared from standard solutions of reagent grade (NH₄)₂[Fe(H₂O)₆](SO₄)₂ and 1,10-phenanthroline. The extinction coefficient at 510 mμ was 0.985 × 10⁴ l./mol cm. The light intensity was measured before and after the photolysis. An average value was used in the calculation of quantum yields. The intensity variation was always less than 5%.

The amount of Fe(II) generated in the photolysis of 3 ml of a freshly prepared 5.9 × 10⁻⁴ *M* (0.0100 g/25.0 ml) solution of Fe(HFA)₃ in absolute ethanol was determined in two ways. First, the absorbance at 540 nm of the photolyzed solution was measured with an equivalent aliquot of the initial stock solution (stored in the dark) in the reference beam. This absorbance was compared to a Beer's law plot of synthetically prepared Fe(HFA)₂·2C₂H₅OH in absolute ethanol. (The extinction coefficient at 540 nm is 1.46 × 10³ l./mol cm.) From the concentration of Fe(II) found, the rate of appearance of Fe(II) in molecules per second was determined. The second method of analysis was also used for all other alcohols. In this case, a 100-fold excess of 1,10-phenanthroline was added to an aliquot of the photolyzed solution. The absorbance was compared to a reference solution prepared in the same manner from an aliquot of the unirradiated solution. The absorbance of the photolyzed solution was compared to a Beer's law plot of standard solutions of Fe(II) and 1,10-phenanthroline dissolved in the various alcohols. A comparison of the two analytical methods was made on solutions of known concentrations. The method of analysis using 1,10-phenanthroline was found to show a 14% larger concentration of Fe(II) than comparison to the standard curve.

Attempts to prepare standard solutions of Fe(II) in the higher molecular weight alcohols were unsuccessful because of the limited solubility of various ferrous salts. To circumvent this problem, Fe(HFA)₂·2THF was used as the standard because of its high solubility in all the solvents used in the photochemical reactions. In *n*-butyl alcohol it was necessary to dissolve the 1,10-phenanthroline in *n*-butyl alcohol due to the immiscibility of water and the alcohol. The molar extinction coefficients at 495 nm of the 1,10-phenanthrolineiron(II) complex were 9.53 × 10³, 8.64 × 10³, and 8.83 × 10³ l./mol cm in *n*-propyl, isopropyl, and *n*-butyl alcohols, respectively.

In all determinations of quantum yield, the absorption of radiation by the sample was greater than 99%, as calculated from spectral data. Generally 15–20% of the Fe(HFA)₃ was consumed during a reaction. The remaining Fe(HFA)₃ was still sufficiently concentrated to absorb more than 99% of the irradiating light. This fact was verified by mounting a solution of the ferric oxalate actinometer directly behind the photolysis cell. We were unable to detect any reaction of the actinometer under these conditions.

The kinetic experiments were carried out at 0° over a con-

(10) (a) C. L. Parker, *Proc. Roy. Soc.*, *Ser. A*, **220**, 104 (1953); (b) C. G. Hatchard and C. A. Parker, *ibid.*, *Ser. A*, **235**, 518 (1953).

(11) J. Lee and H. H. Seliger, *J. Chem. Phys.*, **40**, 519 (1964).

centration range of 7.5×10^{-4} to 6.2×10^{-5} M where the fraction of absorbed light varied from 1.0 to 0.35.

Results

The photochemical behavior of Fe(HFA)$_3$ varies drastically in different solvents: from complete reduction of iron(III) to iron(II) in certain alcohols to no discernible reaction in nonalcoholic solvents. Alcohols in which the reduction is observed include CH_3OH, CH_3CH_2OH, $CH_3(CH_2)_2OH$, $(CH_3)_2CHOH$, $CH_3(CH_2)_3$-OH, $(CH_3)_2CHCH_2OH$, $(CH_3)_3COH$, and 95% CH_3-CH_2OH. Solvents in which no photoreduction of Fe(III) is observed include H_2O, $CHCl_3$, 80% CH_3-CH_2OH, C_6H_6, and $(CH_3CH_2)_2O$.

Preliminary spectral results indicated that there were three major products of the reaction. These products were isolated by vacuum distillation and evaporation. The ultraviolet and infrared spectra of the distillate proved that one product is the protonated ligand. A reddish brown solid was isolated and sublimed. The ultraviolet, visible, and infrared spectra of the sublimate were identical with the spectra of synthetically prepared Fe(HFA)$_2 \cdot 2C_2H_5OH$. In addition, it decomposes at 90° as does Fe(HFA)$_2 \cdot 2C_2H_5OH$. The second major product therefore, results from the loss of a ligand radical by Fe(HFA)$_3$. The adduct molecules, C_2H_5OH, appear necessary to stabilize the iron(II) species. We attempted to determine the amount of free ligand generated during the photolysis (by spectral means), but the results were ambiguous due to the complexity of the ultraviolet spectrum in the region where the ligand absorbs. However, the isolated products seem to indicate that the photochemical reaction is

$$Fe(HFA)_3 \xrightarrow[C_2H_5OH]{h\nu}$$
$$Fe(HFA)_2 \cdot 2C_2H_5OH + HHFA + \text{oxidized solvent}$$
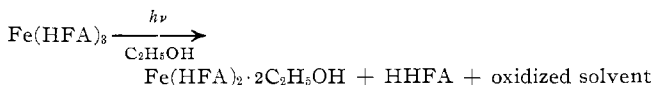
Rate Laws.—The rate of product formation was obtained by measuring the optical density of an aliquot at 540 nm. The product, Fe(HFA)$_2 \cdot 2C_2H_5OH$, absorbs strongly. The reactant, Fe(HFA)$_3$, is transparent at 540 nm. The data show that the rate of product formation is linear with time up to about 80–90% reaction for optically dense solutions, *i.e.*, those in which greater than 99% of the light is absorbed. Solutions more concentrated than 5.0×10^{-4} M in Fe(HFA)$_3$ satisfy this condition. The results show that the rate is independent of the complex concentration for optically dense solutions. The light intensity dependence was determined at 345 nm. The reduction has a first-order dependence on the light intensity as evidenced by the slope of 1.0 ± 0.1 for the plot of the log of the initial rate *vs.* the log of the average light intensity. The light intensity range studied was from 3.0×10^{13} to 6.0×10^{13} quanta/sec. These data indicate that the reduction is a primary process. The rate equation has the form

$$\frac{d(Fe^{2+})}{dt} = \Phi I_a \qquad (1)$$

After 80–90% of the Fe(HFA)$_3$ has reacted, the

reaction rate slows considerably and it appears that an equilibrium is established. Since the forward reaction is a nonequilibrium reaction

$$Fe(HFA)_3 \underset{k_d}{\overset{k_r}{\rightleftharpoons}} Fe(HFA)_2(\text{solvent})_2 \qquad k = k_p/k_d \qquad (2)$$
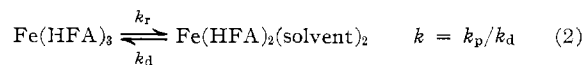
removal of the light source will stop it.[12] If the reverse reaction is thermal, one would expect the amount of product formed to decrease on standing in the dark. Solutions photolyzed for various lengths of time and kept in the dark showed no change in absorbance after 36 hr. A second possibility is that the back-reaction is photoaccelerated[6] where the equilibrium constant, K, is given by

$$K = \frac{\epsilon_{\text{reactant}} \Phi_{\text{reactant}}}{\epsilon_{\text{product}} \Phi_{\text{product}}} \qquad (3)$$

In this case, it implies that Fe(HFA)$_2 \cdot 2C_2H_5OH$ must undergo a photochemical oxidation. Irradiation of solutions of Fe(HFA)$_2 \cdot 2C_2H_5OH$ plus excess ligand in absolute ethanol resulted in no reaction over a 3-hr period. Another possible explanation for the decrease in reaction rate is that the products absorb slightly in the region responsible for the photoreduction of Fe-(HFA)$_3$. Therefore, as the reduction proceeds, a larger fraction of the light is being absorbed by the product. The rate of formation of the product, for 5×10^{-4} M Fe(HFA)$_3$ in ethanol, after 2 hr of photolysis, drops from 3.6×10^{-3} to 5.6×10^{-4} abs unit/min. Assuming that the change in rate is due only to the decrease in light intensity, the final rate should be equal to the initial rate times the fraction of light not being absorbed by the product. When this correction is made, the final rate is calculated to be 6.6×10^{-4} abs unit/min. On the basis of this approximate calculation, it appears that product absorption (inner filter effect) is the major cause of the rate change.

The rate of photoreduction was also studied using solutions in which the fraction of light absorbed is less than 1.0. The concentration range studied was 5.00×10^{-4} to 6.25×10^{-5} M in Fe(HFA)$_3$. The results are presented in Figure 1 where $-\log$ of the initial rate is plotted *vs.* $-\log$ of the initial concentration of Fe(HFA)$_3$ in ethanol. The straight line whose slope is 1.1 ± 0.2 indicates a first-order dependence on Fe(HFA)$_3$ in this concentration range. The zero-order dependence of the rate on reactant concentration in optically dense solutions and the first-order dependence in solutions in which a fraction of the light is absorbed is strong evidence that the reduction is a primary process.[13]

Irradiation of Fe(HFA)$_3$ in other alcoholic solvents produces the same products as in ethanol. However, the rate increases with increasing stability of the solvent radical, *e.g.*, *t*-butyl alcohol > isopropyl alcohol >

(12) The fact that Fe(HFA)$_3$ is thermally stable in absolute ethanol at room temperature was determined by storing the solutions in the dark and recording the ultraviolet–visible spectrum periodically. The solutions showed no spectral changes when stored for several days under these conditions. We have no evidence that the solutions are not stable indefinitely.

(13) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 580.
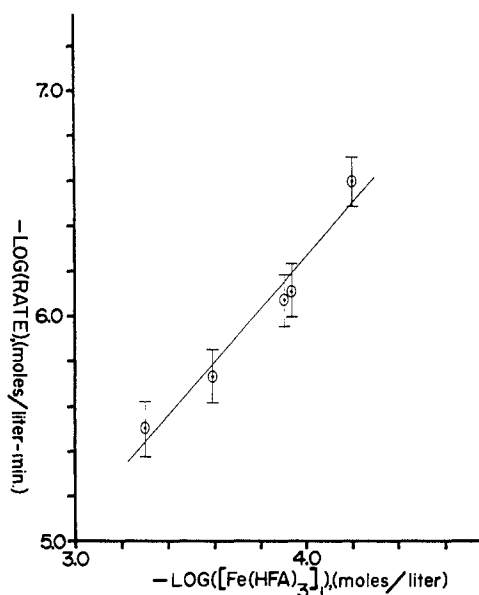
Figure 1.—Log of the initial rate *vs.* log of the initial concentration of Fe(HFA)₃ for irradiation in ethanol at 345 mμ.

ethanol. Preliminary data are consistent with eq 1 in these systems.

Temperature variation over the range 0–50° did not produce a rate change above experimental error.

Quantum Yields.—The dependence of the quantum yield on irradiating wavelength was investigated in the region 450–253 nm. This dependence is shown in Table I.

TABLE I
QUANTUM YIELD FOR PHOTOREDUCTION AS A
FUNCTION OF IRRADIATING WAVELENGTH

Irradiating wavelength, nm	Initial concn of Fe(HFA)₃ × 10⁴, M	Av quantum yield	Variation, %
253	5.91	0.14	±5
275	5.91	0.12	±6
302	5.91	0.10	±5
312	5.91	0.08	±10
345	5.91	0.13	±7
450	5.91	0.0	

Effect of Water.—The effect of water on the photoreduction is pronounced. The rate in 95% ethanol decreases by a factor of 20 from the corresponding rate in absolute ethanol. The quantum yield of Fe(II) in 95% ethanol is 3.5×10^{-3} at 302 nm. The spectrum of Fe(HFA)₃ in 95% ethanol consists of a single strong peak in the ultraviolet region. This strong peak at 305 (313) nm corresponds to the anion form of the free ligand. The resistance of solutions made by dissolving Fe(HFA)₃ in various ethanol–water mixtures was measured in order to detect any appreciable concentration of charged species. These values were compared to the resistances of comparable ethanol–water solutions but without Fe(HFA)₃. The resulting resistance decrease for the Fe(HFA)₃ solution is slightly less than the decrease in the ethanol–water mixtures. Thus, there is no evidence for an appreciable concentration of charged species. The possibility of coordinated water was also checked by determining the quantum yield of

Fe(II) for irradiation of [Fe(H₂O)₆]Cl₃ in absolute ethanol and comparing this value to that obtained for Fe(HFA)₃ in 95% ethanol. The quantum yield of Fe(II) was 4.8×10^{-3} for [Fe(H₂O)₆]Cl₃ and 3.5×10^{-3} for Fe(HFA)₃. Irradiation was at 302 nm.

The infrared spectrum of the Fe(III) complex isolated from 95% ethanol was identical with authentic Fe(HFA)₃ except for bands characteristic of bonded water at 3500–3300, 983, 962, and 906 cm⁻¹. This complex reverted to anhydrous Fe(HFA)₃ in 6 weeks when stored in a stoppered vial.

Absorption and Emission Spectra of the Complex and Ligand.—The absorption spectra of the complex and the ligand in the 200–400-nm region are shown in Figure 2.
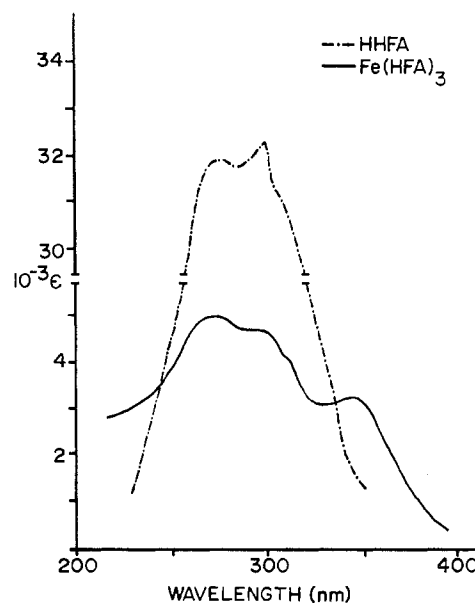

Figure 2.—Absorption spectra of HHFA and Fe(HFA)₃ in ethanol.

The only absorption characteristic of the complex appears at 345 nm and is assigned to a charge-transfer transition. The absorptions at 275 and 320 (313) nm are basically intraligand $\pi \rightarrow \pi^*$ transitions. The solvent dependence of the 302 (313) nm transition suggests that there is $^1O_n \rightarrow ^1\pi^*$ character.

The phosphorescence spectra of the ligand and complex in ethanol at 77°K are shown in Figure 3. The emission spectra are consistent with the assignment of the 302 (313) nm band to a singlet–singlet transition primarily within the ligand.[14] In addition, they allow one to assign a ligand triplet state at 450 nm, which is present in the absorption spectra with $\epsilon \approx 3 \times 10^{-2}$ l./mol cm. This ligand triplet state is relatively unaffected by the presence of the metal.

Additional experiments showed that the rate of photoreduction is independent of the presence of oxygen. The rate did not change if dry nitrogen, helium, or dry air were bubbled through the reaction vessel.

Discussion

The results of the kinetic study indicate that the

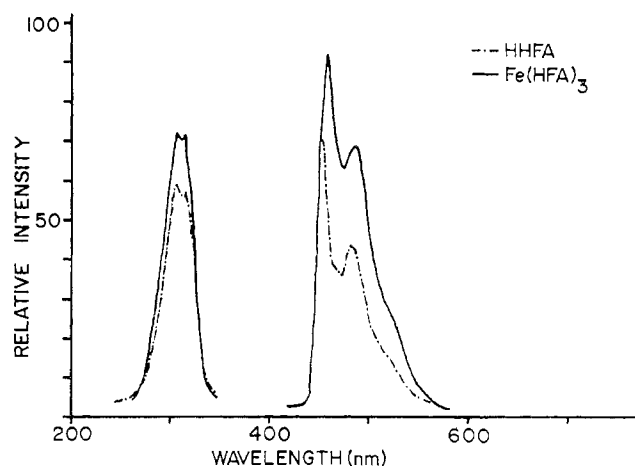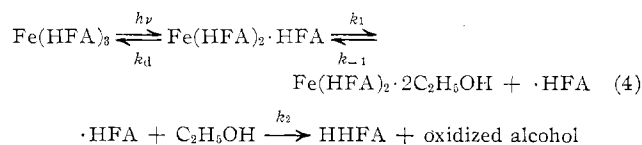(14) F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.*, **40**, 2790 (1963); **41**, 147 (1963).

Figure 3.—Phosphorescence spectra of HHFA and Fe(HFA)₃ at 77°K. The concentration of HHFA is 1.67×10^{-3} M. The concentration of Fe(HFA)₃ is 10^{-4} M.

Fe(II) complex is formed in a primary process when irradiating in the 345-nm region. The resistance of the solution shows only a very small change during photolysis, indicating dissociated charged species are not present in appreciable concentrations. Since the protonated ligand is isolated and the rate of reaction increases with increasing stability of the solvent radical,[15] the suggested mechanism is

$$\text{Fe(HFA)}_3 \underset{k_d}{\overset{h\nu}{\rightleftharpoons}} \text{Fe(HFA)}_2 \cdot \text{HFA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$
$$\text{Fe(HFA)}_2 \cdot 2\text{C}_2\text{H}_5\text{OH} + \cdot\text{HFA} \quad (4)$$
$$\cdot\text{HFA} + \text{C}_2\text{H}_5\text{OH} \overset{k_2}{\longrightarrow} \text{HHFA} + \text{oxidized alcohol}$$

A comparison of the absorption spectra of the protonated ligand and the complex, Figure 2, shows that two types of states may be formed upon initial excitation. First, irradiation at 275 nm and 302 (313) nm would result in excited states primarily associated with the ligand. Second, irradiation at 345 nm would result in an excited state characteristic of the complex. The band at 345 nm is logically assigned to a charge-transfer transition. The fact that irradiation at 345 nm results in photoreduction as the primary process argues for the assignment of the band to a ligand-to-metal charge transfer. The variation of the quantum yield with wavelength, as shown in Table I, indicates that different states are initially formed on excitation at different wavelengths. Since reduction must take place through some mechanism that populates the reactive charge-transfer state, it is reasonable to expect direct irradiation of the charge-transfer absorption to result in a high quantum yield. It is observed that the Fe(II) quantum yield at 345 nm is larger than at 302 nm. Although the 275 and 302 (313) nm transitions occur primarily within the ligand, irradiation at these wavelengths results in the formation of the Fe(II) complex. Thus, a mechanism exists in which excitation energy localized in the ligand excited states is transferred to the reactive charge-transfer state from which

(15) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

reduction takes place.[16,17] Direct transfer of energy from the excited ligand singlet state to the metal ion is possible through a dipole–dipole mechanism.[14,18,19] This transfer from the excited singlet (π^*) to the charge-transfer state occurs with the conservation of total spin multiplicity of the complex. The allowed singlet–singlet dipole transition overlaps the allowed charge-transfer dipole transition, as shown in Figure 2. The result is a large overlap integral and absorption band areas. A high probability of energy transfer through a dipole–dipole mechanism is reasonable because of the short distance between the ligand "sensitizer" and the metal "activator." Thus, an energy-transfer process might be expected to compete effectively with other deactivating processes.

The increase in quantum yield at 275 nm could be due to a decrease in the number of deactivating processes, since no phosphorescence is observed when the 275-nm transition is irradiated. It is interesting to note, if the only difference between excitation to the ligand singlet and the charge transfer is the intersystems crossing process, that with loss of this process, as in the 275-nm transition, the quantum yield is the same. However, the probability of transfer between the 275-nm state and the charge-transfer state would be expected to be much less, whether through a dipole–dipole mechanism or through an exchange mechanism. Thus the photochemical reaction is occurring from the excited ligand state or there exists a nonobserved reactive state similar to the charge-transfer state through which the photoreduction is occurring.

Since we were unable to detect spectrally any difference in the products formed in the reaction with increasing energy of the irradiating light, it is difficult to attribute the increase to photodecomposition, which becomes more important with decreasing wavelength.[20] However, Nagakura[3] has assigned a transition in Fe(AA)₃ occurring at 240 nm to a mixing of the ligand doublet and ligand singlet through a charge-transfer configuration. Although a higher energy transition is not directly observable in ethanol, it does appear (Figure 2) that there might be a band at higher energy. We did observe a transition at 225 nm in higher molecular weight alcohols. If this transition is a mixing of ligand states through a charge-transfer configuration, the increasing quantum yield of the ferrous complex could be due to the charge-transfer character of the transition.

The positions of the ligand triplet state (450 nm) and

(16) The presence of O$_n$ character in the ligand transitions may be important since the protonated ligand is a major product, and as Hammond and Leermakers have pointed out, excitation of a nonbonded electron results in a radical that would favor hydrogen atom abstraction. On the other hand, excitation from a π orbital requires extensive electronic reorganization for hydrogen atom extraction: G. S. Hammond and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 207 (1962).

(17) According to Hanazaki, *et al.*,[3] the π–π^* transitions occurring within the ligand are localized in each ligand. Photochemically, a localized transition would favor the observed reaction since this reaction requires excitation in one ligand followed by metal–oxygen bond breaking and migration of the ligand out of the solvent cage.

(18) G. A. Crosby, *J. Chem. Phys.*, **34**, 743 (1961).

(19) D. C. Dexter, *ibid.*, **21**, 836 (1953).

(20) See ref 13, p 660.

the charge-transfer state (345 nm) are of interest in connection with recent investigations of the laser properties of rare earth 1,3-diketonates.[14,18,21] Crosby[18] has suggested that the energy transfer in the rare earth chelates occurs through the ligand triplet state. However, in $Fe(HFA)_3$ the ligand triplet state is 20 kcal lower in energy than the reactive charge-transfer state. Thus, transfer from the ligand triplet state is an unimportant process due to the photoreduction. The Fe(II) quantum yield of zero for irradiation at 450 nm indicates that this is the case. A reasonable explanation for the lack of laser emission in the transition metal 1,3-diketonates is the presence of reactive charge-transfer states at somewhat higher energies than the ligand triplet states.

The effect of water on the photochemical behavior of $Fe(HFA)_3$ is striking. The spectral data are consistent with coordinated water and a free anionic ligand molecule in 95% ethanol. However, conductance measurements show that there is not an appreciable concentration of charged species present. These facts are explained by outer-sphere complex formation, [Fe(H-

(21) M. L. Bhaumik, *J. Chem. Phys.*, **40**, 3711 (1964).

$FA)_2(H_2O)_2]HFA$, in the presence of sufficient quantities of water. Lister and Rivington[22] have shown that for the iron(III) aquo ion the stabilities of inner- and outer-sphere complexes are very similar for ligands which are anions of strong acids. Hexafluoroacetylacetone is a relatively strong acid. Formation of an outer-sphere complex may be expected to decrease the quantum yield of photoreduction, since it presents an efficient mechanism for the dissipation of the exciting energy into the solvent through hydrogen bonding.[14] The observed Fe(II) quantum yield for irradiation at 302 nm in 95% ethanol is 0.05 times the quantum yield in absolute ethanol.

(22) M. W. Lister and D. E. Rivington, *Can. J. Chem.*, **33**, 1572, 1591, 1603 (1955).

Reversible Addition of Carbon Monoxide to Tertiary Phosphine Complexes of Cobalt(II) and Their Reduction to Cobalt(I) Carbonyl Derivatives

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The reactions of carbon monoxide with complexes of the type $Co(PR_3)_2X_2$ (PR_3 = tertiary phosphine, X = mononegative ion) have been studied in $C_2H_4Cl_2$ and benzene. The reaction under ambient conditions leads to reversible formation of five-coordinate adducts $Co(PR_3)_2(CO)X_2$. The stability of the adducts is strongly influenced by the nature of R and X. The stability constants of the equilibria $Co(PR_3)_2X_2 + CO \rightleftarrows Co(PR_3)_2(CO)X_2$ have been measured for several complexes in $C_2H_4Cl_2$ at 25°. Further reaction with carbon monoxide can lead to formation of the cobalt(I) derivatives $Co(PR_3)_2(CO)_2X$. The stability of the carbonyl adducts $Co(PR_3)_2(CO)X_2$ is discussed in terms of influence of the organic group R and is compared with that of the corresponding tertiary phosphine complexes $Co(PR_3)_3X_2$.

Introduction

As part of our investigations on the stability of low-spin five-coordinate complexes of cobalt(II) and nickel-(II), we wish to report the results of studies on the reversible uptake of carbon monoxide by the four-coordinate complexes $Co(P)_2X_2$ (P = phosphorus atom of a tertiary phosphine; X = mononegative ion).[1-6]

By the reaction of carbon monoxide with benzene solutions of compounds of the type $Co(PR_3)_2X_2$ (PR_3 =

(1) T. Boschi, M. Nicolini, and A. Turco, *Coord. Chem. Rev.*, **1**, 269 (1966).

(2) P. Rigo, C. Pecile, and A. Turco, *Inorg. Chem.*, **6**, 1636 (1967).

(3) P. Rigo, M. Bressan, and A. Turco, *ibid.*, **7**, 1460 (1968).

(4) P. Rigo, B. Corain, and A. Turco, *ibid.*, **7**, 1623 (1968).

(5) T. Boschi, P. Rigo, C. Pecile, and A. Turco, *Gazz. Chim. Ital.*, **97**, 1391 (1967).

(6) P. Rigo, G. Guastalla, and A. Turco, *Inorg. Chem.*, **8**, 375 (1969).

$P(C_2H_5)_n(C_6H_5)_{3-n}$; X = Cl, Br, I), Booth and Chatt prepared the complexes $Co(P(C_2H_5)_3)_2(CO)X_2$. The phosphines $P(C_2H_5)_2C_6H_5$ or $P(C_6H_5)_2C_2H_5$ were reported to give rather intractable products.[7] Later, Sacco described the preparation of the compound $Co(P(C_6H_5)_3)_2(CO)_2I$ by the reaction of $Co(P(C_6H_5)_3)_2I_2$ with carbon monoxide at 170 atm and 80°. He also obtained the corresponding bromide by indirect methods.[8] Finally, Hieber and Duchatsch obtained $Co(P(C_6H_5)_3)_2(CO)_2X$ (X = Cl, Br, I) by mild halogenation of $Na[Co(P(C_6H_5)_3)(CO)_3]$.[9]

Experimental Section

Starting Materials.—The complexes of the type $Co(PR_3)_3X_2$

(7) G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).

(8) A. Sacco, *Gazz. Chim. Ital.*, **93**, 542 (1963).

(9) W. Hieber and Duchatsch, *Chem. Ber.*, **98**, 2530 (1965).