

- (18) E. O. Fischer and L. Knauss, *Chem. Ber.*, **102**, 223 (1969).
 (19) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. Fr.*, **29**, 1301 (1962).
 (20) J. A. Connor, E. M. Jones, and G. K. McEwen, *J. Organomet. Chem.*, **43**, 357 (1972).
 (21) E. O. Fischer, E. Louis, and R. J. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **7**, 136 (1968).
 (22) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **95**, 7516 (1973).
 (23) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1970, p 114.
 (24) (a) J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, N.Y., 1966, p 783; (b) *ibid.*, p 737.
 (25) (a) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 4336 (1971); (b) M. Wrighton, G. S. Hammond, and H. B. Gray, *Inorg. Chem.*, **11**, 3122 (1972).
 (26) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).
 (27) The concentration of CO in cyclohexane at saturation is 0.016 M.
 (28) R. Mathieu and R. Poilblanc, *Inorg. Chem.*, **11**, 1858 (1972).
 (29) The quantum yield for formation of *cis*-W(CO)₄(PPh₃)₂ varies inversely as a function of W(CO)₃PPh₃ concentration. We have evidence that in the absence of an entering ligand the following reaction occurs: 2W(CO)₃PPh₃ + hν → W(CO)₆ + *cis*-W(CO)₄(PPh₃)₂. The concentration dependence of the quantum yield may be a result of this reaction. Further studies are in progress.
 (30) E. O. Fischer, E. Louis, and W. Bathelt, *J. Organomet. Chem.*, **20**, 147 (1969).
 (31) M. Poliakoff, *Inorg. Chem.*, **15**, 2022 (1976).
 (32) W. D. Covey and T. L. Brown, *Inorg. Chem.*, **12**, 2820 (1973).
 (33) G. Schwenzer, M. Y. Darenbourg, and D. J. Darenbourg, *Inorg. Chem.*, **11**, 1967 (1972).
 (34) D. J. Darenbourg, personal communication.
 (35) (a) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 3155 (1976); (b) *ibid.*, **98**, 3160 (1976).
 (36) B. R. Higginson, D. R. Lloyd, J. A. Connor, and J. H. Hillier, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1418 (1974).
 (37) D. L. Lichtenberger and R. F. Fenske, *Inorg. Chem.*, **15**, 2015 (1976).
 (38) M. Wrighton, D. L. Morse, H. B. Gray, and D. K. Ottesen, *J. Am. Chem. Soc.*, **98**, 1111 (1976).
 (39) F. A. Cotton, W. T. Edwards, F. C. Rauch, M. A. Graham, R. N. Perutz, and J. J. Turner, *J. Coord. Chem.*, **2**, 247 (1973).
 (40) This MCD study is in collaboration with Professor A. F. Schreiner, North Carolina State University, Raleigh, N.C.
 (41) R. M. E. Vlieg and P. J. Zandstra, *Chem. Phys. Lett.*, **31**, 487 (1975).
 (42) M. J. Incorvia and J. I. Zink, *Inorg. Chem.*, **13**, 2489 (1974).
 (43) R. F. Fenske, *Pure Appl. Chem.*, **27**, 61 (1971).
 (44) D. L. Lichtenberger, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, **12**, 702 (1973).
 (45) The HOMO's of W(CO)₆ lie lower in energy than those of class 1 compounds due to a higher positive charge on the metal in the former case when the unique ligand, CO, is not a strong σ donor and can accept electron density from the metal into ligand π* orbitals. Phosphorus-donor complexes, which also can accept electron density from the metal due to π interactions, have HOMO energies intermediate between the class 1, strong σ donors, and the hexacarbonyl.
 (46) M. A. M. Meester, R. C. J. Vriends, D. J. Stufkens, and K. Vrieze, *Inorg. Chim. Acta*, **19**, 95 (1976).
 (47) W. G. Richards, *Trans. Faraday Soc.*, **63**, 257 (1967).
 (48) N. A. Beach and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5713 (1968).
 (49) E. O. Fischer, C. G. Kreiter, H. J. Kollmeier, J. Müller, and R. D. Fischer, *J. Organomet. Chem.*, **28**, 237 (1971).
 (50) T. F. Block and R. F. Fenske, *J. Am. Chem. Soc.*, **99**, 4321 (1977).

Contribution No. 3719 from the Department of Chemistry,
 University of California, Los Angeles, California 90024

Photolabilization of Ligands Including Carbon Monoxide from Low-Spin d⁶ Iron(II) Macrocyclic Complexes

MICHAEL J. INCORVIA and JEFFREY I. ZINK*

Received October 1, 1976

AIC607229

The photochemistry of low-spin d⁶ [Fe(TIM)(X)(Y)](PF₆)₂ (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; X and Y = MeCN, CO, imidazole, and triethyl phosphite) is studied in various organic solvents. The electronic absorption spectra contain an intense metal-to-ligand charge-transfer band in the visible region characteristic of the Fe²⁺-α-diimine moiety. The energy of this band varies with the π interaction between the metal and the axial ligands. The photochemistry of [Fe(TIM)CH₃CN(CO)](PF₆)₂ shows two reaction modes: loss of CH₃CN in acetone and loss of CO in acetonitrile. The bis(triethyl phosphite) complex undergoes photosolvation when the MTLCT band is irradiated in pyridine to form [Fe(TIM)(py)₂]²⁺. The bis(imidazole) complex is photoinert. The photoreactivity of the Fe(II)-TIM complexes is discussed in terms of ligand field and charge-transfer excited-state origins. The temperature dependence of the quantum yield for the photosolvation of the bis(triethyl phosphite) complex in pyridine is examined. The quantum yield varies from 0.0018 at 10 °C to 0.0038 at 40 °C. The activation energy for the photoreaction is 4.1 kcal/mol.

Introduction

Six-coordinate low-spin d⁶ complexes of the first, second, and third transition series constitute the largest category of photochemically studied coordination complexes.^{1,2} With the use of strong-field ligands, Fe(II) can form low-spin six-coordinate complexes.³ To date, most of the photochemical studies of Fe(II) complexes, including those of Fe(II) macrocyclic complexes,⁴ have dealt with their photoredox properties.^{1,5}

Six-coordinate Fe(II) complexes containing the quadridentate, macrocyclic ligand TIM (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene), first synthesized by Rose et al.,⁶ were chosen in order to study the ligand substitution photochemistry of low-spin Fe(II). Since this strong-field macrocyclic ligand only adopts a planar configuration in the metal's coordination sphere,^{6,7} a variety of trans-disubstituted low-spin complexes can be prepared. Consequently, their photochemical properties can be examined and compared to those of other low-spin d⁶ metal systems.⁸

In addition to providing a number of low-spin d⁶ iron compounds, the Fe(II)-TIM system has two other important characteristics. First, it binds carbon monoxide. Photochemical studies of carbonyl complexes of iron macrocyclic

systems may provide a bridge between the photochemistry of the zerovalent metal carbonyls and the classical ionic "Werner" complexes. In addition, these ionic carbonyl complexes may act as model systems for the photoactivity of carbon monoxide on myoglobin and hemoglobin.^{5,9-12} Second, the most intense spectroscopic feature in the visible electronic absorption spectrum is an iron to TIM charge-transfer band. These complexes may help to further elucidate the effect of the CT excited state on ligand photosubstitution reactions.

Experimental Section

Synthesis. [Fe(TIM)(CH₃CN)₂](PF₆)₂, [Fe(TIM)(im)₂](PF₆)₂, and [Fe(TIM)CH₃CN(CO)](PF₆)₂ were prepared according to the methods of Baldwin et al.⁶

[Fe(TIM)(P(OEt)₃)₂](PF₆)₂. The bis(acetonitrile) complex (0.5 g) was dissolved in 10 mL of acetonitrile and filtered. Triethyl phosphite (2.5 mL) was added to the filtrate. In about 45 s, the solution turned from red to pink-purple. The solution was rotovapped at room temperature until crystals formed and then was filtered. The crystals were washed with diethyl ether and recrystallized from acetone and diethyl ether; yield 80%. Anal. Calcd for FeC₂₆H₅₄F₁₂N₄O₆P₄: C, 33.7; H, 5.8. Found: C, 33.9; H, 5.8.

[Fe(TIM)(NH₃)₂](PF₆)₂. Dry ammonia gas was vigorously bubbled through a filtered, saturated solution of the bis(acetonitrile) complex in CH₂Cl₂ until the solution was reduced to half its original volume.

Table I. Electronic Absorption Band Maxima of Fe(II)-TIM Complexes

Compd	Solvent	Maxima, nm (e)
[Fe(TIM)CH ₃ CN(CO)]-(PF ₆) ₂	Acetonitrile	431 (6200)
	Acetone	431, 550 sh
[Fe(TIM)(P(OEt) ₃) ₂](PF ₆) ₂	Acetonitrile	513 (9200), 388 sh
	Dichloro-methane	513, 400 sh
	Acetone	513, 400 sh
	Pyridine	513, 400 sh
[Fe(TIM)(CH ₃ CN) ₂](PF ₆) ₂	Acetonitrile	550 (9870), 513 (5766) 463 sh
[Fe(TIM)(im) ₂](PF ₆) ₂	DMA	658 (9550), 613 sh
[Fe(TIM)(NH ₃) ₂](PF ₆) ₂	Acetone	700 (5970), 638 sh

A baby blue powder was obtained when the solution was filtered. Anal. Calcd for FeC₁₄H₃₀F₁₂N₆P₂: C, 26.8; H, 4.8. Found: C, 27.1; H, 5.2.

Photochemistry. All solvents used in the photochemical studies were purified according to the methods described by Jolly.¹³ Each complex gave an accurate elemental analysis. All visible-ultraviolet spectra were recorded on a Cary 14. A 200-W mercury-xenon lamp was used for all irradiations. A 436-nm solution band-pass filter was used to irradiate into the 431-nm band of [Fe(TIM)CH₃CN(CO)](PF₆)₂.^{14a} The 669-nm band used to irradiate into the 670-nm band of the bis(imidazole) complex was isolated using the following filter system: 10 cm of a crystal violet solution (2.5 mg in 200 mL of 95% ethanol), 1 cm of 9,10-dibromoanthracene in toluene (20 mg in 100 mL), a Dirac 630.0-nm cutoff filter, and a Corning 1-69 filter. Irradiation into the 513-nm band of the bis(triethyl phosphite) complex was accomplished with the following filter system: 6 cm of NaNO₂ (30 g in 200 mL of water), a Dirac 500.0-nm cut-on filter, and a Dirac 540.0-nm cutoff filter. The band maximum of the filter system was 531 nm.

Determination of Quantum Yields. Before each photolysis, a stock solution (10⁻⁴ M) of the complex was prepared in the dark and maintained at the same temperature as the thermal holder of the photolysis cell: 10 °C for [Fe(TIM)CH₃CN(CO)](PF₆)₂ and [Fe(TIM)(im)₂](PF₆)₂ and room temperature for [Fe(TIM)(P(OEt)₃)₂](PF₆)₂. All samples to be photolyzed were drawn from the stock solution along with the thermal blanks. After each irradiation the optical density of an aliquot of the stock solution was measured. In all but a few cases, its optical density was equal within experimental error to that taken prior to the irradiation. However, over the time span of a complete study, consisting of up to 40 randomly selected irradiation periods ranging in time from 4 to 120 s, the optical density of the stock solution did change. This thermal reaction was small compared to the observed photochemical reaction and was taken into account for all quantum yield calculations. Concentration changes, both thermal and photochemical, were measured on a Hitachi Perkin-Elmer Model 139 UV-vis spectrophotometer by monitoring the metal-to-ligand charge transfer (MTLCT) band maximum of the complex.

Ferric oxalate actinometry^{14b} was used for the 436-nm irradiation, Reinecke actinometry¹⁵ for the 513-nm irradiations, and chromium urea¹⁵ actinometry for the 669-nm irradiations. All irradiations were carried out in the same 1-cm quartz cell. All photoreactions exhibited isobestic points in the electronic spectra.

Quantum yields were calculated from plots of the concentration of photoreactant vs. time. The amount of photoproduct produced in a given time interval was equal to the amount of photoreactant consumed in the interval. The number of photons absorbed by the photoreactant in the time interval was determined from the area under the curve. In the case of [Fe(TIM)MeCN(CO)](PF₆)₂ where inner

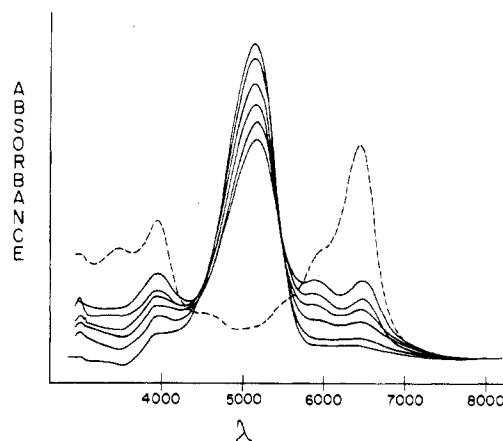


Figure 1. Electronic absorption spectra of [Fe(TIM)(P(OEt)₃)₂](PF₆)₂ in pyridine (—) and [Fe(TIM)(py)₂]²⁺ (---) offset to facilitate comparison. The decreases in absorbance at 5130 Å correspond to irradiations of the original sample and the sample after 2.5 h in the dark and irradiations of 15, 30, and 60 min, respectively.

filter effects were important,¹⁶ the amount of light absorbed by the interfering bis(acetonitrile) complex was subtracted from the total number of photons absorbed by the sample at 431 nm to give the number of photons absorbed by the [Fe(TIM)MeCN(CO)](PF₆)₂ complex.

Results

Electronic Absorption Spectra. The electronic absorption spectra of Fe(II)-TIM complexes are dominated by an intense absorption whose energy is dependent upon the axial ligands as shown in Table I. This band is assigned to an iron to TIM charge-transfer transition with the electron transfer occurring from the d_{xz} or d_{yz} orbital of the metal to a π-antibonding orbital of the α-dimine moiety of TIM.

In addition to the intense CT band, less intense bands which appear as shoulders on the main band are observed for several of the compounds. These shoulders are probably ligand field transitions (vide infra).

Photochemistry. All of the compounds exhibit some degree of thermal solvation. Three complexes, [Fe(TIM)(P(OEt)₃)₂](PF₆)₂, [Fe(TIM)(im)₂](PF₆)₂, and [Fe(TIM)CH₃CN(CO)](PF₆)₂, exhibit slow enough rates of solvation to permit accurate photochemical studies. For these complexes the optical density of a control solution kept in the dark at the same temperature as the photolyzed sample does not change during the time span of the photolysis. In contrast, the bis(ammonia) complex, a highly labile complex, is thermally completely solvated in less than 1 min at 0 °C in acetonitrile. In all cases the thermal and photochemical solvation products are identical. Quantitative results of the photochemical studies are given in Table II.

The photochemical reactions of the bis(triethyl phosphite) complex were studied qualitatively in dichloromethane and acetonitrile and quantitatively in pyridine. In all cases isobestic points were observed. In all of the solvents except pyridine the charge-transfer absorption band of the product developed near the main MTLCT band of the bis(triethyl phosphite) complex, shifting the peak maximum to lower

Table II. Quantum Yield Data

Photoreactant	Solvent	Product	Quantum yield	Temp, °C
[Fe(TIM)(im) ₂] ²⁺	DMA	No observable reaction	Less than 3 × 10 ⁻⁴	10
[Fe(TIM)CH ₃ CN(CO)] ²⁺	CH ₃ CN	[Fe(TIM)(CH ₃ CN) ₂] ²⁺	0.60 ± 0.06	10-25
	Acetone	Loss of CH ₃ CN	0.80 ± 0.30	25
[Fe(TIM)(P(OEt) ₃) ₂] ²⁺	py	[Fe(TIM)(py) ₂] ²⁺	0.0018	10
			0.0022	15
			0.0027	24
			0.0034	37
			0.0038	40

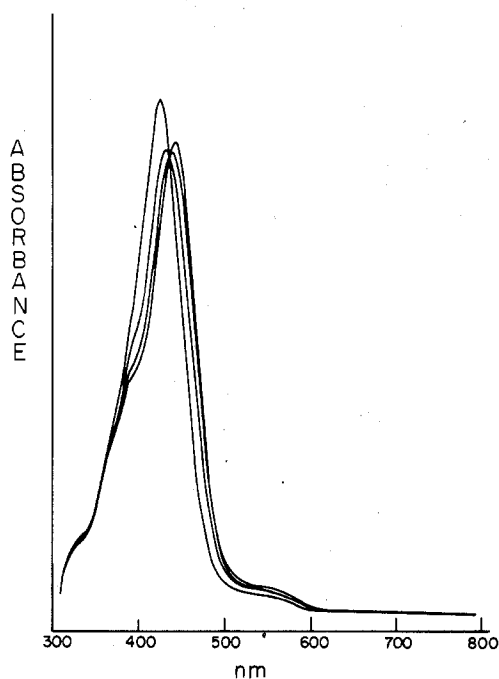


Figure 2. Electronic absorption spectral changes of $[\text{Fe}(\text{TIM})\text{-CH}_3\text{CN}(\text{CO})](\text{PF}_6)_2$ in acetone illustrating the small changes in the observed peak maximum to lower energies caused by increased irradiation times.

energy. The photoproduct in pyridine, $\text{Fe}(\text{TIM})(\text{py})_2^{2+}$, was identified by visible spectroscopy (Figure 1). The MTLCT bands of the photoproduct coincided with those of $\text{Fe}(\text{TIM})(\text{py})_2^{2+}$ formed by dissolving the bis(acetonitrile) complex in neat pyridine. The photochemical reaction was unaffected by the presence of oxygen or water.

The photochemistry of the bis(imidazole) complex was studied in dimethylacetamide (DMA). In the dark, a slow thermal reaction took place to form a solvation product. No measurable photochemical reaction occurred when the bis(imidazole) complex was irradiated in the MTLCT band. The upper limit to the quantum yield of loss of the bis(imidazole) complex was 3×10^{-4} .

The photochemistry of $[\text{Fe}(\text{TIM})\text{MeCN}(\text{CO})](\text{PF}_6)_2$ is unique because it shows different modes of reactivity in different solvents. In both solvents studied, the photoreactions are identical with the corresponding thermal reactions, loss of CO in acetonitrile and loss of acetonitrile in acetone. In acetonitrile the photoreaction produces the bis(acetonitrile) complex with an isosbestic point at 463 nm in the electronic absorption spectrum. In acetone the photoreaction was again clean (Figure 2) with the MTLCT band gradually shifting a few nanometers to lower energy as the photolysis proceeds. In addition, the reaction in acetone shows a slow shift of the carbonyl stretching frequency to lower energy as the reaction proceeds. The photoproduct's peak occurs at 2020 cm^{-1} , 8 cm^{-1} lower in energy than that of the reactant. Both the small electronic spectral shift and the IR peak characteristic of a coordinated carbonyl indicate that the carbonyl ligand is not lost in the photosolvation reaction. The photoproduct is probably either five-coordinate $[\text{Fe}(\text{TIM})\text{CO}]^{2+}$ or six-coordinate $[\text{Fe}(\text{TIM})(\text{acetone})(\text{CO})]^{2+}$ where acetone is weakly coordinated.

Numerous unsuccessful attempts were made to determine the extent of the photolabilization of the coordinated nitrile ligand in acetonitrile. Substituted nitriles such as benzonitrile, trimethylacetonitrile, and propionitrile were coordinated trans to carbon monoxide. Mass spectrometry, gas chromatography, and electronic spectroscopy were not sensitive enough to detect the photochemical labilization of the coordinated nitrile ligand

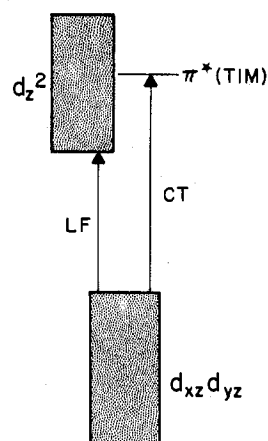


Figure 3. A one-electron energy level diagram for the orbitals involved in the low-energy electronic transitions of $\text{Fe}(\text{II})\text{-TIM}$ complexes.

in acetonitrile and were hampered by the thermal lability of the coordinated substituted nitriles.

Temperature Dependence of Quantum Yields. The quantum yield for the photoproduction of $[\text{Fe}(\text{TIM})(\text{py})_2]^{2+}$ from $[\text{Fe}(\text{TIM})(\text{P}(\text{OEt})_3)_2]^{2+}$ in pyridine is temperature dependent, ranging from 0.0018 at 10°C to 0.0038 at 40°C (Table II). The quantum yield for the photolabilization of carbon monoxide from $[\text{Fe}(\text{TIM})\text{MeCN}(\text{CO})](\text{PF}_6)_2$ in acetonitrile shows no temperature dependence in the range from 10 to 25°C . Temperatures higher than 25°C could not be studied because of competing thermal reactions.

Discussion

Spectroscopic Assignments. The visible absorption spectra of $\text{Fe}(\text{II})\text{-TIM}$ complexes consist of both metal to ligand charge-transfer and ligand field (LF) transitions. The transitions are discussed in terms of the qualitative one-electron orbital diagram given in Figure 3.

The visible spectrum of each of the five $\text{Fe}(\text{II})\text{-TIM}$ complexes studied has as its predominant feature an intense band (ϵ 5000–10 000 $\text{L cm}^{-1} \text{ mol}^{-1}$) characteristic of the MTLCT in iron(II)- α -diimine complexes.¹⁷ This intense CT band is assigned as a MTLCT where an electron is transferred from a d_{xy} or d_{yz} orbital of π symmetry on the metal to an empty π^* orbital of the α -diimine moiety.^{17–19} The energy of the MTLCT band is dependent upon the π -acceptor ability of the axial ligands. As the π -acceptor ability increases, the energy of the d_{xz} and d_{yz} orbitals decreases relative to that of the $\pi^*(\text{TIM})$ orbital, causing the MTLCT band to move to higher energies.²⁰

Ligand field transitions are also expected in the visible absorption spectrum. The lowest energy d-d transitions in tris(diimine) complexes are generally centered between 600 and 900 nm.^{18,21–23} The energy of the d_{xz} or $d_{yz} \rightarrow d_{z^2}$ LF transition will not only be affected by the π -bonding ability of the axial ligand but also by its σ -bonding ability. As the σ -donor ability of the axial ligand increases, the d_{z^2} orbital will move to higher energy relative to that of the d_{xz} , d_{yz} orbitals. Because of this dual dependence on the axial ligand's σ and π interactions, the LF transition energies will not, in general, parallel those of the CT.

The one-electron model can be used to interpret the spectroscopy of the $\text{Fe}(\text{II})\text{-TIM}$ complexes. In $[\text{Fe}(\text{TIM})\text{-CH}_3\text{CN}(\text{CO})](\text{PF}_6)_2$ the d_{xz} and d_{yz} orbitals are strongly stabilized by the π -accepting ability of CO, giving rise to the highest energy MTLCT transition observed in the series (431 nm). A low-intensity peak is observed at 550 nm for this complex in acetone and by Rose in nitromethane.²⁴ It is uncertain whether this low-energy transition is a d-d transition or the charge-transfer transition from trace $\text{Fe}(\text{TIM})\text{-}$

(CH₃CN)₂²⁺ impurities. In the bis(imidazole) complex, the MTLCT band is found at a lower energy (658 nm) than that of the suspected $d_{yz}d_{xz} \rightarrow d_z$ transition (613 nm). This ordering is due to the poor π -acceptor properties and the strong σ -donating ability of the nitrogens in imidazole. The spectroscopic properties of bis(triethyl phosphite) complex lie between those of [Fe(TIM)CH₃CN(CO)](PF₆)₂ and [Fe(TIM)(im)₂](PF₆)₂. The ligand π -acceptor abilities decrease in the order CO > P(OEt)₃ > CH₃CN > im > NH₃.

Photochemistry. Interpretation of the Reactivity. The quantum yields of the Fe(II)-TIM complexes studied here range from 0.60 to less than 3×10^{-4} . The observed behavior can be interpreted using two different explanations: ligand labilization caused by populating antibonding orbitals in ligand field excited states or reactivity caused by formally oxidizing the metal thereby decreasing metal-ligand π back-bonding in the excited state.

The interpretation based upon the ligand field excited states requires that there be rapid energy transfer from the directly populated photoinactive charge-transfer excited state to a lower lying ligand field excited state. The lowest energy ligand field state has bonding properties different from those of the ground state: weakened metal-ligand σ bonding caused by the population of the d_z σ -antibonding orbital and weakened (or strengthened) metal-axial ligand π bonding caused by depopulation of the d_{xz} and d_{yz} π bonding (or antibonding) orbitals, respectively. Theoretical treatments of ligand field reactivity have been published.^{1,2,25-28}

According to the ligand field interpretation, when the ligand field excited state is lower in energy than the CT excited state, the former will be populated and axial ligand labilization will occur.²⁵⁻²⁸ If the ligand field state is higher in energy than the CT state, the latter will be populated and no ligand labilization will occur. The relative energies of the MTLCT and the LF transitions are "tuned" by the π -acceptor and σ -donor abilities of the axial ligands. Similar tuning of the excited-state energies and photochemical reactivity has been demonstrated for Ru(NH₃)₅X²⁺^{29,30} and W(CO)₅X³⁺ d⁶ complexes (X = substituted pyridine), where the energy of the metal to unique ligand charge-transfer transition was varied by changing the substituents on the pyridine ligand. [Fe(TIM)CH₃CN(CO)](PF₆)₂ and [Fe(TIM)(P(OEt)₃)₂](PF₆)₂ would be reactive because their CT excited states are respectively higher than and equal to the energies of their LF states. The bis(imidazole) complex would be photoinactive because its CT band is lower in energy than its LF band.

The second interpretation of the reactivity patterns is based on the reactivity expected from the formally oxidized iron center. Populating the MTLCT excited state will remove an electron from the degenerate d_{xz} or d_{yz} orbitals of the metal causing a loss of π bonding along the z axis for π -acceptor ligands. In addition, the metal will be oxidized from Fe(II) to Fe(III) thereby decreasing the amount of π back-bonding and increasing the σ -bonding interactions. Both effects would be expected to weaken the metal-ligand bonds for good π -acceptor ligands like CO and triethyl phosphite. Ligands with poor π -back-bonding characteristics but strong σ -donor properties such as imidazole would not be affected by π -bonding changes but would have increased σ bonding due to the metal being in a higher formal oxidation state. Thus, the photoactivity of the complexes containing π -acceptor ligands and the photoactivity of the complex containing strong σ -donor ligands could be explained in terms of reactivity directly out of a CT excited state.

Definitive experimental differentiation between the two explanations of the reactivity cannot be made because of the extreme thermal lability of many of the complexes and the difficulty in synthesizing as wide of a variety of substituted

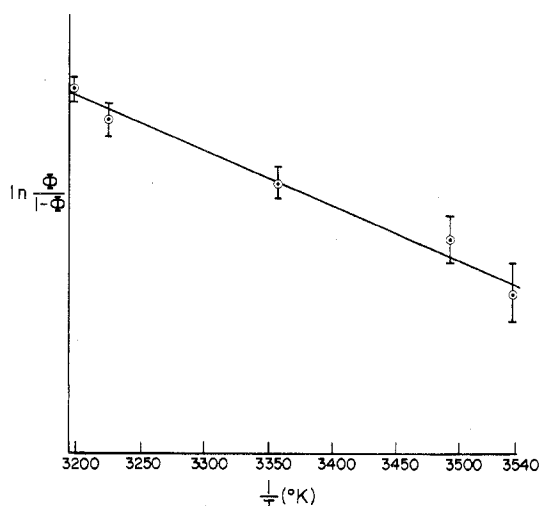


Figure 4. Plot of the experimental values of $\ln(\Phi/(1-\Phi))$ vs. $1/T$ (K^{-1}) for the photoreaction of [Fe(TIM)(P(OEt)₃)₂]²⁺ in pyridine.

Fe(II)-TIM complexes as would be desired. On the basis of our available data, we favor the ligand field bond labilization explanation. The primary argument against the CT explanation is that the acetonitrile ligand is readily labilized from [Fe(TIM)CH₃CN(CO)](PF₆)₂ in acetone.

Temperature Dependence. The rate constant of a photochemical reaction, k_r , for a nonphotoluminescent complex can be expressed in terms of the reaction quantum yield, Φ , and the rate constant of the nonradiative, nonreaction processes, k_n , as shown in eq 1. The temperature dependence of the rate

$$k_r = \frac{\Phi k_n}{1 - \Phi} \quad (1)$$

of reaction is commonly expressed in terms of the Arrhenius equation (eq 2) where E_a is the activation energy. Substituting

$$k = A e^{-E_a/RT} \quad (2)$$

eq 1 into eq 2 yields a relationship between the reaction quantum yield and the temperature

$$\frac{k_n \Phi}{1 - \Phi} = A e^{-E_a/RT} \quad (3)$$

The point-slope form of eq 3 is

$$\ln\left(\frac{\Phi}{1 - \Phi}\right) = \frac{-E_a}{R} \left(\frac{1}{T}\right) + \ln\left(\frac{A}{k_n}\right) \quad (4)$$

A plot of the experimental values of $\ln(\Phi/(1-\Phi))$ vs. the inverse of the absolute temperature gives a straight line with a r^2 coefficient of 0.98 as shown in Figure 4. The energy of activation obtained from the plot is 4.1 ± 0.7 kcal/mol. The energy of activation for the thermal reaction is 23.4 kcal/mol.

The temperature dependence of the viscosity of a liquid is

$$\eta = A' e^{\Delta E_{vis}/RT} \quad (5)$$

where η is the coefficient of viscosity measured in centipoise, A' is an undetermined constant, and ΔE_{vis} is the energy of activation for viscous flow.³² For pyridine, ΔE_{vis} is 2.4 kcal/mol as calculated from the data given by Telang.³³

The photosolvation of [Fe(TIM)(P(OEt)₃)₂](PF₆)₂ in pyridine can be considered to be diffusion controlled due to the closeness in energy of the photochemical activation energy and ΔE_{vis} . That E_a is larger than ΔE_{vis} may be due to the larger bulk of triethyl phosphite compared to that of pyridine which could cause the energy of the diffusion process to be slightly larger.

The photosolvation of $[\text{Fe}(\text{TlM})\text{MeCN}(\text{CO})]^{2+}$ in acetonitrile shows no temperature dependence over the temperature range studied, 10–25 °C. The lack of an observed temperature dependence may be due to the small temperature range examined. If the excited-state activation energy is small, the change of k_r over the temperature range studied could be insignificant.

Acknowledgment. We are grateful to the UCLA research committee for support of this work. J. I. Zink gratefully acknowledges the support provided by the Camille and Henry Dreyfus Teacher-Scholar Award, 1974–1979. We thank Professor Norman Rose for helpful discussions.

Registry No. $[\text{Fe}(\text{TlM})\text{CH}_3\text{CN}(\text{CO})](\text{PF}_6)_2$, 43223-43-4; $[\text{Fe}(\text{TlM})(\text{P}(\text{OEt})_3)_2](\text{PF}_6)_2$, 64070-43-5; $[\text{Fe}(\text{TlM})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$, 43223-41-2; $[\text{Fe}(\text{TlM})(\text{im})_2](\text{PF}_6)_2$, 43223-42-3; $[\text{Fe}(\text{TlM})(\text{NH}_3)_2](\text{PF}_6)_2$, 64070-41-3; $[\text{Fe}(\text{TlM})(\text{py})_2](\text{PF}_6)_2$, 64070-39-9.

References and Notes

- V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y., 1970.
- A. W. Adamson and P. O. Fleischer, "Concepts of Inorganic Photochemistry", Wiley, New York, N.Y., 1975.
- F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry: A Comprehensive Text", 3rd ed, Interscience, New York, N.Y., 1972, pp 860–863.
- D. Reichgott and N. J. Rose, *J. Am. Chem. Soc.*, **99**, 1813 (1977).
- D. V. Stynes, *J. Am. Chem. Soc.*, **96**, 5942 (1974).
- D. A. Baldwin, R. M. Pfeiffer, D. W. Reichgott, and N. J. Rose, *J. Am. Chem. Soc.*, **95**, 5152 (1973).
- (a) S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **11**, 2893 (1972); (b) D. P. Rillema and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 8711 (1972).
- J. I. Zink, D. Schwendiman, and M. J. Incorvia, Abstracts, 169th National Meeting of the American Chemical Society, Philadelphia, Pa., 1975, No. INOR 143; J. I. Zink and M. J. Incorvia, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., 1976, No. INOR 37.
- M. T. Wilson, M. Brunori, J. Bonaventura, and C. Bonaventura, *Biochem. J.*, **131**, 863 (1973); C. Bonaventura, J. Bonaventura, E. Antonini, M. Brunori, and J. Wyman, *Biochemistry*, **12**, 3424 (1973).
- A. Szabo and M. Karplus, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 673 (1973).
- M. Brunori, J. Bonaventura, C. Bonaventura, E. Antonini, and J. Wyman, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 868 (1972).
- G. M. Giacometti, A. Focesi, Jr., M. Brunori, and J. Wyman, *J. Mol. Biol.*, **98**, 333 (1975).
- W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1970, pp 114–121.
- J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1967: (a) p 737; (b) pp 783–786.
- E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
- V. O. Kling, E. Nikolaiski, and H. L. Schläfer, *Ber. Bunsenges. Phys. Chem.*, **67**, 883 (1963).
- D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956).
- P. Krumholz, *Struct. Bonding (Berlin)*, **9**, 139 (1971).
- J. C. Dabrowiak and D. H. Busch, *Inorg. Chem.*, **14**, 1881 (1975).
- D. F. Shriver and J. Posner, *J. Am. Chem. Soc.*, **88**, 1672 (1966).
- T. Ito and N. Tanaka, *J. Inorg. Nucl. Chem.*, **32**, 155 (1970).
- R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966).
- P. Krumholz, O. A. Serra, and M. A. DePaoli, *Inorg. Chim. Acta*, **15**, 25 (1975).
- N. J. Rose, private communication.
- J. I. Zink, *J. Am. Chem. Soc.*, **94**, 8039 (1972); *Inorg. Chem.*, **12**, 1018 (1973); *J. Am. Chem. Soc.*, **96**, 4464 (1974); *Inorg. Chem.*, **14**, 446 (1975).
- M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 165 (1973).
- M. J. Incorvia and J. I. Zink, *Inorg. Chem.*, **13**, 2489 (1974).
- N. Rösch, R. P. Messmer, and K. H. Johnson, *J. Am. Chem. Soc.*, **96**, 3855 (1974).
- T. L. Kelly and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 1797 (1972).
- G. Malouf and P. C. Ford, *J. Am. Chem. Soc.*, **96**, 601 (1974).
- M. S. Wrighton, H. B. Abramson, and D. L. Morse, *J. Am. Chem. Soc.*, **98**, 4105 (1976).
- G. M. Barrow, "Physical Chemistry", 2nd ed, McGraw-Hill, San Francisco, Calif., 1966, pp 544–545.
- M. S. Telang, *J. Phys. Chem.*, **50**, 373 (1946).

Contribution No. 3835 from the Department of Chemistry, University of California, Los Angeles, California 90024

Charge-Transfer Photochemistry of Halonitrosylbis(*o*-phenylenebis(dimethylarsine))iron(II)

PO-HSIN LIU and JEFFREY I. ZINK*

Received May 26, 1977

AIC70386B

Charge-transfer band irradiation of solutions of $[\text{Fe}^{\text{II}}\text{X}(\text{NO})(\text{das})_2](\text{ClO}_4)_2$ (X = Cl, Br, or I and das = *o*-phenylenebis(dimethylarsine)) in acetone, acidified methanol, and acidified methanol containing excess halide ions produces $[\text{Fe}^{\text{III}}\text{X}_2(\text{das})_2]^+$. The quantum yield is independent of wavelength (255, 313, 366, 405, and 435 nm), the concentration of starting material, the incident light intensity, and the concentration of halide ion. However, the quantum yield is sensitive to the solvents and to the halide ligands. The photoactive excited state is assigned to the $b_2(d_{xy}) \rightarrow e(\pi^*(\text{NO}))$ transition which causes the formal oxidation of Fe(II) to Fe(III) and the formal reduction of NO^+ to NO radical. Mechanisms of the reaction are discussed.

The photoreactivity of charge-transfer excited states of transition-metal complexes is poorly understood in comparison with the photoreactions originating from ligand field excited states.¹ Whereas the latter excited states most commonly lead to ligand labilization¹ caused by population of metal–ligand antibonding orbitals, the former can lead to photoredox processes in addition to ligand labilization. For example, photoexcitation into ligand to metal charge-transfer (LTMCT) excited states of tris(dithiocarbamate)iron(III) complexes led to a series of reactions which were interpreted in terms of free radical ligands and a reduced metal center in the excited state.^{4–6} Similarly, the metal to ligand charge-transfer (MTLCT) photochemistry of hexakis(aryl isocyanide) complexes of group 6B metals was interpreted in terms of a

formally oxidized metal center.⁷ The charge-transfer photochemistry of complexes containing more classical ligands has recently been reviewed.¹

Low-lying MTLCT excited states are in general expected in complexes containing good π -acceptor ligands which are coordinated to metals in low oxidation states. The nitrosyl ligand was chosen for study because it fulfills the qualities of being a good π acceptor. Although the ground-state properties of metal nitrosyl complexes have been well studied and are well explained by the Enemark–Feltham theory,⁸ excited-state properties have not received much attention. Quantitative studies of the photochemistry of nitrosyltetracarbonylmanganese⁹ and pentacyanonitrosylferrate¹⁰ have been reported. The former compound undergoes photosubstitution