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Photochemistry of Low-Spin Iron(III) Complexes with Macrocyclic Ligands

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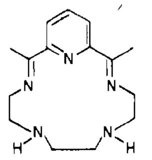
Received March 26, 1980

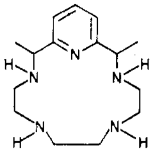
The charge-transfer photochemistries of $Fe(TIM)(OCH_3)CH_3OH^{2+}$ and $Fe(DMG)_2(OCH_3)CH_3OH$ can be described as a photooxidation of coordinated methanol and the reduction of the metal center. Reduction of $Fe(TIM)(OCH_3)CH_3OH^{2+}$ by hydroxymethyl radicals ($k = 1.9 \times 10^6$ M^{-1} s^{-1}) and the reoxidation of the Fe(II)–TIM product by dioxygen were investigated by flash photolysis. Quantum yields of the photolysis products were determined as a function of the excitation wavelength. Limiting yields $\phi_L = 4.0 \times 10^{-2}$ for $Fe(TIM)(OCH_3)CH_3OH^{2+}$ and $\phi_L = 7.0 \times 10^{-2}$ for $Fe(DMG)_2(OCH_3)CH_3OH$ were obtained for photonic energies larger than or equal to 76.3 kcal/mol. The photochemical properties of these complexes are attributed to the population of charge-transfer methoxy to iron(III) states.

Introduction

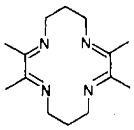
The charge-transfer photochemistry of iron(III) complexes has been extensively investigated.[1-12] The photochemical properties of high-spin iron(III) complexes of the macrocyclic ligands [15]pydieneN_5 (I) and [15]pyaneN_5 (II) have been recently reported.[12] These studies show that the oxidation of ligands coordinated in axial positions, namely, Cl^-, Br^-, I^-, and N_3^-, is the most significant photoreaction. The threshold energies of these processes have been correlated with the electroaffinity of the radical formed in the photooxidation of the ligand and with structural features which depend on the nature of the macrocycle.



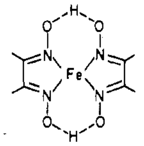
[15] pydiene N_5 (I)



[15] pyane N_5 (II)



TIM (III)



Fe(DMG)$_2$ (IV)

The photochemistries of low-spin iron(III) complexes of the TIM (III) and DMG^- (IV) ligands have been investigated in this work.[13] Previous studies have demonstrated that irradiations of $Fe(TIM)(OCH_3)CH_3OH^{2+}$ with sunlight produce the oxidation of coordinated methanol.[3] A similar photoprocess was found for $Fe(DMG)_2(OCH_3)CH_3OH$. These photoreactions have been attributed to the population of methoxy to iron(III) charge-transfer states.

Experimental Section

Photochemical Procedures. A description of the continuous wave and flash photolysis apparatuses was given elsewhere.[12] The light intensities were measured with tris(oxalato)ferrate(III) and Reinecke's salt.[14,15]

Cells with a slab geometry and 1-cm optical path were used for continuous wave irradiations. The optical density of the solutions was adjusted in order to absorb more than 99.9% of the light. Quantum yields were determined from the slope of the product concentration vs. irradiation time curves, extrapolated to zero irradiation time.

Dioxygen was removed from the photolyte solutions with streams of solvent-saturated argon or with three freeze-thaw cycles. The deaerated liquids were handled in a gastight apparatus.

Electrochemical Procedures. The electromotive force of the cells was measured either by potentiometry or with a high-impedance Beckman pH meter. A calomel electrode was used as a reference electrode. The working electrode was a platinum wire immersed in a methanolic solution of the photolyte. The reference and working hemicells were in contact through a salt bridge made with two solutions, 0.1 M KCl in methanol and a saturated aqueous solution of KCl, respectively.

Analytical Procedures. Formaldehyde was distilled under vacuum and at room temperature from irradiated solutions. Blanks were obtained with solutions kept in the dark. The formaldehyde, collected together with methanol, was analyzed with chromotropic acid.[16]

Iron(II) was measured with 1,10-phenanthroline.[17] The disappearance of the iron(III) complexes in continuous-wave irradiations was determined by means of the ultraviolet absorbances. Cells with 0.2-cm optical path were used for these determinations.[12]

Materials. $[Fe(TIM)(CH_3CN)_2](ClO_4)_2$ and $[Fe(TIM)(OCH_3)CH_3OH](ClO_4)_2 \cdot {}^1/_2H_2O$ were prepared according to the procedures indicated by Rose et al.[3,18] The spectra of these complexes agreed with previous reports.

$Fe(DMG)_2(OCH_3)CH_3OH$ was obtained by adding small fractions of anhydrous $Fe(ClO_4)_3$ (4.0 g) to a methanolic solution of NaDMG (4.5 g). The slow evaporation of the solvent was required in some preparations in order to induce the precipitation of the complex. The brown solid was dried under vacuum. Anal. Calcd for $FeC_{10}N_4H_{21}O_6$: Fe, 19.05. Found: Fe, 19.10.

Spectrometric quality methanol (Aldrich Gold Label) was used without further purification. Other chemicals were analytical grade and used without purification.

Results

a. Continuous Photolysis. Photolyses with monochromatic light, $\lambda_{excit} \leq 500$ nm, of deaerated solutions of Fe(TIM)-

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(13) Abbreviations: TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; DMG^- = dimethylglyoxime.

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Table I. Quantum Yields for Irradiations of $Fe(TIM)(OCH_3)CH_3OH^{2+}$ and $Fe(DMG)_2(OCH_3)CH_3OH$ in Deaerated Methanolic Solutions

λ_{excit}, nm	$10^4 I_0$, einsteins/(L min)	$10^2\phi_{Fe(II)}$	$10^2\phi_{CH_2O}$	$10^2\phi_{Fe(III)}$	conditions[a]
		(a) $Fe(TIM)(OCH_3)CH_3OH^{2+}$			
470	6.0	0.15 ± 0.04	nd[b]	nd	10^{-4} M NaOH
450	6.4	0.42 ± 0.03	0.21 ± 0.03	0.40 ± 0.03	
450		0.57 ± 0.04	0.30 ± 0.02	nd	10^{-6} M NaOH
450		0.85 ± 0.04	0.36 ± 0.03	nd	10^{-5} M NaOH
450		0.84 ± 0.03	0.35 ± 0.03	1.0 ± 0.2	10^{-4} M NaOH
420	3.8	1.0 ± 0.2	nd	nd	10^{-4} M NaOH
390	3.8	1.9 ± 0.2	1.0 ± 0.1	1.8 ± 0.2	
390		3.7 ± 0.3	1.6 ± 0.1	nd	10^{-4} M NaOH
350	3.0	3.9 ± 0.2	nd	nd	10^{-4} M NaOH
320	0.2	3.7 ± 0.3	1.8 ± 0.2	nd	10^{-4} M NaOH
	3.8	3.5 ± 0.3	1.9 ± 0.1	3.2 ± 0.2	10^{-4} M NaOH
		1.8 ± 0.2	0.95 ± 0.05	nd	
300	6.1	3.8 ± 0.4	1.7 ± 0.3	3.6 ± 0.3	10^{-4} M NaOH
		2.0 ± 0.2	1.1 ± 0.1	nd	
280	0.7	3.7 ± 0.1	1.7 ± 0.2	3.9 ± 0.4	10^{-4} M NaOH
		1.8 ± 0.2	nd	2.2 ± 0.3	
		(b) $Fe(DMG)_2(OCH_3)CH_3OH$			
470	6.0	0.04 ± 0.01	0.020 ± 0.005	nd	
450	6.4	0.33 ± 0.03	0.17 ± 0.02	0.30 ± 0.02	
420	3.8	2.5 ± 0.2	1.1 ± 0.3	nd	
400	3.9	4.2 ± 0.2	1.9 ± 0.2	nd	
350	3.0	5.2 ± 0.3	2.6 ± 0.3	5.0 ± 0.2	
300	6.1	5.4 ± 0.3	2.5 ± 0.2	5.0 ± 0.3	

[a] Solutions made in neutral methanol unless specially stated. [b] nd = not determined.

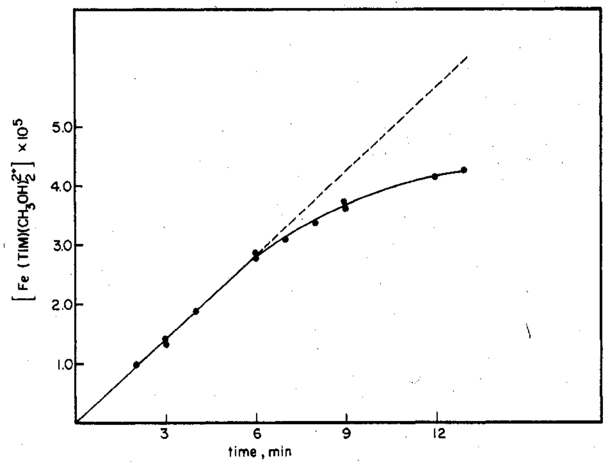

Figure 1. Formation of $Fe(TIM)(CH_3OH)_2^{2+}$ in irradiations of 10^{-3} M $Fe(TIM)(OCH_3)CH_3OH^{2+}$ in deaerated methanol; λ_{excit} = 300 nm.

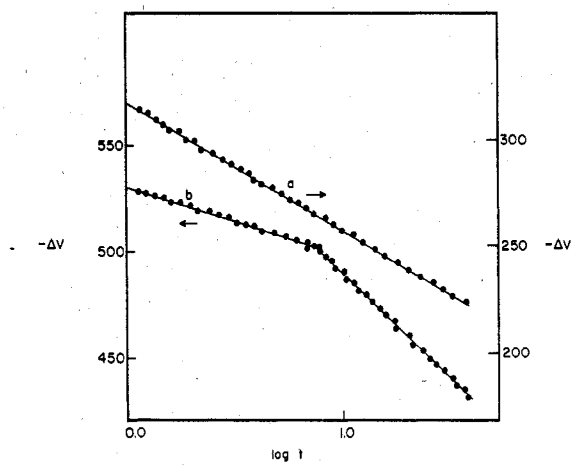

Figure 2. Variation of the electrochemical potential of cells Fe(III)/Fe(II) (calomel electrode (saturated KCl) with the logarithm of the irradiation time): (a) $Fe(TIM)(OCH_3)CH_3OH^{2+}$, λ_{excit} = 360 nm; (b) $Fe(DMG)_2(OCH_3)CH_3OH$, λ_{excit} = 360 nm.

$(OCH_3)CH_3OH^{2+}$ in methanol produce $Fe(TIM)(CH_3OH)_2^{2+}$ and CH_2O. These solutions were irradiated for short periods which resulted in conversions to products smaller than 5%. Conversions larger than 5% produce a significant curvature in product concentration vs. irradiation time plots (Figure 1). This deviation from a linear behavior is probably caused by inner filter effects due to the large absorptivities of the Fe(II) product. In this regard, quantum yields had to be determined by extrapolating to a zero irradiation time.

The yields of the iron(II) product, $\phi_{Fe(II)}$, and formaldehyde, ϕ_{CH_2O}, were in the same stoichiometric relationship, for excitations at distinct wavelengths, 280 nm ≤ λ_{excit} ≤ 520 nm (eq 1 and Table I). In addition the yield for the disappearance

$$\phi_{Fe(II)} = (2.1 \pm 0.3)\phi_{CH_2O} \qquad (1)$$

of $Fe(TIM)(OCH_3)CH_3OH^{2+}$, $\phi_{Fe(III)}$, is in a 1:1 relationship with the yield of the Fe(II) product. Therefore, the reaction stoichiometry between product yields is that expected for the photooxidation of methanol to formaldehyde.

The yield of the Fe(II) and formaldehyde exhibited a marked dependence on the acid concentration. Product yields in basic solutions are larger than those measured in neutral solutions (Table I). Part of this increase in the efficiency of the photoredox reaction can be attributed to a reaction of hydroxymethyl radicals with $Fe(TIM)(OCH_3)CH_3OH^{2+}$ (see below).

Also, the irradiation of $Fe(DMG)_2(OCH_3)CH_3OH$ in methanol produces the reduction of the complex to iron(II) and the oxidation of methanol to formaldehyde. Product yields are in the appropriate stoichiometric relationship for such a photoredox process (eq 2 and Table I). Moreover, the iron(II) and formaldehyde yields were insensitive to complex concentration and extent of the irradiation.

$$\phi_{Fe(II)} = (1.8 \pm 0.2)\phi_{CH_2O} \qquad (2)$$

The photochemical transformations of $Fe(TIM)(OCH_3)CH_3OH^{2+}$ and $Fe(DMG)_2(OCH_3)CH_3OH$ were followed by

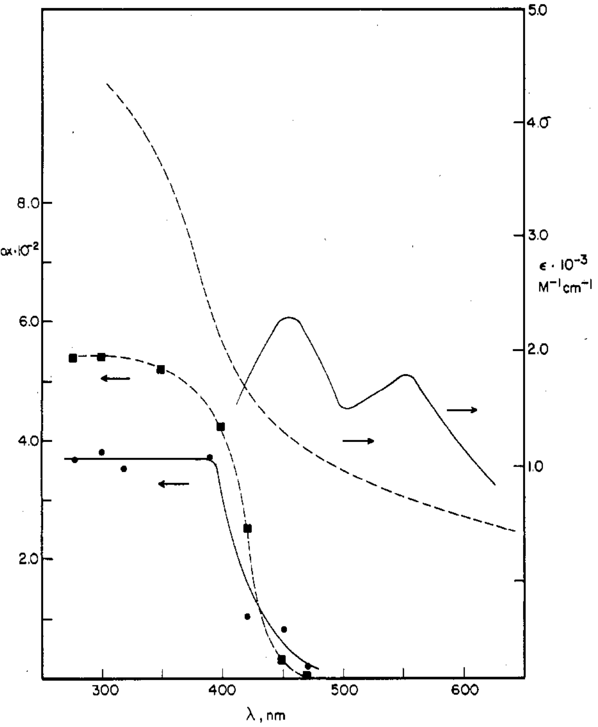

Figure 3. Absorption spectrum and quantum yield dependence on excitation wavelength for $Fe(TIM)(OCH_3)CH_3OH^{2+}$ (—) and $Fe(DMG)_2(OCH_3)CH_3OH$ (---). Yields of $Fe(TIM)(CH_3OH)_2^{2+}$ were obtained in photolyses of $Fe(TIM)(OCH_3)CH_3OH^{2+}$ in 10^{-4} M NaOH; see Table I for other conditions.

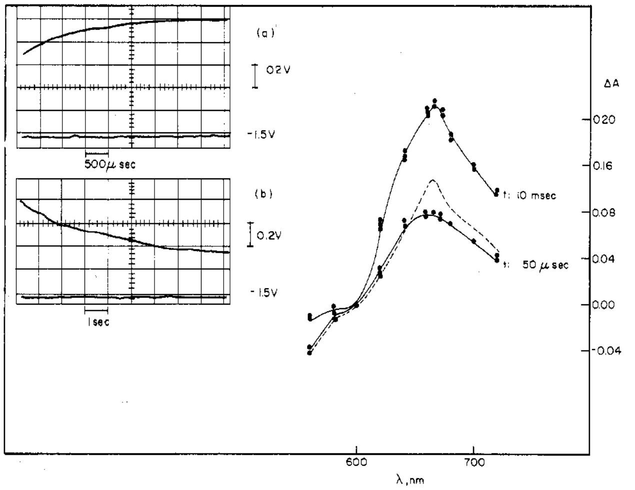

Figure 4. Transient spectrum obtained in flash photolysis of $Fe(TIM)(OCH_3)CH_3OH^{2+}$ in deaerated methanolic solutions at 50-ηs and 10-ms reaction times. The dashed curve shows the spectrum at 150 ms obtained in aerated solutions. Inserts: (a) transient formation of $Fe(TIM)(CH_3OH)_2^{2+}$ in flash irradiations ($\lambda_{excit} > 240$ nm) of $Fe(TIM)(OCH_3)CH_3OH^{2+}$; (b) oxidation of $Fe(TIM)(CH_3OH)_2^{2+}$ in aerated solutions. The reactions were followed at 660 nm.

Table II. Transient Kinetics in the Oxidation of $Fe(TIM)(CH_3OH)_2^{2+}$ in Methanolic Solutions

ΔA_0	$t_{1/2,SLS}$,[b,c] s	$t_{1/2,LLS}$,[b,c] s	conditions[a]
0.147	0.17	4.0	250 J/pulse
0.152	0.17	4.0	250 J/pulse, $[O_2] = 2.5 \times 10^{-3}$ M
0.088	0.20	3.8	122 J/pulse
0.062	0.28	4.2	63 J/pulse
0.150	0.11	5.5	250 J/pulse, 5×10^{-6} M NaOH
0.153	0.13	60.0	250 J/pulse, 10^{-5} M NaOH

[a] Solutions contain 2.5×10^{-3} M O_2 in neutral methanol unless stated. Irradiations of $Fe(TIM)(OCH_3)CH_3OH^{2+}$ at $\lambda \geqslant 240$ nm. [b] Reaction followed at 670 nm. [c] SLS = short-lived stage; LLS = long-lived stage.

means of the redox potentials, ΔV, of electrochemical cells. The change ΔV exhibited a linear dependence in the logarithm of the irradiation time for photolyses of $Fe(TIM)(OCH_3)CH_3OH^{2+}$ (Figure 2). However, irradiations of $Fe(DMG)_2(OCH_3)CH_3OH$ gave plots of ΔV vs. log t which exhibited deviations from linearity (Figure 2). These deviations can be associated with labile equilibria between various iron(III) species.

The photochemical reactivity of the TIM and DMG complexes was investigated for excitations with various photonic energies. Limiting yields, $\phi_L = 4.0 \times 10^{-2}$ for $Fe(TIM)(OCH_3)CH_3OH^{2+}$ and $\phi_L = 7.0 \times 10^{-2}$ for $Fe(DMG)_2(OCH_3)CH_3OH$, were obtained for excitation with photonic energies larger than or equal to 76.3 kcal/mol. However, thresholds for photochemical reactivity were found at photonic energies smaller than 76 kcal/mol but still larger than the thresholds for charge-transfer absorption (Figure 3).

b. Flash Photolysis. Deaerated solutions of $Fe(TIM)(OCH_3)CH_3OH^{2+}$ in methanol were irradiated at wavelengths longer than 320 nm. A growth of the solution absorbance, $\lambda_{max} \approx 670$ nm, was observed after the flash irradiation, namely at 50-μs reaction time (Figure 4). Moreover, a transient growth was detected at reaction times longer than 50 μs for irradiations of the complex in basic solutions (Figure 4). The spectral changes can be attributed to $Fe(TIM)(CH_3OH)_2^{2+}$ which is formed by both the flash irradiation and a slow reaction of the iron(III) complex with hydroxymethyl radicals. Indeed, a second-order rate constant $k = 1.9 \times 10^6$ M^{-1} s^{-1} was obtained from the linear dependence of the reaction rate on $Fe(TIM)(OCH_3)CH_3OH^{2+}$ concentration.

The oxidation of the flash photolytically generated $Fe(TIM)(CH_3OH)_2^{2+}$ by dioxygen was investigated in aerated solutions, $[O_2] \simeq 2.5 \times 10^{-3}$ M. The decay of the 670 nm absorbance takes place in two successive stages. The rate of the short-lived stage was independent of base concentration and exhibited a second-order dependence on the initial concentration of iron(II) complex (Table II). A ratio of the rate constant to the extinction coefficient, $k/\epsilon = 56.7 \pm 0.1$ cm s^{-1}, was obtained from measurements at 670 nm. The long-lived stage exhibited a first-order dependence on the initial concentration of Fe(II) product (Table II). Moreover, the rate of this stage exhibited a complex dependence on base concentration (Table II).

Flash photolysis of $Fe(DMG)_2(OCH_3)CH_3OH$ in deaerated methanolic solutions failed to produce transient absorbances. However, the addition of nitrogen bases, namely, $N(CH_3)_3$, pyridine, and CH_3CN, resulted in transient spectral transformations that can be attributed to solvolysis of the $Fe(DMG)_2B$ species.[19]

Discussion

Rose et al. have demonstrated that reduction of the metal center and oxidation of coordinated methanol or methoxide ions is the only photoreaction in the sunlight photolysis of $Fe(TIM)(OCH_3)CH_3OH^{2+}$.[3] This conclusion is supported by our results obtained with monochromatic irradiations of the complex. Moreover, the photoredox chemistry of $Fe(DMG)_2(OCH_3)CH_3OH$ involves a similar process, namely, reduction to ferrous species and oxidation of coordinated methanol. Neither the DMG^- nor TIM ligands seem to

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(19) The metastable nature of iron(II)–DMG species and the spectra of stable $Fe(DMG)_2B$ (B = pyridine, cyanide, hydrazine) were previously reported: Jillot, B. A.; Williams, R. J. P. *J. Chem. Soc.* **1958**, 462.

participate with a significant yield in the photoredox reactions. In this regard, the primary process in either complex can be described by eq 3. Since methoxy radicals are unstable in

$$FeL(OCH_3)CH_3OH^{2+} \underset{\leftsquigarrow}{\xrightarrow{h\nu}} CT \rightarrow \{FeL(CH_3OH)^{2+},CH_3\dot{O}\} \quad (3)$$

$$L = TIM, (DMG^-)_2$$

metanolic media, they can be scavenged in solvent cages (eq 5) or can undergo diffusive separation (eq 6) and can be scavenged by bulk solvent (eq 7).[20] The disproportionation

$$\{FeL(CH_3OH)^{2+},CH_3\dot{O}\} \rightarrow FeL(OCH_3)CH_3OH^{2+} \quad (4)$$

$$\xrightarrow{CH_3OH} FeL(CH_3OH)_2{}^{2+} + \dot{C}H_2OH \quad (5)$$

$$\xrightarrow{CH_3OH} FeL(CH_3OH)_2{}^{2+} + CH_3\dot{O} \quad (6)$$

$$CH_3\dot{O} + CH_3OH \rightarrow CH_3OH + \dot{C}H_2OH \quad (7)$$

of the hydroxymethyl radical, eq 8 and 9, competes, under the

$$\dot{C}H_2OH \rightarrow \dot{C}H_2O^- + H^+ \quad (8)$$

$$\dot{C}H_2OH + \dot{C}H_2OH \rightarrow CH_2O + CH_3OH \quad (9)$$

$$\dot{C}H_2O^- + FeL(OCH_3)CH_3OH^{2+} \rightarrow CH_2O + FeL(CH_3OH)_2{}^{2+} \quad (10)$$

experimental conditions used for flash photolysis, with the reduction of another $Fe(TIM)(OCH_3)CH_3OH^{2+}$, eq 10. Although stoichiometric relationships, eq 1 and ref 3, do not give kinetic information on these processes, flash photolysis provides evidence on the competition between reactions 8–10. Moreover, the dependence of the reaction on base concentration suggests that the reactive species in eq 10 must be the anion radical $\dot{C}H_2O^-$ rather than the acid form of the radical, $\dot{C}H_2OH$.[21] This reactivity will increase the yields of $Fe(TIM)(CH_3OH)_2{}^{2+}$ by a factor of 2 for base concentrations equal to or larger than 10^{-5} M. Therefore, primary yields will be $\phi = {}^1/_2\phi_{Fe(II)}$ at high base concentrations or $\phi = \phi_{Fe(II)}$ in neutral solutions.

The oxidation of the photochemical product $Fe(TIM)(CH_3OH)_2{}^{2+}$ is a multistep process, namely, eq 11–13, which

$$Fe(TIM)(CH_3OH)_2{}^{2+} + O_2 \xrightarrow{fast} Fe(TIM)(CH_3OH)O_2{}^{2+} \quad (11)$$

$$Fe(TIM)(CH_3OH)O_2{}^{2+} + Fe(TIM)(CH_3OH)_2{}^{2+} \rightarrow [Fe(TIM)(CH_3OH)]_2O_2{}^{4+} \quad (12)$$

$$[Fe(TIM)(CH_3OH)]_2O_2{}^{4+} + CH_3OH \rightarrow 2Fe(TIM)(OCH_3)CH_3OH^{2+} + O_2H_2 \quad (13)$$

re-forms the original Fe(III)–TIM complex. The two stages, observed in flash photolysis studies, suggest a mechanism that involves the formation of a dimeric intermediate with $k/\epsilon = 56.7$ cm s^{-1} at 670 nm, eq 12. If one assumes that the dimeric species has small absorptivity at 670 nm, the rate constant for reaction 12 is $k = (2.0 \pm 0.3) \times 10^5$ M^{-1} s^{-1}. In addition, the dimer will undergo an acid-dependent hydrolysis toward the monomeric iron(III) complex, eq 13, in the second stage.

Transient transformations are not observed in flash photolysis of $Fe(DMG)_2(OCH_3)CH_3OH$. This probably shows that the reduction of the complex by hydroxymethyl radicals, namely, eq 10, is not significant for the mechanism eq 3–10. Moreover, the results obtained in photovoltammetry can be interpreted if one assumes that the dissociation of the primary product, namely, $Fe(DMG)_2(CH_3OH)_2{}^{2+}$, generates various monomeric and dimeric species.

Intense absorptions are placed at low energies in the absorption spectrum of the $Fe(DMG)(OCH_3)CH_3OH$. These bands have been attributed to charge-transfer, DMG^- to iron(III), transitions, $CT_{L\rightarrow Fe(III)}$.[22] In this regard, the same origin can be assigned to bands at 550 and 460 nm in the spectrum of the TIM complex. Such low energies for $CT_{L\rightarrow Fe(III)}$ transitions in DMG^- and TIM complexes contrast with large values of the threshold energies for photochemical reactivity. It seems feasible that the low-lying charge-transfer states, $CT_{L\rightarrow Fe(III)}$, neither are photoactive nor populate reactive methoxy to iron(III) charge-transfer states, $CT_{CH_3OH\rightarrow Fe(III)}$. Furthermore, the $CT_{CH_3OH\rightarrow Fe(III)}$ may be placed at higher energies than $CT_{L\rightarrow Fe(III)}$. Such states, $CT_{CH_3OH\rightarrow Fe(III)}$, can be further classified according to the populated metal orbital, namely, nonbonding t_2 and antibonding e.[23] Distinct Franck–Condon and electronic contributions to threshold energies can be associated with each of these states.[24] Therefore, one can expect that thresholds for photochemistry should be placed at energies equal to or larger than those of the thresholds for charge-transfer absorption in photoreactive states.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2061 from the Notre Dame Radiation Laboratory.

Registry No. $Fe(DMG)_2(OCH_3)CH_3OH$, 74684-27-8; $Fe(TIM)(OCH_3)CH_3OH^{2+}$, 62638-27-1; $Fe(TIM)(CH_3OH)_2{}^{2+}$, 62638-26-0.

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(20) The properties of $CH_3\dot{O}$ and $\dot{C}H_2OH$ have been previously reported: Dainton, F. S.; Salmon, G. A.; Wardman, P. *Proc. R. Soc. London, Ser. A* **1969**, *313*, 1. Gray, P.; Shaw, R.; Thynne, J. C. J. *Prog. React. Kinet.* **1967**, *4*, 63.

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(23) The metal orbitals t_2 and e in a pseudooctahedral symmetry will be further split in a tetragonal C_{4v} symmetry: $t_2 \rightarrow e + b_2$ and $e \rightarrow a_1 + b_1$.

(24) Orgel, L. *Q. Rev., Chem. Soc.* **1956**, *8*, 422. Jørgensen, C. K. In "Orbitals in Atoms and Molecules", Academic: New York, 1962; Chapter 7. These references describe the energy of a charge-transfer transition by $E = (I + \Delta_1) + \epsilon_x + \Delta Q + \Delta S + \Delta(SPE) + ...$ The vertical ionization potential, I, is perturbed by given ligand field energies, Δ_i; ϵ_x is the vertical electron affinity of the radical formed in the charge-transfer oxidation of the ligand; ΔQ and ΔS are energies which account for Franck–Condon and solvent reorganization contributions in nonvertical transitions between ground and CT states. The change in spin pairing energies between the electronic configuration of the two states is indicated as Δ(SPE). This equation predicts differences of, at least, 16 kcal/mol between states produced by charge transfer to t_2, or b_2 in C_{4v}, and e, or $a_1 + b_1$ in C_{4v}.