Photoassisted Oxidation of Methanol Catalyzed by a Macrocyclic Iron Complex

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Abstract: When 10^{-3}-10^{-4} M methanol solutions of an iron complex of TIM (2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) are exposed to sunlight, oxidation of methanol to formaldehyde proceeds according to the net equation: $CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2O + H_2O$. In the absence of O_2 the oxidation of methanol is accompanied by a stoichiometric reduction of $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$, a red low-spin Fe(III) complex, to $[Fe^{II}(TIM)(CH_3OH)_2]^{2+}$, a blue low-spin Fe(II) complex. The initial step in each oxidation-reduction reaction is thought to be a photoassisted homolytic cleavage of an Fe-OCH_3 bond leading to the Fe(II) species and the $\cdot(OCH_3)$ radical. In the presence of O_2, $[Fe^{II}(TIM)(CH_3OH)_2]^{2+}$ is oxidized to $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ and the photoassisted reaction continues. The foregoing processes proceed in a cyclic manner until the available O_2 is consumed or until the Fe(TIM) species are irreversibly degraded.

The photochemistry of Fe(II) and Fe(III) complexes has been a subject of intense interest for several decades.[1] This work has been recently reviewed,[2] and ongoing efforts have afforded significant achievements in both aqueous[3,4] and nonaqueous[3,5,6] media. Although the photochemistry of bidentate chelates of iron[3,5,7] and of the naturally occurring macrocyclic chelates[8,9] has been developed extensively, the photochemistry of synthetic macrocyclic iron chelates is less explored[10,11] to date.

In this paper we report a cyclic, photoassisted oxidation-reduction reaction, which involves methanolic solutions of an iron complex containing the macrocyclic ligand, TIM (2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, Figure 1).[12-14] The structure and chemistry of Fe(II),[10,12,14,15] Co(II),[16,17] Co(III),[14,16,18,19] and Ni(II)[20] complexes of TIM have been previously reported, and the structure of an Fe(III) complex has been determined.[21] From these studies several key points emerge concerning TIM complexes: (1) In none of the seven structural studies nor in the spectroscopic studies is there evidence that the macrocyclic ligand adopts any configuration about the metal other than one in which the metal ion and the four nitrogen donor atoms of TIM are virtually coplanar. Thus, in six-coordinate complexes, the fifth and sixth ligating atoms must be mutually trans, and "axial" with respect to the plane of the metal and the four TIM nitrogen donor atoms. (2) In the case of Fe(II) and Fe(III), all six-coordinate complexes have been found to be low spin. (3) Facile ligand substitution reactions are readily carried out involving the "axial" ligands of the Fe complexes.

The photodissociation of "axial" ligands (involving heterolytic bond cleavage) from d^6 $[Fe(TIM)(nitrile)(CO)]^{2+}$ complexes has been recently reported.[10] The results were found to reinforce the notions developed through a simple molecular-orbital description of Co(III) complexes, considering the influence of d-d transitions on the labilization of ligands.[22] In contrast to the photodissociation studies of d^6 complexes,[22-24] the work described here concerns the photoassisted reduction[25] of a d^5 to a d^6 iron-TIM complex and the concomitant oxidation of methanol. In this scheme, the light absorbing step undoubtedly involves ligand to metal charge transfer (LMCT) rather than a d-d transition and the key step in the reaction mechanism probably involves homolytic bond cleavage between the iron and an axial ligand. The net equations proposed to occur in the system are represented by eq 1, 2, and 3.

$$[Fe(TIM)(CH_3CN)_2](PF_6)_2 \xrightarrow{CH_3OH} [Fe^{II}(TIM)(CH_3OH)_2]^{2+} \text{ (blue)} + 2PF_6^- + 2CH_3CN \tag{1}$$

$$2[Fe^{II}(TIM)(CH_3OH)_2]^{2+} \text{ (blue)} + \tfrac{1}{2}O_2 \xrightarrow{CH_3OH} 2[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+} \text{ (red)} + H_2O \tag{2}$$

$$2[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+} \text{ (red)} + CH_3OH \xrightarrow[\text{sun}]{CH_3OH} 2[Fe^{II}(TIM)(CH_3OH)_2]^{2+} \text{ (blue)} + CH_2O \tag{3}$$

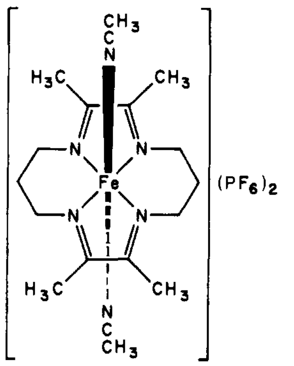
These three equations correspond *respectively* to the three following experiments, which in turn are keyed by number into the larger set of experiments shown in Figure 2. (1) Anaerobic dissolution of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in methanol (to give a blue solution). (2) Exposure of the blue solution to oxygen (to give a red solution). (3) Exposure of the degassed red solution to sunlight (to give the blue solution again). The data and inferences which provide support for the proposed reactions are presented below.

Results and Discussion

Equation 1. When $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ is dissolved in carefully degassed methanol, and successive fractions of methanol are removed and distilled onto the solid, a blue solution results. The blue methanol solution is diamagnetic (within the sensitivity of the measurement) and no ESR signal is observed at room temperature nor in the frozen solution at liquid nitrogen temperature. The spectrum of the blue solution (Figure 3) remains unchanged over several months, provided the solution is carefully protected from oxygen. It is proposed that methanol has replaced acetonitrile in the "axial" sites of the complex (eq 1), and that the six-coordinate complex, $[Fe^{II}(TIM)(CH_3OH)_2]^{2+}$, ($S = 0$), is the predominant complex present. Such a formulation seems likely in that a wide variety of six-coordinate Fe(II) complexes have been prepared of the sort $[Fe(TIM)(X)(Y)]^{2+}$, where X and Y are neutral ligands. All are diamagnetic.[12,15]

Equation 2. Exposure of the blue solution to oxygen (or to air) is accompanied by a rapid color change to red and an uptake of 0.27 (±0.07 maximum estimated error) mol of oxygen per gram-atom of iron.

The spectrum of this red solution (Figure 3) is the same whether it is prepared from reagent methanol or methanol distilled from calcium hydride, and the spectra of freshly prepared solutions are unchanged by the presence of 0.1 M concentrations of water or acetonitrile. In fact the red solution can be prepared directly by dissolving [Fe(TIM)(CH$_3$-



$[Fe(TIM)(CH_3CN)_2](PF_6)_2$
$S = 0$

Figure 1. Structural representation of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ after Lingafelter and Smith.[14]

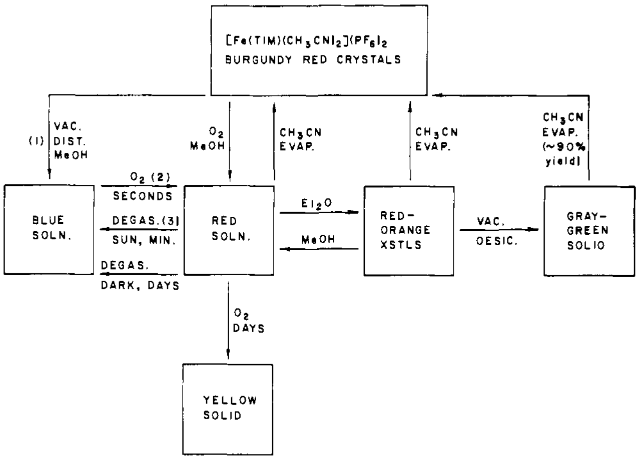


Figure 2. Schematic representation of some reactions of $[Fe(TIM)(X)(Y)](PF_6)_2$.

$CN)_2](PF_6)_2$ in methanol in the presence of air and this is the manner in which it was routinely done.

The gram-magnetic susceptibility of the iron species present in the red methanol solution (freshly prepared) is 1.90 (±0.12) $\times 10^{-6}$ cgs. An ESR signal is observed in methanol at room temperature, and in frozen solution at liquid nitrogen temperature g values of 1.97, 2.13, and 2.19 are obtained; no hyperfine structure is observed. The red methanol solution is slightly acidic. Thus on dissolution of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in the presence of air approximately 0.02 equiv of hydrogen ion is produced per gram-atom of iron. In the presence of low concentrations of trifluoroacetic acid ($[H^+] = 0\text{–}0.001$ M, $[Fe] = 4 \times 10^{-4}$ M) there are no significant changes in the spectrum of the red methanol solution. However, in the presence of higher concentrations of acid ($[H^+] = 0.1\text{–}1.0$ M, $[Fe] = 4 \times 10^{-4}$ M) there is a color change to yellow, the intensity of the absorption at 21.74 kK is diminished, and a new maximum is observed at 23.53 kK (Figure 4).

The assignment of the predominant species present in the red solution is not as straightforward as for the blue solution. The experimentally determined stoichiometry of the reaction with oxygen corresponds very nearly to 0.25 mol O_2 per mol of iron. Thus an oxidation from Fe(II) to Fe(III) is indicated (eq 2). Since the oxidation is accompanied by only a very slight *increase* in hydrogen ion concentration, some anionic oxygen-containing species must be bound to the Fe(III). This anion is undoubtedly OH^-, OCH_3^-, or O^{2-} (formally). The following complexes merit consideration as the predominant Fe containing species present in the red solution. The complexes A and B are dimers, whereas C and D are five- and six-coordinate mononuclear complexes. (In methanol it is assumed that OCH_3^- and CH_3OH are somewhat more likely ligands than OH^- and H_2O, respectively; however, the ultimate argument about the nature of the photoassisted reaction is not materially altered regardless of which is selected.)

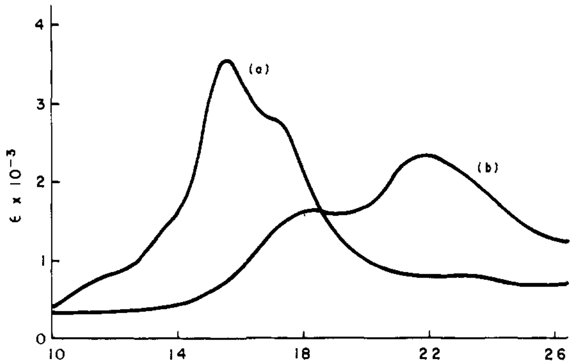


Figure 3. Visible spectra (methanol solution) of (a) $[Fe^{II}(TIM)(CH_3OH)_2]^{2+}$ (max at 15.60 kK), the "blue solution"; and (b) $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ (max at 21.74 kK), the "red solution".

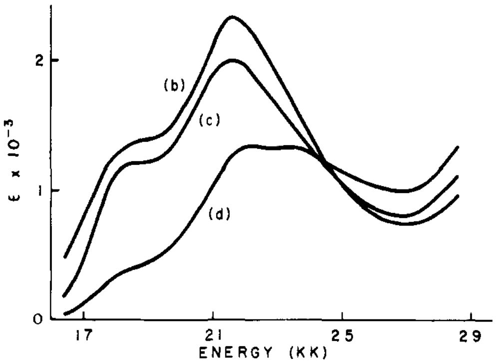


Figure 4. Visible spectra (methanol solution) of $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ in the presence of trifluoroacetic acid. Curve (b) 0.000–0.001 M $[H^+]$, (c) 0.11 M $[H^+]$; (d) 0.54 M $[H^+]$.

$[(Fe^{III}(TIM))_2O]^{4+}$ $\qquad$ $[(Fe^{III}(TIM)(CH_3OH))_2O]^{4+}$
A $\qquad$ B

$[Fe^{III}(TIM)(OCH_3)]^{2+}$ $\qquad$ $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$
C ($S = 1/2$) $\qquad$ D ($S = 1/2$)

Prior to considering the relative merits of the selection of A, B, C, or D it is appropriate to discuss the red-orange solid obtained from the red solution (Figure 2). A microcrystalline red-orange solid is obtained on the addition of diethyl ether to the red methanol solution (see Experimental Section). The visible spectrum of a methanol solution of this solid is identical with that obtained by dissolving $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in methanol (under air). A quantitative comparison of absorbances of these two solutions affords a molecular weight (per iron) of 667 ± 10 amu for the red-orange solid. The positions of the maxima in the visible spectrum of a Nujol mull of this solid (21.98, 18.5 (shoulder) kK) are similar to those in the methanol solution spectrum (21.74, 18.26 kK, Figure 3). The solid has a gram-magnetic susceptibility of 2.31×10^{-6} cgs at 23.8 °C, which increases slightly as the temperature is decreased to 90 °C (2.48×10^{-6} cgs). The infrared spectrum of the solid (as a Nujol mull) exhibits bands characteristic of TIM,[12] PF_6^-,[26] water, and methanol. When the red-orange solid is dissolved in acetonitrile and the resulting solution is evaporated to the atmosphere the solid obtained is $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ as indicated by its magnetic susceptibility and its infrared and ^{1}H NMR spectra.[12] The molecular weight of the red-orange solid determined gravimetrically (based on the known molecular weight of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$) is 661 ± 3 amu per iron.[27] The ^{1}H NMR spectrum taken following the dissolution of the red-orange solid in deuterioacetonitrile shows all the peaks assigned to $[Fe(TIM)(CD_3CN)]^{2+}$,[12] plus approximately ⅔ mol of methanol per mol of complex. The Mössbauer spectrum (20 °C) of the red-orange solid shows two lines; isomer shift = 0.36 mm/s (relative to sodium nitroprusside), and quadrupole splitting = 2.67 mm/s.

On vacuum desiccation, the red-orange solid loses mass, and changes color to gray-green (Figure 2). This solid is hygroscopic, and the infrared spectrum indicates that both water and methanol have been lost from the solid. (A similar color change is observed on heating the red-orange solid to 79 °C.) The gram-magnetic susceptibility of the gray-green solid (20 °C) is 3.5×10^{-6} cgs and the Mössbauer spectrum (20 °C) exhibits four lines.[28] The solid remaining when an acetonitrile solution of the gray-green solid evaporates to dryness is burgundy red with an infrared spectrum characteristic of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$. However, the gram-magnetic susceptibility of the solid thus obtained is slightly higher than expected, -0.17×10^{-6} cgs, $\mu_{eff} = 0.57\ \mu_B$ as compared to -0.37×10^{-6} cgs, $\mu_{eff} = 0.36\ \mu_B$ for an authentic sample of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$.[12]

A consideration of the properties of the red-orange solid and the red solution permits the selection of D as the most likely species present in the red solution. The oxo-bridged dimeric structures A and B can be eliminated as likely candidates via two lines of evidence, one based on magnetic data, the other on ESR spectra. In oxo-bridged species the two Fe(III) centers are commonly coupled antiferromagnetically.[29,30] Although the magnetic moment of the iron present in the red solution at 30 °C, 1.94 (±0.06) μ_B,[31] is not itself indicative of the absence of antiferromagnetism, the red-orange solid derived from the red solution clearly does not exhibit the expected temperature dependence of χ_g for two coupled Fe(III) centers.[29] The solid exhibits a magnetic moment of 2.10 μ_B at 23.8 °C and 1.91 μ_B at −90 °C.[31] Given the magnetic data and the strikingly similar electronic spectra of the red solution and the red-orange solid it seems likely that the same mononuclear low-spin Fe(III) complex is present in both phases.

A consideration of ESR spectra provides the second line of evidence. Oxo-bridged dimeric complex ions containing Fe(III) have been extensively studied, but to date only limited ESR data have appeared.[29,32] It is significant that no ESR signal is observed for $[Fe(salen)]_2O{\cdot}CH_2Cl_2$[33] nor for $[Fe(TPP)]_2O$[32,34] at room temperature or at liquid nitrogen temperature. For $[Fe(sal\text{-}N\text{-}n\text{-}Pr)_2]_2O$ one isotropic line is observed[29] at $g \simeq 4.3$. This is in contrast to the ESR spectrum of the red methanol solution (which yields three g values at liquid nitrogen temperature) and of the spectra of other complex ions containing low-spin Fe(III), 14-membered macrocyclic ligands, and one or two axial ligands[35-41] (Table I). Clearly the ESR data are also consistent with a mononuclear Fe(III) ($S = \frac{1}{2}$) complex being the predominant one present in the red solution (structure C or D).

As seen in Table I both five-[38] and six-coordinate[34-41] low-spin Fe(III) complexes with macrocyclic ligands somewhat similar to TIM (i.e., four sp^2 nitrogen atoms bound to the iron) can all give grossly similar ESR spectra. A consideration of the Mossbauer spectra, however, permits a reasonable selection between C and D to be made. (The assumption again required is that the red-orange solid and the solution from which it formed contain the same Fe complex.) The quadrupole splitting of the red-orange solid (2.67 mm/s) is similar to two six-coordinate low-spin Fe(III) complexes[42] (2.73 mm/s for $[Fe[14]1,3,8,10\text{-tetraene-}N_4)Cl_2]^+$ and 2.73 mm/s for $[Fe(TIM)cl_2]^+$) but different from that of a five-coordinate low-spin Fe(III) complex[41] (3.60 mm/s for $Fe(Dh_2[14]N_4)(SPh)]$). Thus, D seems the most likely choice for the complex present in solution, eq 2. This assignment has been reinforced by the x-ray determination of the structure of $[Fe(TIM)(H_2O)_2](ClO_4)_3$,[21] a low-spin, six-coordinate Fe(III) complex, which deprotonates readily in water.

Table I. ESR g Values for Some Fe(III) Complexes

Complex	Coordination No.	g	Ref
$[Fe(HDf)_2(py)_2]Br$	6	1.962, 2.244, 2.280	36
$[Fe(HDf)_2(py)_2]I$	6	1.969, 2.240, 2.273	36
$[Fe(Ph_2[14]N_4)(Br)(DMF)]$	6	1.99, 2.06, 2.09	41
$[Fe(Ph_2[14]N_4)(I)(DMF)]$	6	1.99, 2.06, 2.09	41
$[Fe(Ph_2[14]N_4)(SPh)(DMF)]$	6	1.99, 2.04, 2.12	41
$[Fe(Ph_2[14]N_4(SPh)(py)]$	6	2.00, 2.03, 2.13	41
$[Fe(Ph_2[14]N_4)(py)_2]^+$	6	2.00, 2.02, 2.08	41
$[Fe(Ph_2[14]N_4)(NMeIm)_2]^+$	6	1.99, 2.04, 2.10	41
$[Fe(Me_6[14]tetraene\text{-}N_4)(Cl)_2]PF_6$	6	1.925, 2.288, 2.428	39
$[Fe(Me_6[14]tetraene\text{-}N_4)(Br)_2]PF_6$	6	1.919, 2.338, 2.490	39
$[Fe(Ph_2[14]N_4)(SPh)]$	5	2.01, 2.04, 2.11	41
$[Fe(TIM)(CH_3OH)(OCH_3)]^{2+}$	6	1.97, 2.13, 2.19	This work

Equation 3. Red solutions prepared by dissolving $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in methanol ($0.77\text{–}1.56 \times 10^{-3}$ M in iron) in the presence of air were degassed by three successive freeze–pump–thaw cycles, maintained under anaerobic conditions, and exposed at room temperature to direct sunlight for 1 h. The solutions turned blue in color in a matter of minutes and the visible spectrum of the blue solution is identical with that obtained from a methanol solution of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ prepared anaerobically (see Figure 2 and the preceding discussion of eq 1). In conjunction with the red to blue conversion there is no gas evolved from the solution. The course of the color change is readily followed by periodically interrupting the exposure to sunlight and recording the spectrum of the solutions. A family of such spectra exhibit an isosbestic point at the intersection of the curves shown in Figure 3.

Clearly the $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ is being reduced to $[Fe^{II}(TIM)(CH_3OH)_2]^{2+}$ (Figure 2). The species being oxidized is CH_3OH or OCH_3^- in that the color change from red to blue is accompanied by the production of formaldehyde (no formaldehyde is produced when the red solution is prepared by dissolution of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in methanol in the presence of air). The formaldehyde content of ten different solutions averaged 0.43 mol of CH_2O per mol of iron present. The standard deviation of the ten measurements is 0.02 mol of CH_2O per mol of iron present and the estimated maximum error (accuracy) in the analytical method used is 8% or, in our application, 0.03 mol of CH_2O per mol of Fe present. Equation 3 features a stoichiometry reasonably close to that observed experimentally. Thus, the measured formaldehyde production is consistent with 90% of the $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ reduction proceeding via the reaction represented by eq 3.

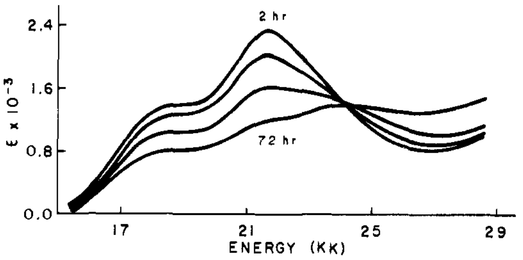


Figure 5. Visible spectra (methanol solution) of $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ after contact with air for 2 (upper spectrum at left), 6, 24, and 72 h (lowest spectrum at left). See text.

There is a striking difference between reactions conducted in sunlight and those done in the dark. The characteristic color change from red to blue also occurs in the dark but more slowly; days are required in the dark, minutes in the sunlight. Further, lower amounts of formaldehyde are detected in the reactions done in the dark. Using a degassed solution which was 8.0×10^{-4} M in iron complex, 0.13 mol of formaldehyde per mol of iron was detected after the color of the solution had changed to blue (3 days). To explore the possibility that formaldehyde could itself serve as a reducing agent for $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$, a red methanol solution was made up to contain 0.60 mol of formaldehyde per mol of iron complex (analyzed following vacuum degassing), degassed, and kept in the dark. After 10 days, by which time the solution had clearly changed color to blue, the solution was found to contain 0.47 mol of formaldehyde per gram-atom of iron. In contrast, the observed yield of formaldehyde produced in the "sunlight" reaction is unaffected by storing the resulting blue solution in the dark for 10 days. It is concluded that (a) a photoassisted reduction of $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ to $[Fe^{II}(TIM)(CH_3OH)_2]^{2+}$ occurs in sunlight with a concomitant oxidation of CH_3OH or OCH_3^- to CH_2O; (b) CH_2O reduces $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ via a "slow" thermal reaction in the dark; and (c) disproportionation of CH_2O in the presence of $[Fe^{II}(TIM)(CH_3OH)_2]^{2+}$ is not significant. In the "sunlight" reaction it is likely that the products which represent the approximately 10% of the stoichiometric yield of $[Fe^{II}(TIM)(CH_3OH)_2]^{2+}$ from $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ not accounted for by eq 3 include ethylene glycol[5] and further oxidation products of methanol (or formaldehyde) such as formic acid.

The color change from red to blue occurs in solutions (kept in Pyrex flasks and partially deoxygenated by bubbling N_2 through them) whether they are exposed to direct sunlight or sunlight transmitted through window glass or sunlight transmitted through Corning filters with "cutoffs" of 35.7, 29.4, 26.3, and 22.7 kK. The color change also occurs in the presence of sunlight for degassed solutions which contain trifluoroacetic acid ($[H^+] = 0.9$ M, $[Fe] = 8 \times 10^{-4}$ M), but the color change occurs significantly slower than for a solution of the same iron concentration which contains no added acid. The color change is also produced in sealed capillary tubes exposed to the radiation of an argon-krypton laser in the 21.84–19.2-kK region. It is clear from the experiments that the system is "active" with high energy visible light, but quantum yields will be required to establish the wavelength of maximum efficiency. This wavelength may be in the near ultraviolet region of the spectrum. In view of the spectral changes caused by appreciable amounts of H^+ (Figure 4) it is not surprising that the relative rate of the photoassisted reaction is in some way dependent on $[H^+]$ (vide infra).

General Considerations. It is to be noted that the sum of eq 2 and 3 is simply the oxidation of CH_3OH by O_2 to CH_2O,

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow CH_2O + H_2O \qquad (4)$$

Since the $\Delta G°$ for eq 4 is negative[43] we conclude that the net effect of the sunlight is to provide the activation energy for the oxidation.

There is reason to believe that the iron complex $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ can serve a catalytic role in the oxidation of methanol. Thus, when the red solution is not carefully degassed (of O_2) by a succession of freeze-pump-thaw cycles prior to its exposure to sunlight, quantities of CH_2O in excess of those predicted by eq 3 are found. For example, when a red methanol solution is degassed by bubbling nitrogen gas through the solution for 30 min, then stoppered and exposed to sunlight, 6.6 mol of formaldehyde per mol of iron present is detected. This is consistent with the proposed reaction sequence in which the reactions indicated by eq 2 and 3 proceed in a cyclic manner until the available O_2 is consumed. The cyclic character of the system can be more directly demonstrated by simply taking a blue solution (which has been prepared from a red solution by exposure to sunlight), exposing it to O_2, thereby turning it red, bubbling N_2 through it, and finally exposing it to sunlight again to turn it blue. This cycle from red to blue may be repeated several times with the same solution. However, there is a gradual diminution in the absorption of the bands in the visible spectrum. We associate this diminution with the known decomposition of the this red solution in the presence of air. When the methanol solution is left exposed to the air, changes occur in the spectrum over several hours, as depicted in Figure 5. If the solution is exposed to the air (or to oxygen) for several days in the presence of sunlight, a color change to yellow occurs, and a yellow crystalline solid is deposited (Figure 2). This change will also occur in the dark, but it requires a longer period of time. The crystalline solid contains carbon, hydrogen, and iron, but no nitrogen; it has not been further characterized.

The obvious decomposition of $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ required to make the yellow solid is not involved to a measurable extent in the first cycle of a red to blue conversion. Thus, when a red solution is prepared by dissolving $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in methanol in air, degassed by the freeze-pump-thaw technique, exposed to sunlight (and turned blue), and then exposed to air again for several minutes, the resulting red solution has a spectrum indistinguishable from the initial solution. Further, the spectrum of a freshly prepared red solution exposed to air was monitored over a period of approximately 30 min and showed no measurable change in that time interval.

The iron–TIM–methanol system described here is similar to the photochemically active iron–phenathroline–methanol system previously studied.[5] In the latter system formaldehyde is also produced and it has been proposed[5] that the primary photoprocess involves homolytic cleavage of an Fe(III)–methanol bond, thus producing CH_3OH^+ and Fe(II). Secondary products include $CH_3O\cdot$ and $CH_2OH\cdot$ with a major final product being formaldehyde. Although the reaction discussed here (eq 3) probably occurs by a similar mechanism, it may be that the photochemically significant step in the Fe(III)–TIM–methanol system involves the homolytic cleavage of an Fe(III)–OCH_3 bond,[44] thus producing Fe(II) and $CH_3O\cdot$ directly. We infer this because, under acidic conditions (vide supra), where a coordinated OCH_3^- would be converted to a coordinated $HOCH_3$, the conversion of a red to a blue solution in sunlight is significantly slower (see Figure 4 and recall that the visible spectra of the solutions are marked by dependence on acid concentrations above 0.1 M).

In our system, as in the Fe(III)–phenathroline–methanol system,[5] the electronic transition which is photochemically important is most likely a ligand-to-metal charge transfer (LMCT). A proposed sequence of events starting with a LMCT is shown in Figure 6. If LMCT involves the d_{z^2} orbital, then not only does this account for the generation of Fe(II) and

$CH_3O\cdot$, but the $CH_3O\cdot$ will be labilized due to the presence of the electron in the d_{z^2} orbital.[22] The dissociation of $CH_3O\cdot$ from Fe(II) followed by the reduction of another $[Fe^{III}(TIM)(CH_3OH)(OCH_3)]^{2+}$ by $CH_3O\cdot$ (or the hydroxymethyl free radical[45]), accounts for the production of CH_2O in the observed stoichiometry.

It is to be noted that similar color changes to that observed in methanol solutions have also been seen in ethanol. Thus the use of Fe(III) complexes of the sort mentioned here may be useful for photochemically catalyzing a variety of oxidations with O_2.

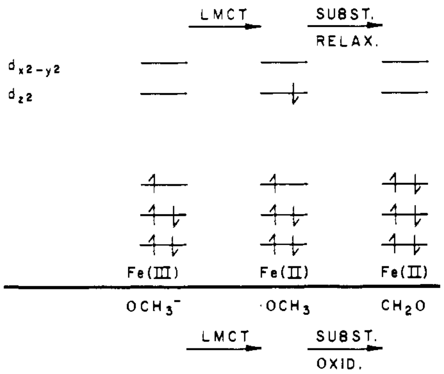


Figure 6. Suggested steps in the photoreduction of the Fe(III) species and concomitant oxidation of the CH_3OH. In the top portion of the figure the photoreduction is illustrated using a crystal-field diagram and population of the 3d orbitals. In the bottom portion the oxidation of the methanol is shown (SUBST. = substitution).

Experimental Section

The reagents used as starting materials were obtained commercially and used without further purification, except where noted.

$[Fe(TIM)(CH_3CN)_2](PF_6)_2$. An improved preparation to that described previously[12] follows.

Nitrogen was bubbled through methanol (125 ml) for 15 min and then iron powder (3.0 g, 0.053 mol, excess) was added. The stream of nitrogen was maintained throughout the following procedure. Anhydrous $FeCl_3$ (8.62 g, 0.053 mol) was added and the mixture was brought to a gentle boil. $SnCl_2{\cdot}2H_2O$ (1.0 g, 0.004 mol) was added and the solution (now ~0.08 M Fe(II)) was allowed to cool.

Methanol (100 ml) was cooled to −10 °C and maintained at temperatures between −5 and 5 °C during the sequential additions of 1,3-diaminopropane (13.4 ml, 0.16 mol), glacial acetic acid (9.2 ml, 0.16 mol), and a solution of 2,3-butanedione (14 ml, 0.16 mol) in 14 ml of methanol. The solution was stirred for 15 min, while a stream of nitrogen was bubbled through.

Under a blanket of nitrogen, the iron solution was filtered into a dropping funnel, and then added dropwise to the ligand solution (approximately 2 drops/s). Immediately after the start of the addition, *dry* potassium acetate (15.6 g, 0.16 mol) was added as a solid. Nitrogen was bubbled through the solution for 15 min following the completion of the addition, and then the flask was stoppered. The opaque blue reaction mixture was slowly warmed to about 40 °C over 6 h.

After a total time of 24 h the solution was cooled to 10 °C. Acetonitrile (25 ml, 0.472 mol) and glacial acetic acid (25 ml, 0.436 mol) were added, and the nitrogen atmosphere was no longer maintained. The resulting burgundy red mixture was filtered with suction and a yellow solid was discarded. A solution of NH_4PF_6 (10 g, 0.061 mol) in 80 ml of water was added to the filtrate, causing the precipitation of a burgundy red solid. The product was collected immediately by suction filtration, washed with absolute ethanol until the filtrate became clear, then washed with diethyl ether, and dried under a stream of dry air: yield, 11.7 g, 22%.

The product was recrystallized from acetonitrile and ethanol. Following recrystallization samples of the solid were prepared as powders from acetonitrile solutions by the rapid addition of an excess of ethanol.

$[Fe(TIM)(CH_3OH)(OCH_3)](PF_6)_2{\cdot}\frac{1}{2}H_2O$. A sample of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ (0.5 g, prepared in powdered form) was dissolved in methanol (250 ml) with vigorous stirring for 30 min. The resulting solution was filtered, and its volume was reduced to 30 ml on a rotary evaporator. The solution was again filtered and then diethyl ether (100 ml) was added dropwise (about 2 drops/s) while the solution was stirred continuously. The red-orange microcrystalline solid was collected via suction filtration, washed with diethyl ether, and dried under a stream of dry air: yield, 0.38 g, 77%; see ref 27.

Solutions in methanol were prepared (typically $0.4{-}1.0 \times 10^{-3}$ M) by stirring a powdered sample of $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in methanol in the presence of air, for 30 min, except where noted. Methanolic solutions were degassed by three freeze-pump-thaw cycles (except where noted) under a vacuum of about 5×10^{-5} Torr.

The O_2 uptake of an $[Fe^{II}(TIM)(CH_3OH)_2]^{2+}$ containing solution was done on a vacuum line of known volume by measuring the O_2 pressure before exposure to the solution and after both exposure and freeze-degassing of the solution with a Toeppler pump.

Except where noted, the source of visible light was direct sunlight, filtered by window glass and Pyrex laboratory glassware. The sunlight exposure time for all solutions in which formaldehyde was to be determined was 1 h.

Analyses for formaldehyde were determined colorimetrically using a technique adapted from other sources.[5,47] A column containing Dowex 50W-X8 cation-exchange resin (of total exchange capacity 20 mequiv and with an excluded volume of approximately 16 ml) was loaded with aqueous NaCl solution, and then flushed thoroughly with methanol. Methanol solutions (5.00 ml) exposed to the sunlight or maintained in the dark were poured onto the column and then eluted with methanol. The eluate was collected in 10.0-ml fractions. The first fraction was used as a blank. From each fraction a 1.00-ml aliquot was taken and 0.5 ml of water and 0.5 ml of a freshly prepared solution of 4,5-dihydroxy-2,7-naphthalenedisulfonic acid disodium salt (0.1 g/ml in water) were added. Concentrated sulfuric acid (5.0 ml) was added slowly while cooling in a cold water bath. The solution was incubated at 85 °C (±5 °C) for 1 h, cooled, and the volume was adjusted to 10.0 ml. Absorbance data were taken at 570 nm using a Cary 14 recording spectrophotometer, employing the sample from the first fraction in the reference beam. In no case was any formaldehyde detected in the fifth fraction. Formaldehyde concentration was determined by comparison to a calibration curve derived from solutions of known formaldehyde concentration.

Magnetic susceptibility was determined in methanol solution by the Evans technique,[48] employing a concentric NMR tube, with Me_4Si as reference. NMR shifts were measured on a Varian HA-100 NMR spectrometer at 30 °C (±0.5 °C) with methanol ($-CH_3$) serving as the internal lock. All solution magnetic susceptibility data were corrected for density.

Magnetic susceptibility was determined for solid samples by the Faraday technique. Susceptibility measurements were taken between −90 °C and ambient temperatures. Visible spectra were taken on a Cary 14 recording spectrophotometer. ESR spectra were taken at X-band on a Varian E9 ESR spectrometer. DPPM was used as an external standard.

Mössbauer spectra were obtained at ambient temperatures (21 ± 2 °C) using a Doppler-shifted 5-mCi ^{57}Co source and a 97% Xe/3% CO_2 gas proportional detector. Data were recorded on a 512-channel multichannel analyzer and computer fit using the National Bureau of Standards program PARLORS.[49] Sodium nitroprusside was used as the reference standard.

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References and Notes

(1) (a) N. Uri, *Chem. Rev.*, **50**, 375 (1952); (b) J. H. Baxendale and J. Magee, *Trans. Faraday Soc.*, 205 (1955).
(2) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y., 1970.
(3) P. G. David, J. G. Richardson, and E. L. Wehry, *J. Inorg. Nucl. Chem.*, **34**, 1333 (1972).
(4) (a) R. J. Stoltzberg and D. C. Hume, *Env. Sci. Technol.*, **9**, 654 (1975); (b) C. N. Chen and N. N. Lichtin, *Science*, **190**, 879 (1975).
(5) P. G. David and E. L. Wehry, *J. Mol. Photochem.*, **5**, 21 (1973).
(6) J. T. Grooves and W. W. Swanson, *Tetrahedron Lett.*, 1953 (1975).
(7) J. H. Baxendale and N. K. Bridge, *J. Phys. Chem.*, **59**, 783 (1955).

(8) D. G. Whitten, T. J. Meyer, F. R. Hopf, J. A. Ferguson, and G. Brown, *Ann. N.Y. Acad. Sci.*, **206**, 516 (1973).
(9) C. Yu, Y. L. Chiang, L. Yu, and T. E. King, *J. Biol. Chem.*, **250**, 6218 (1975).
(10) (a) J. I. Zink, D. Schwendiman, and M. J. Incorvia, Abstracts, 169th National Meeting of the American Chemical Society, Philadelphia, Pa., 1975, No. INOR-143; (b) J. I. Zink, personal communication.
(11) D. V. Stynes, *J. Am. Chem. Soc.*, **96**, 5942 (1974).
(12) D. A. Baldwin, R. M. Pfeiffer, D. W. Reichgott, and N. J. Rose, *J. Am. Chem. Soc.*, **95**, 5152 (1973); D. W. Reichgott, Thesis, University of Washington, 1976.
(13) An alternative nomenclature for this chelate is (Me_4[14]tetraene-N_4). See V. L. Goedken, P. H. Merrell, and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 3397 (1972).
(14) H. W. Smith, G. W. Svetich, and E. C. Lingafelter, Program and Abstracts of the American Crystallographic Association Meeting, 1973, Series 2, Vol. 1, No. M5, p 174.
(15) D. W. Reichgott and N. J. Rose, Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., August 1973, No. INOR-061.
(16) S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **11**, 2893 (1972).
(17) D. P. Rillema and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 8711 (1972).
(18) S. C. Jackels, Thesis, University of Washington, 1974.
(19) D. P. Rillema, J. F. Endicott, and J. R. Barber, *J. Am. Chem. Soc.*, **95**, 6987 (1973).
(20) (a) L. P. Torre and E. C. Lingafelter, Program and Abstracts of the American Crystallographic Association Meeting, Columbia, S.C., Jan. 1971; (b) L. P. Torre, Thesis, University of Washington, 1971; (c) D. A. Baldwin and N. J. Rose, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1968, No. INOR-202.
(21) M. D. Glick and J. F. Endicott, personal communication.
(22) J. I. Zink, *J. Am. Chem. Soc.*, **96**, 4464 (1974).
(23) P. C. Ford, *Inorg. Chem.*, 14, 1440 (1975).
(24) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, **79**, 630 (1975).
(25) The authors of ref 10 and 24 have also considered photoredox pathways in addition to their photodissociation studies.
(26) N. J. Rose, M. S. Elder, and D. H. Busch, *Inorg. Chem.*, **6**, 1924 (1967).
(27) Elemental analyses of the red-orange solid are 27.2% C, 4.8% H, and 8.7% N. The percent nitrogen calculated for four N atoms for a molecular weight of 666 amu is 8.41%. The observed carbon-to-nitrogen ratio is 3.63, which corresponds to 14.5 carbon atoms per four nitrogen atoms in the formula unit. (It is likely that the carbon analysis is low because methanol present in the crystal lattice is undoubtedly lost during the initial sweep-purge in the analysis procedure.)
(28) Two lines (19% of total area) are symmetric about an isomer shift of 0.36 mm/s (relative to sodium nitroprusside) and have a quadrupole splitting of 2.77 mm/s. Two other lines (81% of total area) have isomer shift and quadrupole splitting of 0.46 and 0.92 mm/s, respectively.
(29) K. S. Murray, *Coord. Chem. Rev.* **12**, 1 (1974), and references cited therein.
(30) T. H. Moss, H. R. Lillienthal, C. Moleski, G. A. Smythe, M. C. McDaniel, and W. S. Caughey, *J. Chem. Soc., Chem. Commun.*, 263 (1972).
(31) The magnetic susceptibility of the Fe containing complex (per Fe atom) is calculated using a molecular weight of 666 per iron atom and a diamagnetic susceptibility correction of -2.96×10^{-4} cgs.
(32) R. H. Felton, G. S. Owen, D. Dolphin, A. Forman, D. C. Borg, and J. Fager, *Ann. N.Y. Acad. Sci.*, **206**, 504 (1973).
(33) P. Coggon, A. T. McPhail, F. E. Mabbs, and V. N. McLachlan, *J. Chem. Soc. A*, 1014 (1971).
(34) K. M. Kadish, G. Larson, D. Lexa, and M. Momenteau, *J. Am. Chem. Soc.*, **97**, 282 (1975).
(35) Y. Nishida, S. Oshio, and S. Kida, *Chem. Lett.*, 78 (1975).
(36) E. V. Suntsov, D. G. Batyr, I. I. Bulgak, and V. E. Zubareva, *J. Struct. Chem.*, **16**, 24 (1975).
(37) J. P. Collman, T. N. Sorrell, and B. M. Hoffman, *J. Am. Chem. Soc.*, **97**, 913 (1975).
(38) S. Koch, S. C. Tang, R. H. Holm, R. B. Frankel, and J. A. Ibers, *J. Am. Chem. Soc.*, **97**, 916 (1975).
(39) A. B. Manner, Thesis, The Ohio State University, 1975.
(40) $[Fe(TIM)(H_2O)_2](ClO_4)_3$ shows a room temperature ESR spectrum similar to the red methanol solution in this study (ref 21).
(41) S. Koch, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, **97**, 6714 (1975).
(42) J. C. Dabrowiak, P. H. Merrell, J. A. Stone, and D. H. Busch, *J. Am. Chem. Soc.*, **95**, 6613 (1973); E. Fey and N. J. Rose, unpublished results.
(43) Values selected for gaseous molecules: F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Natl. Bur. Stand.* (*U.S.*), *Circ.*, **No. 500**, 1 (1952).
(44) An equivalent reaction would be the homolytic cleavage of an Fe(III):OH bond, with a rapid secondary process producing HOH and $(CH_3O)\cdot$.
(45) Other workers[46] have shown that free radicals may be trapped following irradiation of frozen aqueous solutions containing alcohols and Fe(III) complexes. However, the irradiation of a frozen methanol solution containing $[Fe(TIM)(CH_3OH)(OCH_3)]^{2+}$ with an unfiltered mercury lamp has produced neither color changes nor changes in the ESR spectrum at liquid nitrogen temperature.
(46) A. L. Poznyak, S. I. Arzhankov, and G. A. Shagisultanova, *Russ. J. Phys. Chem.*, **46**, 445 (1972).
(47) C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 400 (1945).
(48) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(49) J. T. Spijkerman, D. K. Sneidiker, F. C. Ruegg, and J. R. Devoe, *Natl. Bur. Stand.* (*U.S.*), *Spec. Publ.*, **No. 260**, 13 (1967).

Preparation and Properties of Iron(III)–Amino Acid Complexes. 2. The Crystal and Molecular Structure of Monoclinic Tri-μ_3-oxo-triaquohexakis(glycine)triiron(III) Perchlorate

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Abstract: The crystal and molecular structure of tri-μ_3-oxo-triaquohexakis(glycine)triiron(III) perchlorate, $[Fe_3O\cdot(C_2H_5O_2N)_6\cdot(H_2O)_3](ClO_4)_7$, has been determined using single crystal x-ray techniques and refined by full matrix least squares to a conventional R factor of 0.074. The dark red-brown prismatic crystals of monoclinic space group $P2_1$ have unit cell dimensions $a = 19.26$ (2), $b = 15.61$ (1), $c = 16.69$ (2) Å, and $\beta = 100.71$ (6)°. The structure is similar to that of basic iron acetate, $[Fe_3O(CH_3COO)_6\cdot 3H_2O]ClO_4$, with a trimeric unit having an oxygen atom at the center. The remaining coordination sites of each iron are occupied by four carboxylate oxygens from bridging glycines and a single water molecule.

The study of non-heme iron proteins has been of great interest in recent years. In an effort to study model systems for certain of these iron-containing proteins, we have prepared several iron amino acid complexes. The absorption spectra and Mössbauer and room temperature magnetics of these complexes have shown that these properties resemble those of ferritin.[2] Preliminary x-ray studies have indicated the presence of Fe_3O^{7+} clusters. The results of a detailed magnetic study done at a wide range of temperature are in agreement with the proposed trimeric iron structure.[3] To further elucidate the