Volume 31

Number 7

April 1, 1992

Inorganic Chemistry

Communications

Attenuation of Antiferromagnetic Exchange Interactions via H_2O Hydrogen Bonding to Oxo-Bridged Diiron(III) Complexes

Hemerythrin[1] (Hr) is the prototypical example of a class of nonheme iron proteins which includes ribonucleotide reductase,[2] methane monooxygenase,[3] and purple phosphatases.[4] These so-called iron–oxo proteins have been the focus of much attention recently and have spawned the preparation of many oxo-bridged iron model complexes.[5] Of the group of iron–oxo proteins under investigation, Hr is by far the best characterized. High-resolution X-ray crystallographic studies have been reported on the met and azidomet forms of Hr.[6] Since the basic structure of the diiron core is by now fairly well-established, efforts over the past several years have begun to focus on the mechanism of O_2 binding in the protein. Stenkamp et al.[6a] have proposed on the basis of their crystallographic results a mechanism for the conversion of deoxyHr to oxyHr involving hydrogen atom transfer from a μ-OH deoxy species to dioxygen during electron transfer to yield hydroperoxo-bound oxyHr. Shiemke et al.[7] have since presented resonance Raman data which in general support Stenkamp's model of hydrogen bonding to the μ-oxo bridge in oxyHr. These results allow for a relatively straightforward explanation of magnetic susceptibility data on the protein which indicate a decrease in the magnitude of coupling between the Fe^{III} ions upon conversion from N_3metHr ($J = -134$ cm^{-1}) to oxyHr ($J = -77$ cm^{-1}).[8] This modulation of exchange interactions is presumably due to the hydrogen bonding of the bound hydroperoxide to the μ-oxo bridge of the complex. To shed additional light on how hydrogen bonding can affect magnetic properties in oxo-bridged dinuclear complexes,[9] we wish to report the structural and magnetic properties of (μ-oxo)bis(μ-carboxylato)diiron(III) complexes of a polyimidazole ligand which we have examined as a possible model for the basic core of Hr. It is established that H_2O crystallizing as a lattice solvate is hydrogen bonded to the μ-oxo bridge and this hydrogen bonding results in a significant attenuation of the antiferromagnetic exchange interactions between the two Fe^{III} ions in the complexes.

Dinuclear iron complexes containing the tridentate ligands bis((1-methylimidazole-2-yl)methyl)amine (bmima) were prepared following the "self-assembly" method.[10] An ethanolic solution containing 1 equiv each of bmima, Et_3N, and either of benzoic or acetic acid was added with stirring to a solution containing $Fe(ClO_4)_3{\cdot}9H_2O$. The resulting mixture was stirred for 1 h, whereupon a light green precipitate was isolated by filtration. Recrystallization of the complexes from CH_3CN[11] afforded crystals of $[Fe_2O(bmima)_2(O_2CPh)_2](ClO_4)_2{\cdot}2CH_3CN{\cdot}2H_2O$ (**1**) and $[Fe_2O(bmima)_2(O_2CCH_3)_2](ClO_4)_2{\cdot}2CH_3CN{\cdot}1.5H_2O$ (**2**). Additional purification results in a decrease in the amount of cocrystallized solvent; complex **3** isolated after several recrys-

---

(1) (a) Klotz, I. M.; Kurtz, D. M., Jr. *Acc. Chem. Res.* **1984**, *17*, 16. (b) Wilkins, P. C.; Wilkins, R. G. *Coord. Chem. Rev.* **1987**, *79*, 195. (c) Que, L., Jr.; Scarrow, R. C. *ACS Symp. Ser.* **1988**, *No. 372*, 152. (d) Sanders-Loehr, J.; Loehr, T. M. *Adv. Inorg. Biochem.* **1979**, *1*, 235. (e) Wilkins, R. G.; Harrington, P. C. *Adv. Inorg. Biochem.* **1983**, *5*, 51. (f) Que, L., Jr.; True, A. E. *Prog. Inorg. Chem.* **1990**, *38*, 97–200. (g) Sanders-Loehr, J. In *Physical Bioinorganic Chemistry*; Loehr, T. M., Ed.; VCH Publishers: New York, 1989; Vol. 5.

(2) (a) Reichard, P.; Ehrenberg, A. *Science* **1983**, *221*, 514. (b) Sjöberg, B.-M.; Gräslund, A. *Adv. Inorg. Biochem.* **1983**, *5*, 87. (c) Lynch, J. B.; Juarez-Garcia, C.; Munck, E.; Que, L., Jr. *J. Biol. Chem.* **1989**, *264*, 8091. (d) Joelson, T.; Uhlin, U.; Eklund, H.; Sjoberg, B.-M.; Hahne, S.; Karlsson, M. *J. Biol. Chem.* **1984**, *259*, 9076. (e) Norlund, P.; Sjoberg, B.-M.; Eklund, H. *Nature* **1990**, *345*, 593.

(3) (a) Fox, G. G.; Sereus, K. K.; Munck, E.; Lipscomb, J. D. *J. Biol. Chem.* **1988**, *263*, 10553. (b) Ericson, A.; Hedman, B.; Hodgson, K. O.; Green, J.; Dalton, H.; Bentson, J. G.; Beer, R. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2330. (c) Prince, R. C.; George, N. G.; Sara, J. C.; Cramer, S. P.; Patel, R. N. *Biochim. Biophys. Acta* **1988**, *452*, 220. For a recent paper on functional modelling of MMO, see: (d) Fish, R. H.; Konings, M. S.; Oberhausen, K. J.; Fong, R. H.; Yu, W. M.; Christou, G.; Vincent, J. B.; Coggin, D. K.; Buchanan, R. M. *Inorg. Chem.* **1991**, *30*, 3002.

(4) (a) Antanaitis, B. C.; Aisen, P. *Adv. Inorg. Biochem.* **1983**, *5*, 111. (b) Antanaitis, B. C.; Aisen, P. *J. Biol. Chem.* **1984**, *259*, 2066, and references therein. (c) Davis, J. C.; Averill, B. A. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 4623.

(5) For recent reviews, see: (a) Vincent, J. B.; Olivier-Lilley, G. L.; Averill, B. A. *Chem. Rev.* **1990**, *90*, 1447. (b) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344. (c) Kurtz, D. M., Jr. *Chem. Rev.* **1990**, *90*, 585. For the most recent modeling work, see: (d) Mashuta, M. S.; Webb, R. J.; Oberhausen, K. J.; Richardson, J. F.; Buchanan, R. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 2745. (e) Stassinopoulous, A.; Cardonna, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 7071. (f) Menage, S.; Brennan, B. A.; Juarez-Garcia, C.; Munck, E.; Que, L., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 6423. (g) Borovik, A. S.; Hendrich, M. P.; Holman, R. R.; Munck, E.; Papaefthymiou, V.; Que, L., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 6031. (h) Norman, R. E.; Yan, S.; Que, L., Jr.; Backes, G.; Ling, J.; Sanders-Loehr, J.; Zhang, J. H.; O'Connor, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 1554.

(6) (a) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H.; McCallum, J. D.; Sanders-Loehr, J. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 713. (b) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618. (c) Hendrickson, W. A. In *Invertebrate Oxygen-Binding Proteins: Structure, Active Site and Function*; Lamy, J., Lamy, J., Eds.; Dekker: New York, 1981; p 503. (d) Sheriff, S.; Hendrickson, W. A.; Smith, J. L. *J. Mol. Biol.* **1987**, *197*, 273.

(7) Shiemke, A. K.; Loehr, T. M.; Sanders-Loehr, J. *J. Am. Chem. Soc.* **1986**, *108*, 2437.

(8) Dawson, J. W.; Gray, H. B.; Hoenig, H. E.; Rossman, G. R.; Schredder, J. M.; Wang, R.-H. *Biochemistry* **1972**, *11*, 461.

(9) The effect of protonation on magnetic exchange and electron transfer has been examined by other authors. See: (a) Hagen, K. S.; Westmoreland, D.; Scott, M. J.; Armstrong, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 1907. (b) Thorp, H. H.; Sarneski, J. E.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 9249. (c) Sarneski, J. E.; Thorp, H. H.; Brudvig, G. W.; Crabtree, R. H.; Schulte, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 7255. (d) Landrum, J. T.; Grimmett, D.; Haller, K. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 2640.

(10) (a) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4837. (b) Wieghardt, K.; Pohl, K.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 727.

(11) Both complexes **1** and **2** can also be crystallized from CH_3NO_2, yielding X-ray-quality crystals. The structures and magnetic properties of these solvates will be reported elsewhere.

0020-1669/92/1331-1123$03.00/0 © 1992 American Chemical Society

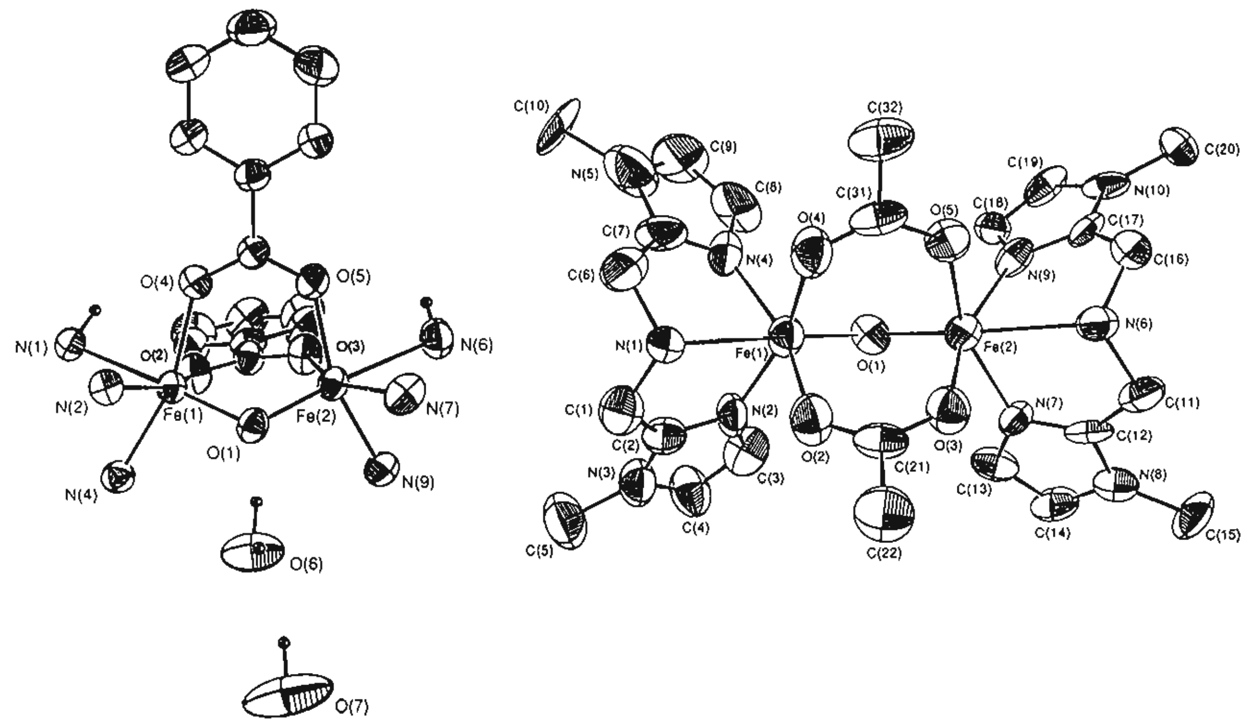

Figure 1. ORTEP drawings of the cations of $[Fe_2O(bmima)_2(O_2CPh)_2](ClO_4)_2 \cdot 2CH_3CN \cdot 2H_2O$ (**1**) (left) and $[Fe_2O(bmima)_2(O_2CCH_3)_2](ClO_4)_2 \cdot 2CH_3CN$ (**3**) (right). Selected bond distances (Å) and angles (deg) are as follows. Complex **1**: Fe1–O1 = 1.809 (3), Fe1–O2 = 2.025 (4), Fe1–O4 = 2.056 (4), Fe1–N1 = 2.263 (4), Fe1–O2 = 2.087 (4), Fe1–N4 = 2.104 (5), Fe2–O1 = 1.804 (3), Fe2–O3 = 2.058 (3), Fe2–O5 = 2.029 (3), Fe2–N6 = 2.290 (4), Fe2–N7 = 2.100 (4), Fe2–N9 = 2.079 (4), Fe1–Fe2 = 3.0976 (9); Fe1–O1–Fe2 = 118.0 (2). Complex **3**: Fe1–O1 = 1.773 (6), Fe1–O3 = 2.008 (7), Fe1–O5 = 2.036 (7), Fe1–N1 = 2.300 (8), Fe1–N2 = 2.068 (9), Fe1–N4 = 2.094 (8), Fe2–O1 = 1.785 (6), Fe2–O2 = 2.031 (7), Fe2–O4 = 2.048 (7), Fe2–N6 = 2.323 (7), Fe2–N7 = 2.094 (7), Fe2–N9 = 2.071 (8), Fe1–Fe2 = 3.059 (2); Fe1–O1–Fe2 = 116.9 (3).

tallizations is formulated as $[Fe_2O(bmima)_2(O_2CCH_3)_2](ClO_4)_2 \cdot 2CH_3CN$.

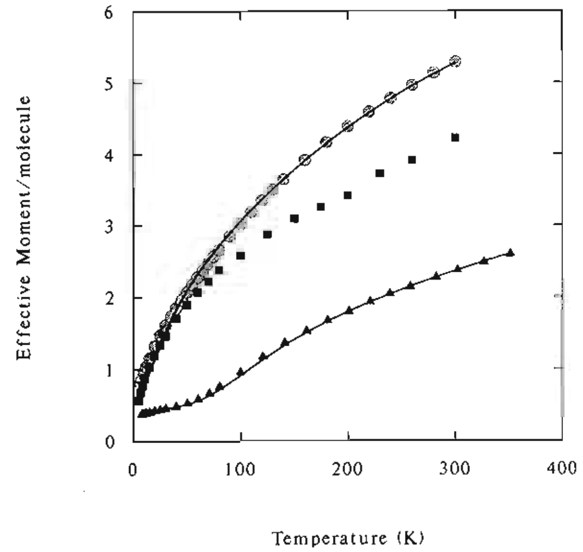

Figure 2. Plots of effective magnetic moment versus temperature for $[Fe_2O(bmima)_2(O_2CPh)_2](ClO_4)_2 \cdot 2CH_3CN \cdot 2H_2O$ (**1**, ■), $[Fe_2O(bmima)_2(O_2CCH_3)_2](ClO_4)_2 \cdot 2CH_3CN \cdot 1.5H_2O$ (**2**, ○), and $[Fe_2O(bmima)_2(O_2CCH_3)_2](ClO_4)_2 \cdot 2CH_3CN$ (**3**, ▲). Solid lines indicate fits to theoretical susceptibility equations. See text for details.

Crystal structures were determined for compounds **1** and **3**;[12] ORTEP drawings of cations for **1** and **3** are shown in Figure 1. Each complex has a triply bridged μ-oxo bis(μ-carboxylato) core with the bmima chelating ligands completing the octahedral coordination about each metal center. The core structures of the two compounds are in general very similar, and bond distances found are typical for high-spin Fe^{III} ions.[13] The largest disparity between the structures of complexes **1** and **3** occurs for the Fe–μ-O and Fe–N(amine) bond lengths. For complex **1**, the Fe–μ-O distances average 1.807 (5) Å, while, for complex **3**, this average is 1.780 (5) Å. The longer oxo bond lengths in complex **1** results in a weaker trans effect on the Fe–N(amine) bonds (average 2.276 (5) Å) compared to the average length of 2.314 (5) Å for complex **3**. This lengthening of the Fe–μ-O bond and concomitant shortening of the Fe–N(amine) bond in complex **1** is due to a hydrogen-bonding interaction which is evident in complex **1** between the μ-O and one of the lattice H_2O molecules.[14] The *μ-O···H*-OH distance is 1.76 (4) Å with an angle of 169 (1)°, while the O--O separation is 2.749 (5) Å. This is to be compared with the hydrogen-bonding interaction in oxyHr, estimated at 1.7 Å with an angle of 130°.[7] The O--O distance between the bridging oxo group and the hydrogen-bonded hydroperoxo group in oxyHr is 2.8 Å.[15] The hydrogen-bonding interaction in complex **1** would appear to be stronger than that found in oxyHr on the basis of

---

(12) Crystallographic details. Complex **1**: $C_{38}H_{48}Cl_2Fe_2N_{12}O_{15}$, fw = 1097.49, space group $P2_1/n$ with a = 10.493 (2) Å, b = 24.569 (3) Å, c = 19.088 (4) Å, β = 90.78 (1)°, V = 4920.3 Å^3, Z = 4, D_c = 1.48 g cm^{-3}, μ = 7.71 cm^{-1}, and R = 0.055 (R_w = 0.062) for 5928 observed reflections ($I > 3\sigma(I)$) and 647 variables at 25 (1) °C. Complex **3**: $C_{28}H_{40}Cl_2Fe_2N_{12}O_{13}$, fw = 935.30, space group $P2_1/n$ with a = 12.193 (3) Å, b = 12.036 (3) Å, c = 29.088 (3) Å, β = 101.48 (2)°, V = 4183.3 Å^3, Z = 4, D_c = 1.36 g cm^{-3}, μ = 8.9 cm^{-1}, and R = 0.058 (R_w = 0.062) for 2571 observed reflections and 485 variables. Data were collected to 35° in 2θ after which the crystal decomposed (new sample currently being prepared).

(13) ^{57}Fe Mössbauer spectra for each complex at 300 K can be fit to a single quadrupole-split doublet with hyperfine parameters consistent with high-spin Fe^{III}. (Compound **1**: ΔE_Q = 1.173 (5) mm/s, δ = 0.377 (3) mm/s. Compound **2**: ΔE_Q = 1.167 (4) mm/s, δ = 0.380 (2) mm/s.)

(14) The compound $[Fe_2O(bmima)_2(O_2CPh)_2](ClO_4)_2 \cdot 2CH_3CN$ has been isolated after several recrystallizations of compound **1** and found to crystallize in the space group $C2/c$ with a = 19.456 (5) Å, b = 9.584 (3) Å, c = 27.151 (5) Å, β = 106.4 (2)°, V = 4857.5 Å^3, Z = 4, R = 0.048 and R_w = 0.054 at −100 °C. Fe···Fe = 3.0555 (8) Å, Fe–μ-O = 1.793 (3) Å, Fe–N_t = 2.304 (3) Å, and Fe–O–Fe′ = 116.9 (3)°.

(15) Holmes, M. A.; Le Trong, I.; Turley, S.; Sieker, L. C.; Stenkamp, R. E. *J. Mol. Biol.* **1991**, *218*, 583.

the μ-O···H distance, bond angle, and O--O distance.[16]

In Figure 2 are shown plots of effective monomer per molecule versus temperature in an applied field of 10.00 kG. Data for complex **3** are readily fit to a Heisenberg exchange Hamiltonian of the form $\mathbf{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ with $g = 2.00$ and $J = -134$ cm^{-1}; contributions from TIP and the paramagnetic impurity were held fixed at 3.00×10^{-4} cgsu and 0.002, respectively.[18] This value for J is typical for an oxo-bridged Fe$^{III}_2$ complex[5] and is in fact identical to that found in N$_3$metHr. The data for complexes **1** and **2**, however, show a dramatic change in the magnitude of the pairwise exchange interaction as evidenced by both the larger effective moments and as well larger values of $\partial\mu_{eff}/\partial T$ at low temperature. The data for complex **2** can be fit reasonably well to the above Hamiltonian for $g = 2.00$ and $J = -26$ cm^{-1} (impurity = 0.008; TIP as above). The data for complex **1**, however, *cannot* be fit to a simple Heisenberg expression. It is our opinion that the J values for both complexes **1** and **2** are temperature dependent. This conclusion was reached on the basis of attempts to fit the data for complex **1** in different temperature regions. If only the data below 100 K are considered, a value of $J \approx -30$ cm^{-1} is obtained, obviously similar to that for complex **2**. However, the resulting theoretical curve substantially overshoots the experimental data at higher temperatures. Conversely, a consideration of the high temperature data (i.e., $T \geq 150$ K), affords $J \approx -70$ cm^{-1}, but such a value undershoots the low-temperature data. Similar results are found for complex **2**, but since the variation with temperature is much less pronounced ($\Delta J \approx 10$ cm^{-1}), a presentable fit assuming a temperature-independent J term can be obtained. Regardless of the details of the data fitting, it is quite clear that the antiferromagnetic exchange interactions in complexes **1** and **2** are considerably weaker than that in complex **3**.

We suggest that the temperature dependence of J is a result of the hydrogen-bonding interaction of the solvate with the μ-oxo bridge. As temperature is increased, the increase in available thermal energy and resultant expansion of the crystal are expected to weaken hydrogen bonds. Weakening of the hydrogen bond to the oxo-bridge leads to an increase in the magnitude of the antiferromagnetic exchange interaction between the Fe^{III} ions as the bridge loses its μ-O···H character, resulting in a smaller moment (i.e., larger J value) at higher temperatures. The more pronounced effect seen for complex **1** versus complex **2** can be explained by considering the nature of the bridging carboxylates in the two compounds. The benzoate bridges of complex **1** will, in general, produce a lattice which is more susceptible to thermal expansion/contraction than that for the acetate complex. The lattice characteristics will affect the strength of the hydrogen bond, resulting in a larger temperature coefficient for the exchange parameter in the case of complex **1**. These data are further evidence of the importance of this subtle hydrogen-bonding interaction in determining the magnetic properties of these molecules. There is one other example in the literature where exchange interactions propagated by hydrogen-bonding contacts have shown a pronounced temperature dependence.[19]

Acknowledgment. These studies were supported by the National Science Foundation Grants CHE-9016947 and RII861067 and Commonwealth of Kentucky EPSCoR Program (R.M.B.), the National Institutes of Health Grant HL13652 (D.N.H.), and an NSF equipment grant (CHE-9016978) (J.F.R.).

Supplementary Material Available: Tables of positional parameters and bond distances and angles for complexes **1** and **3** and tables of magnetic data for complexes **1–3** (18 pages). Ordering information is given on any current masthead page.

---

(16) Reem, R. C.; McCormick, J. M.; Richardson, D. E.; Devlin, F. J.; Stephens, P. J.; Musselman, R. L.; Solomon, E. I. *J. Am. Chem. Soc.* **1989**, *111*, 4688.

(17) Reference deleted in proof.

(18) Magnetic data were fit using a relative error minimization routine (E. A. Schmitt, unpublished results).

(19) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1974**, *13*, 2929.

(20) Present address: Nalco Corp., Naperville, IL.

Department of Chemistry
University of Louisville
Louisville, Kentucky 40292

Kenneth J. Oberhausen
John F. Richardson
Robert J. O'Brien
Robert M. Buchanan*

Department of Chemistry
University of California at San Diego
La Jolla, California 92093-0506

James K. McCusker
Robert J. Webb[20]
David N. Hendrickson*

Received October 23, 1991

Photosubstitution of Fe(CO)$_5$ with PEt$_3$ in Cyclohexane: Fe(CO)$_4$PEt$_3$ and Fe(CO)$_3$(PEt$_3$)$_2$ as Single-Photon Products

The photochemistry of Fe(CO)$_5$ has proven to be very complex, and even though it was one of the first organometallic compounds to be studied, it is still actively investigated.[1-5] In the gas phase, UV photolysis of metal carbonyls (M(CO)$_n$) leads to multiple, stepwise CO dissociations since the energy of a UV photon is in excess of two or more of the metal–CO bond energies.[6] The number of CO's lost and the distribution of M(CO)$_x$ formed (x varies) depends on the wavelength.[6] In contrast, it is generally believed that UV photolysis of metal carbonyls in condensed phases results in only one CO dissociation since further CO dissociation is not expected to compete with vibrational relaxation of M(CO)$_{n-1}$.[6-8] This is supported by the photochemistry of group VI metal carbonyls where only monosubstitution of the metal carbonyl is observed in solution.[9,10] When disubstitution has been detected, it has been rationalized as the result of secondary photolysis (i.e., photolysis of primary photoproducts, eqs 1 and 2). This was the case in a recent study of Fe(CO)$_5$ photosubstitution by (E)-cyclooctene in n-hexane, where the authors reported a quantum yield of 0.8 for monosubstitution.[2,11] Only once has the quantum yield for disubstitution as a primary photoprocess been published.[12,13] In that account, the photolysis of Fe(CO)$_5$

$$\mathrm{M(CO)}_n \xrightarrow{h\nu,\,-\mathrm{CO}} \mathrm{M(CO)}_{n-1} \xrightarrow{+\mathrm{L}} \mathrm{M(CO)}_{n-1}\mathrm{L} \qquad (1)$$

$$\mathrm{M(CO)}_{n-1}\mathrm{L} \xrightarrow{h\nu,\,-\mathrm{CO}} \mathrm{M(CO)}_{n-2}\mathrm{L} \xrightarrow{+\mathrm{L}} \mathrm{M(CO)}_{n-2}\mathrm{L}_2 \qquad (2)$$

---

(1) Warburg, O.; Neglein, E. *Biochem. Zeit.* **1929**, *204*, 495.

(2) Angermund, H.; Bandyopadhyay, A. K.; Grevels, F.-W.; Mark, F. *J. Am. Chem. Soc.* **1989**, *111*, 4656.

(3) Norwood, K.; Ali, A.; Flesch, G. D.; Ng, C. Y. *J. Am. Chem. Soc.* **1990**, *112*, 7502.

(4) Majima, T.; Ishii, T.; Matusumoto, Y.; Takami, M. *J. Am. Chem. Soc.* **1989**, *111*, 2417.

(5) See ref 6 for other leading references.

(6) Poliakoff, M.; Weitz, E. *Acc. Chem. Res.* **1987**, *20*, 408.

(7) Waller, I. M.; Hepburn, J. W. *J. Chem. Phys.* **1988**, *88*, 6658.

(8) Rayner, D. M.; Ishikawa, Y.; Brown, C. E.; Hackett, P. A. *J. Chem. Phys.* **1991**, *94*, 5471.

(9) (a) Nasielski, J.; Colas, A. *Inorg. Chem.* **1978**, *17*, 237. (b) Nasielski, J.; Colas, A. *J. Organomet. Chem.* **1975**, *101*, 215.

(10) Nayak, S. K.; Burkey, T. J. *Organometallics* **1991**, *10*, 3745.

(11) From a kinetic model the authors predicted the concentrations of species as the reaction progressed and reported a minor deviation with the experimental results. They suggested the formation of disubstituted product formed directly from Fe(CO)$_5$ may account for the minor deviation but did not indicate a yield for disubstituted product in this account.

(12) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551.

(13) The quantum yield for disubstitution of Fe(CO)$_5$ with P(OCH$_3$)$_3$ (0.43) was recently reported: Angermund, H.; Bandyopadhyay, A. K.; Grevels, F.-W.; Mark, F.; Schappert, K. Presented at the Eighth International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Santa Barbara, CA, Aug 1989. The analogous value for (E)-cyclooctene photosubstitution was reported to be 0.07. These values were obtained from an abstract for the meeting.