propagation will therefore be retarded while the resulting increased local concentration of peroxyls near the surface will increase chain termination. That is, the nonhomogeneous distribution of peroxyls in the bilayer will lead to an apparent decrease in k_p and increase in $2k_t$.

In summary, our results suggest that the physical structure of lecithin bilayers makes them more resistant to autoxidation than would be expected on the basis of their chemical composition. Thus, although these bilayers appear to follow the normal kinetic law for autoxidation, the initiation process appears to be rather inefficient (probably because of its high microviscosity), and oxidizability appears to be reduced (possibly because of the "expulsion" of the peroxyls from the autoxidizable region of the bilayer). We hope that our results will stimulate additional kinetic work on bilayer and biomembrane autoxidation and that our suggestions will prove valuable in understanding these complex systems.

Acknowledgment. We thank Dr. G. W. Burton for his continued help and advice. We are also grateful to Dr. J. A. Howard, Dr. B. F. Johnson, Mrs. Anne Joyce, Mr. D. Lindsay, and Dr. I. C. P. Smith for their assistance and/or helpful suggestions.

---

(14) A referee suggested that the DBHN may be sequestered only in the polar region of the bilayer, near the head groups, and that this would slow down propagation because only unreactive $-CH_2-$ would be available for reaction. This is equivalent to our own suggestion except insofar as the process which causes the first peroxyl to be near the surface of the bilayer. However, the initiating *tert*-butoxyl does not abstract alkane hydrogen atoms all that rapidly, and so it should have time to diffuse to a position where it can attack the much more reactive allylic and doubly allylic hydrogens (unless it, too, is sequestered in the polar region).

(15) On sabbatical leave from Mount Allison University, Sackville, New Brunswick.

L. R. C. Barclay,[15] K. U. Ingold*
Division of Chemistry, National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6

Received June 19, 1980

Mechanistic Aspects of the Photochemistry of Metal-Metal Bonds. Evidence for the Intervention of Two Different Primary Photoproducts in the Photochemistry of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$

Sir:

The results of recent photochemical and related[1-4] studies on transition-metal compounds containing metal-metal single bonds have been consistently interpreted by a primary photochemical act in which homolytic cleavage of the metal-metal bond occurs (eq 1).[1-4] In particular, for the iron dimer, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$,

$$\text{M-M} \xrightarrow{h\nu} 2\text{M}\cdot \qquad (1)$$

both halogen atom abstraction from halocarbon solvents and substitution of phosphines and phosphites for CO have been attributed to $(\eta^5\text{-}C_5H_5)Fe(CO)_2$.[2] However, flash-photolysis studies on the dimers $Mn_2(CO)_{10}$[5] and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$[6] have provided evidence for both homolytic cleavage and additional transients, and the roles that the different intermediates play in the net photochemistry are unclear. For example, for the iron dimer, Tyler, Schmidt, and Gray[7] obtained low temperature spectroscopic (IR) evidence for a photochemical intermediate thought to be $(\eta^5\text{-}C_5H_5)(CO)_2Fe(\mu\text{-}CO)Fe(\eta^5\text{-}C_5H_5)(CO)(L)$ (L = $P(O\text{-}i\text{-}Pr)_3$) but whose structure and composition are uncertain. They suggested that the observed photochemistry of the starting dimer may occur solely via the dinuclear intermediate rather than through $(\eta^5\text{-}C_5H_5)Fe(CO)_2$.

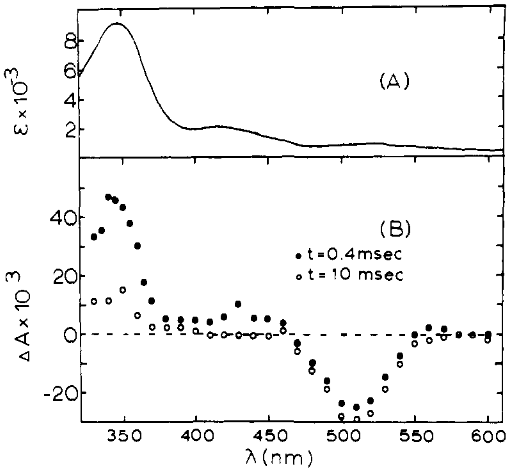


Figure 1. (A) Absorption spectrum of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ in cyclohexane. (B) Difference spectrum observed following flash photolysis of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ in cyclohexane. ΔA is the absorbance change observed from before the flash to t = 0.4 ms after initiation of the flash (O) and from before the flash to 10 ms after the flash (●). $\Delta A > 0$ corresponds to a decrease in absorbance of the solution after the flash.

In order to resolve the apparent mechanistic ambiguities in the iron dimer system, we have investigated its photochemistry by flash photolysis under both net photochemical and nonphotochemical conditions in inert solvents (cyclohexane, benzene). Under nonphotochemical conditions (freeze-pump-thaw-degassed, flame sealed), the samples were completely photochromic and stable for a period of at least several weeks. The electronic spectrum of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ has a characteristic, intense absorption band at 345 nm which has been assigned to the transition ($\sigma^* \leftarrow \sigma$(Fe-Fe))[8a] but which is probably more appropriately assigned to a $\pi^* \leftarrow \pi$ transition of the $Fe_2(CO)_2$ bridge.[8b] Either UV (λ > 250 nm) or visible (λ > 400 nm) flash photolysis of the dimer leads to the formation of two distinct intermediates. Both of the intermediates are present immediately following the flash (50 μs) and can be studied separately because their subsequent decay processes occur on substantially different time scales.

The more short-lived of the intermediates returns to $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ by equal concentration, second-order kinetics within 2 ms after the flash. The difference spectrum for the transient process observed (Figure 1B; t = 0.4 ms) shows a bleaching of the absorption band at 345 nm, and the reaction occurring is almost surely recombination of the monomeric fragments formed by photolysis during the flash (eq 2; k_2(20 ± 2 °C) = 3.2×10^9 M^{-1} s^{-1} (cyclohexane), 1.0×10^9 (benzene)).

$$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4 \underset{k_2}{\overset{h\nu}{\rightleftharpoons}} 2(\eta^5\text{-}C_5H_5)Fe(CO)_2 \qquad (2)$$

The long-lived (seconds) intermediate, I, also returns to the original dimer, and the difference spectrum for this process (Figure 1B; t = 10 ms) shows that I has a broad absorption centered at 510 nm which decays by first-order kinetics. The decay rate increases in a roughly linear manner with increasing monitoring light intensity. The results obtained suggest that I undergoes both secondary photolysis and a thermal reaction and that both re-

---

(1) Hudson, A.; Lappert, M. F.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* **1977**, 551.

(2) Abrahamson, H. B.; Palazotto, M. C.; Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 4123.

(3) Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 4123.

(4) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246.

(5) Hughey, J. L., IV; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49.

(6) Hughey, J. L., IV; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440.

(7) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2753.

(8) (a) Harris, D. C.; Gray, H. B. *Inorg. Chem.* **1975**, *14*, 1215. (b) Mitschler-, A.; Rees, B.; Lehman, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 3390; Bernard, M. *Inorg. Chem.* **1979**, *18*, 2782. Temmis, E. D.; Pinhos, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, *100*, 7259.

(9) Waltz, W. L.; Hackelberg, A.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259.

0002-7863/80/1502-7794$01.00/0

actions return it to $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$.

Having observed two intermediates, we studied their reactivity with added substrates, again by flash photolysis. Two reactions were investigated, substitution and oxidation by CCl_4. For the long-lived intermediate, I, in cyclohexane saturated with CO, a quantitative return to $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ was observed following flash photolysis and the difference spectrum for the process was unaffected. However, the observed first-order rate constant for return to the dimer had increased from $0.34\ s^{-1}$ to $280\ s^{-1}$ and was no longer light sensitive. The reaction with added potential ligands is not limited to CO. The lifetime of the intermediate was also markedly decreased in solutions containing PPh_3, CH_3CN, and Me_2SO in excess. It is more difficult to obtain reliable rate information under these conditions because net photochemistry is occurring, and only data from the first flash can be used reliably. However, a series of experiments at varying PPh_3 concentrations (10^{-3}–10^{-4} M) in cyclohexane showed that the observed first-order rate constant varies linearly with $[PPh_3]$ and that $k(20 \pm 2\ °C) = 1.5 \times 10^5\ M^{-1}\ s^{-1}$ for the disappearance of I. By contrast, there appears to be no or at best a very small contribution to photosubstitution from the homolytic cleavage pathway, at least for PPh_3 under our concentration conditions. The difference spectrum and recombination rate constants for $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ (eq 2) are *unaffected* by the presence of added CO (saturated) or PPh_3 (0.1 or 0.001 M). Since net photosubstitution to give $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3L$ is known to occur under the conditions of the flash experiment,[4,7,10] intermediate I is necessarily the origin of the observed photosubstitution with PPh_3, at least for $[PPh_3] \leq 0.1$ M.[12]

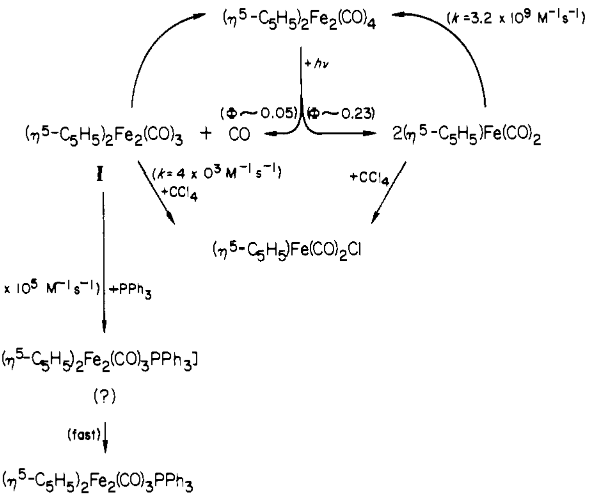
Flash photolysis experiments in cyclohexane with added CCl_4 (0.02–0.002 M), under conditions where photoredox chemistry is known to occur (eq 3), show clearly that I undergoes a reaction

$$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4 \xrightarrow[h\nu]{CCl_4} (\eta^5\text{-}C_5H_5)Fe(CO)_2Cl^{2,11} \quad (3)$$

with CCl_4. The transient decay rate for the intermediate is enhanced ($k(20 \pm 2\ °C) = 4 \times 10^3\ M^{-1}\ s^{-1}$) and the absorbance change observed is consistent with the appearance of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ as the product. However, it is equally clear that a reaction also occurs between CCl_4 and the monomers as shown by the loss of the transient absorbance increase at 345 nm (Figure 1). Clear evidence for the intervention of two intermediates in a reaction with CCl_4 has also been obtained by Fox and Poë by a kinetic study of the photochemical reaction between $Mn_2(CO)_{10}$ and CCl_4.[13] In fact, at high concentrations of CCl_4 the majority of the photoredox reaction for the iron dimer appears to occur through $(\eta^5\text{-}C_5H_5)Fe(CO)_2$. From the data of Abrahamson et al.[2] and Tyler et al.,[7] the quantum yield at 366 nm for the redox reaction ($\Phi = 0.23$ in CCl_4) is 4–5 times greater than that for PPh_3 substitution ($\Phi = 0.05$ in benzene). The yield for PPh_3 substitution, which only occurs through I, should also be a measure of the contribution of I to the redox yield at sufficiently high concentrations of PPh_3 and CCl_4, and it seems clear that the majority of the reaction with CCl_4 occurs via $(\eta^5\text{-}C_5H_5)Fe(CO)_2$.

From our results and the earlier results of Tyler et al. and of Abrahamson et al., it is possible to construct an overall reactivity scheme which accounts for the observed photochemistry of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. The basis for the scheme is the thermal reactivity of two distinct photointermediates, both of which appear to be primary photoproducts or are immediately derived from different primary photoproducts. From its reactivity toward added ligands like CO or PPh_3, we assume that intermediate I is a CO-loss products. In order to explain the earlier results of Tyler et al. at low temperature,[7] the suggestion is made in Scheme I that in the reaction between I and PPh_3, there is a second intermediate, the intermediate observed by Tyler et al. The two intermediates are clearly different: from Figure 1, I clearly absorbs strongly in the visible; the second intermediate has no obvious absorption features in the visible.[7] Presumably the second intermediate is a CO-bridged dimer without an Fe–Fe bond which is an unstable isomer of the final product, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$. However, it should be pointed out that we have *no* direct evidence on this point. If a second intermediate is involved, its conversion to the final product is more rapid than its rate of formation under our conditions (20 ± 2 °C).

Scheme I



Acknowledgment is made to the Department of Energy for support of this research through Grant No. ER-78-S-05-6034.

Jonathan V. Caspar, Thomas J. Meyer*

Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Received August 8, 1980

---

(10) Haines, R. J.; duPreez, A. L. *Inorg. Chem.* **1969**, *8*, 1459.

(11) Giannotti, C.; Merle, G. *J. Organomet. Chem.* **1976**, *105*, 96.

(12) It seems clear that the reactivity of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ toward substitution may be strongly dependent on the nature of the added ligand. For example, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(P(OMe)_3)_2$ is the major photoproduct observed following irradiation of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ in the presence of $P(OMe)_3$[2] suggesting a direct reaction between $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ and $P(OMe)_3$.

(13) Fox, A.; Poë, A. *J. Am. Chem. Soc.* **1980**, *102*, 2497.

H-Bond and Deprotonation Effects on the Resonance Raman Iron–Imidazole Mode in Deoxyhemoglobin Models: Implications for Hemoglobin Cooperativity[1]

Sir:

The recent assignment[2,3] of the iron–imidazole stretching mode, $\nu_{Fe\text{–}Im}$, in the resonance Raman (RR) spectrum of deoxyHb (Hb = hemoglobin) has provided a direct monitor of the strength of this important bond. Although no change in this frequency could be observed in R vs. T states of Hb Kempsey,[2] Nagai and Kitagawa,[4] using isolated chains, Hb Milwaukee, Hb Boston, and valency hybrids, have shown that there is an appreciable decrease of the normal (isolated chains or R state) Fe–Im frequency (222 and 224 cm^{-1} for α and β chains) in (T state) deoxyHb A, and that the shift is greater for α chains (207 cm^{-1}) than for β chains (220 cm^{-1}). These shifts were interpreted by Nagai and Kitagawa[4] in terms of the tension model of Hb cooperativity.[5] They assumed a linear force exerted by the protein on the proximal imidazole,

---

(1) This work was supported by NIH Grant HL 12526.

(2) Kincaid, J.; Stein, P.; Spiro, T. G. *Proc. Natl. Acad. Sci., U.S.A.* **1979**, *76*, 549–552; 4156.

(3) (a) Kitagawa, T.; Nagai, K.; Tsubaki, M. *FEBS Lett.* **1979**, *104*, 376–378. (b) Nagai, K.; Kitagawa, T.; Morimoto, H. *J. Mol. Biol.* **1980**, *136*, 271–289. (c) Hori, H.; Kitagawa, T. *J. Am. Chem. Soc.* **1980**, *102*, 3608–3613.

(4) Nagai, K.; Kitagawa, T. *Proc. Natl. Acad. Sci.* U.S.A. **1980**, *77*, 2033–2037.

(5) (a) Perutz, M. F.; Ladner, J. E.; Simon, S. R.; Ho, C. *Biochemistry* **1974**, *13*, 2163–2173. (b) Perutz, M. F.; Heidner, E. J.; Ladner, J. E.; Beetlestone, J. G.; Ho, C.; Slade, E. F. *Ibid.* **1974**, *13*, 2187–2200.

0002-7863/80/1502-7795$01.00/0