An important result of the analysis is the high sensitivity of QS to the trigonal distortion parameter b_1. This effect is illustrated in Figure 1 (II), where the solid curve represents the best fit to the data with $b_1 = 0.96$ whereas the dotted line is the best simulation obtained with b_1 fixed to 0.93. The latter curve exhibits a broad maximum and then drops appreciably at 4.2 K. This behavior becomes more pronounced as one approaches octahedral symmetry for which $b_1 = 0.816$. We therefore conclude that an increase or at least a constant value of QS at liquid helium temperature relative to the value at liquid nitrogen temperature may be used as a diagnostic feature for a symmetry intermediate between the octahedral and trigonal-prismatic limits, provided that the room-temperature value is substantially lower.

The variation of the QS with temperature is influenced to a lesser extent by the parameter c_1 which we take as a measure of the C_2 distortion. Although the range of values of c_2 is not so narrow as that for b_1, we have found that the QS behavior cannot be accounted for by omitting the C_2 distortion.

The similar thermal dependence of the quadrupole splittings as well as the very close crystal field parameters and the almost identical isomer shifts between I and the iron(IV) dithiocarbamates suggests that the structural characteristics and the detailed nature of iron bonding in these two classes of iron(IV) compounds are very similar. This is confirmed by the nearly identical structures of I and II. The same arguments lead to the conclusion that the exact environment at the iron is also similar in compounds II–V. Finally, we remark that the successful interpretation of Mössbauer data by a method based on ligand field theory offers substantial support to the fact that in these FeS_6 compounds we are concerned with iron in a well-established +4 oxidation level.

Registry No. II, 39838-28-3; III, 35270-33-8; IV, 39838-24-9; V, 35270-36-1.

References and Notes

(1) National Research Foundation Fellow.
(2) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).
(3) F. J. Hollander, R. Pedelty, and D. Coucouvanis, *J. Am. Chem. Soc.*, **96**, 4032 (1974).
(4) R. L. Martin, N. M. Rohde, G. B. Robertson, and D. Taylor, *J. Am. Chem. Soc.*, **96**, 3647 (1974).
(5) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Aust. J. Chem.*, **26**, 2533 (1973).
(6) G. Cauquis and L. Lachenal, *Inorg. Nucl. Chem. Lett.*, **9**, 1095 (1973).
(7) G. S. F. Hazeldean, R. S. Nyholm, and R. V. Pavish, *J. Chem. Soc. A*, 162 (1966).
(8) T. H. Moss, A. Ehrenberg, and A. J. Bearden, *Biochemistry*, **8**, 4159 (1969).
(9) R. H. Felton, G. S. Owen, D. Dolphin, and J. Fajer, *J. Am. Chem. Soc.*, **93**, 6332 (1971).
(10) J. L. Martin and J. Takats, *Inorg. Chem.*, **14**, 1358 (1975).
(11) V. Petrouleas, A. Kostikas, A. Simopoulos, and D. Coucouvanis, *J. Phys.*, **37**, Colloque C6, 507 (1976).
(12) R. M. Golding, C. M. Harris, K. J. Jessop, and W. C. Tennant, *Aust. J. Chem.*, **25**, 2567 (1972).
(13) N. H. Gangas, N. Gaitanis, A. Kostikas, and A. Simopoulos, *Nucl. Instrum. Methods*, **106**, 409 (1973).
(14) E. A. Paez, D. L. Weaver, and W. T. Oosterhuis, *J. Chem. Phys.*, **57**, 3709 (1972).
(15) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, N.Y., 1962, p 68.
(16) V. Petrouleas, A. Kostikas, and A. Simopoulos, *Phys. Rev. B*, **12**, 4666 (1975).
(17) B. N. Figgis, "Introduction to Ligand Fields", Wiley, New York, N.Y., 1966.
(18) For a review on ferrous compounds data see F. Varret, *J. Phys.*, **37**, Colloque C6, 481 (1976).

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Photooxidation of a Tetranuclear Cluster Complex in the Presence of Halocarbons. Photochemistry of the Carbonyl(η^5-cyclopentadienyl)iron(I) Tetramer

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Received November 5, 1976 AIC608035

The photochemistry and electronic absorption spectra of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ in the presence of halocarbons are reported. Irradiation of the complex at the appropriate wavelengths results in photooxidation, giving initially quantitative yields of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4^+$. This is the only photoreaction observed for any irradiation wavelength longer than 300 nm. In the absence of charge-acceptor solvents no photooxidation is found: the complex is photoinert in either benzene or CH_3CN. The quantum efficiency in the presence of halocarbons depends on cosolvent, the halocarbon, and wavelength. For example, in 1:1 CH_3CN–CCl_4 (by volume) the initial quantum yields are 0.21 at 313 nm, 0.03 at 366 nm, 0.002 at 405 nm, and ~0.0005 at 436 nm. But in pure CCl_4 the 313-nm quantum yield is only 0.05. The 313-nm yield for 1:1 CH_2Cl_2–CH_3CN is 0.0007. The absorption spectra reveal a halocarbon dependence in the near-UV, consistent with a charge-transfer-to-solvent excitation (CTTS). The CTTS maximum correlates with the ease of reduction of the halocarbons, and the wavelength dependence of the photooxidation substantiates the conclusion that the CTTS excitation is responsible for the photochemistry.

Introduction

Photochemical reactions of metal–metal bonded complexes have only been extensively investigated for dinuclear complexes.[2-6] Some qualitative reports concern the trinuclear species $M_3(CO)_{12}$ (M = Fe, Ru, Os).[6-10] In all of the cases studied thus far, the dominant form of excited-state chemical decay is rupture of the metal–metal bond(s) to ultimately yield mononuclear complexes. For larger clusters where one metal atom is bonded to more than one or two other metal atoms one might expect that one-electron excited states may not result in enough labilization to give photodeclusterification. Thus, ligand photosubstitution and photoredox processes may be important and lead to new ways to modify clusters, while retaining the essential framework bonding associated with the metal–metal core.

In this report we describe the photochemical behavior of the tetranuclear cluster $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$. This species has been known[11] for some time and is known[12] to undergo reversible reduction and oxidation, but no photochemical studies have been reported. We have examined the photochemical behavior of the complex in the presence of potential nucleophiles which could replace CO, but we found the complex to be essentially inert to ligand substitution. We do find that $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ can undergo photooxidation in the

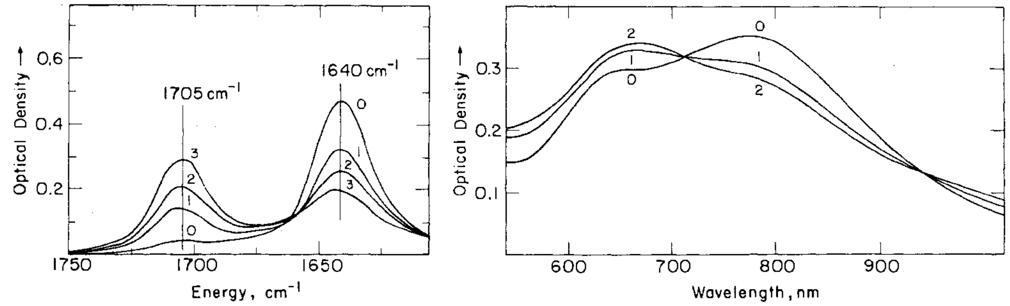

Figure 1. Infrared and visible spectral changes accompanying 313-nm irradiation of 1 × 10^{-3} M $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ at 25 °C in degassed $CH_3CN\text{-}CCl_4$, 1:1 by volume. Curves 0, 1, 2, and 3 correspond to 0, 0.5, 1.0, and 2.0 h of irradiation, respectively. The 1640-cm^{-1} peak is characteristic of the starting material and that at 1705 cm^{-1} is due to the cationic tetramer, $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4^+$. Both spectra were recorded with 1.0-mm cells.

Table I. Stoichiometry for Photooxidation of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ in 1:1 $CH_3CN\text{-}CCl_4$[a]

	Change in concn, M × 10^4	
Irrdn time, h	Fe_4	Fe_4^+
0.5	−3.3	+2.6
1.0	−4.8	+4.5
2.0	−5.9	+6.6

[a] 313-nm irradiation of 1.0 × 10^{-3} M $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ in $CH_3CN\text{-}CCl_4$, 1:1 by volume, at 25 °C. Spectral data for this experiment are given in Figure 1.

Table II. Quantum Yields for Disappearance of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ in the Presence of CCl_4[a]

Irrn wavelength, nm	Φ (±0.10)	Irrn wavelength, nm	Φ (±0.10)
313	0.21	436	~0.0005
366	0.03	514.5	<0.0001
405	0.002	632.8	<0.0001

[a] Degassed 1:1 v/v $CH_3CN\text{-}CCl_4$ solutions of 2 × 10^{-4} M $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ irradiated at 25 °C.

Table III. Photooxidation Quantum Yields for $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ as a Function of Halocarbon[a]

Solvent	Φ_{366nm}	Φ_{313nm}
$CCl_4\text{-}CH_3CN$ (1:1)	0.03	0.21
$HCCl_3\text{-}CH_3CN$ (1:1)	0.003	0.05
$H_2CCl_2\text{-}CH_3CN$ (1:1)		~0.0007[b]
$H_2CBr_2\text{-}CH_3CN$ (1:1)	≤0.005[b]	0.15
CH_3CN		<0.001[b]

[a] Irradiation at indicated wavelength in degassed solvent systems at 25 °C. Quantum yields are ±10%. [b] Quantum yield is for disappearance of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$.

Table IV. Solvent Dependence of Quantum Yields for Photooxidation of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$[a]

S-CCl_4 (1:1 v/v)	Φ_{313nm}	S-CCl_4 (1:1 v/v)	Φ_{313nm}
$CH_3CN\text{-}CCl_4$	0.21	$CH_2Cl_2\text{-}CCl_4$	0.07
$MeOH\text{-}CCl_4$	0.19	$C_6H_6\text{-}CCl_4$	0.10
$EtOH\text{-}CCl_4$	0.21	CCl_4	0.05
i-$PrOH\text{-}CCl_4$	0.19		

[a] Degassed S-CCl_4 (1:1 v/v) solutions containing 2 × 10^{-4} M $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ irradiated at 313 nm.

presence of certain halocarbons, and we now report the main findings concerning this photochemistry. To interpret our results we draw on the rich precedence[13] associated with the photooxidation of $Fe(\eta^5\text{-}C_5H_5)_2$ in the presence of chlorocarbons.

Results and Discussion

a. Photochemistry of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$. Prolonged near-UV or visible (λ >300 nm) irradiation of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ in degassed CH_3CN solution at 25 °C results in no observable spectral changes, and the complex can be recovered unchanged from the solution. However, near-UV irradiation of degassed, 25 °C CCl_4 solutions of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ rapidly yields precipitation of a dark green solid. The $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ is thermally stable in CCl_4 under the photoreaction conditions. Collection and identification of the product from the photoreaction show that it is the one-electron oxidation product $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4^+$. By comparison to a sample prepared by Cl_2 oxidation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_4]$ the chemical yield of the photoproduct is >90% based on the starting neutral complex. The photoproduct does not readily precipitate from more polar media so we have made quantitative measurements in $CH_3CN\text{-}CCl_4$ 1:1 by volume. Low-energy visible absorption spectral changes accompanying 313-nm irradiation are shown in Figure 1. Two isosbestic points are observed, 715 and 942 nm, and the same spectral changes with the same isosbestic points are found using Br_2 chemical oxidation of the tetramer. Regeneration of the starting tetramer from the photooxidation product is possible by addition of the strong reducing agent N_2H_4.[12] Infrared spectral changes accompanying the photooxidation are included in Figure 1. Quantitative measures of the decline of the band at 1640 cm^{-1} and the growth of the band at 1705 cm^{-1} show nearly 100% initial yield of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4^+$ from the neutral tetramer. Representative data associated with the spectral changes in Figure 1 are given in Table I. All spectral properties of the photooxidation product are in accord with those obtained on samples of the same ion generated chemically or electrochemically. The characteristic IR band at 1705 cm^{-1} and the UV–vis spectral features show that the cationic tetramer is the product in the various halocarbon solvent systems to be described below.

We observed qualitatively that $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ is largely insensitive to visible light, even in the presence of CCl_4 and despite its extensive near-IR and visible absorption. A wavelength dependence of the quantum efficiency for photooxidation is shown by the data in Table II. The near-UV quantum efficiency of 0.21 at 313 nm is very respectable, but the efficiency falls rapidly at the longer wavelengths, and at least for low-energy visible irradiation we find no efficient photochemistry of any sort.

The efficient 313-nm reaction in the presence of CCl_4 and the low reactivity in pure CH_3CN parallel earlier observations for $Fe(\eta^5\text{-}C_5H_5)_2$ which undergoes photooxidation in the presence of halocarbons but is essentially photoinert in solvents such as benzene, CH_3CN, alkanes, etc. We have carried out additional studies of the photoreactivity of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ in the presence of various halocarbon donors, Table III. The quantum yields are ordered in the chlorocarbon series CH_2Cl_2 < $CHCl_3$ < CCl_4. Additionally, CH_2Br_2 is significantly more reactive than CH_2Cl_2. These reactivity patterns can be

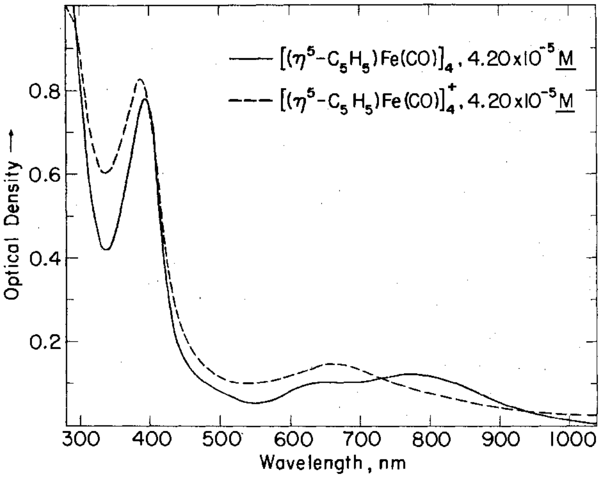

Figure 2. Optical absorption spectra of neutral and cationic clusters in CH_3CN at 25 °C in a 1.00-cm path length cell. The cation is as the PF_6^- salt.

Table V. Optical Absorption Spectral Data for $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ in Several Solvents at 25 °C

Solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
CH_3CN	775 (2.90×10^3), 394 (1.83×10^4)
CCl_4	775 (3.02×10^3), 396 (1.90×10^4)
$CHCl_3$	775 (3.00×10^3), 394 (1.83×10^4)
CH_2Br_2	775 (3.00×10^3), 396 (1.83×10^4)
$CHBr_3$	775 (3.10×10^3), 396 (1.90×10^4)
CH_2Cl_2	775 (3.10×10^3), 394 (1.90×10^4)
EtBr	775 (3.00×10^3), 395 (1.80×10^4)
THF	775 (2.98×10^3), 394 (1.85×10^4)
Benzene	775 (3.00×10^3), 396 (1.90×10^4)

correlated with the ease of reduction of the halocarbon.

One final set of results is important, regarding the photochemistry of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$. Table IV shows the effect of solvent on the quantum yields for photooxidation using CCl_4 as the halocarbon. Not unexpectedly, we find that the more polar solvents give larger quantum yields for the photooxidation process. This result seems to be consistent with the charge-transfer nature of the overall chemical process. Perhaps surprisingly, we find no evidence for photosubstitution in the cyclopentadienyl ring as reported[14] for $Fe(\eta^5\text{-}C_5H_5)_2$ in halocarbon–ethanol mixtures. It is likely, though, that cyclopentadienyl substitution is a secondary process, in any event.

b. Electronic Spectra and Nature of the Reactive Excited State. The spectra of the $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ and the photooxidation product are shown in Figure 2 for CH_3CN solution at 25 °C. For both the neutral and the cationic tetramer the spectra consist of a low-energy, low-intensity vis–near-IR band system and a near-UV high-intensity band. The similarity of the two spectra likely reflects the importance of the common Fe_4 core in each species. We do not make a detailed assignment here, but the absorptions are logically associated with electronic transitions between orbitals delocalized over the Fe_4 core. As shown by the data in Table V the positions and intensities of the main features of the spectrum of the neutral tetramer are independent of solvent. As described below, however, careful comparisons in the near-UV show some small, but important solvent dependencies.

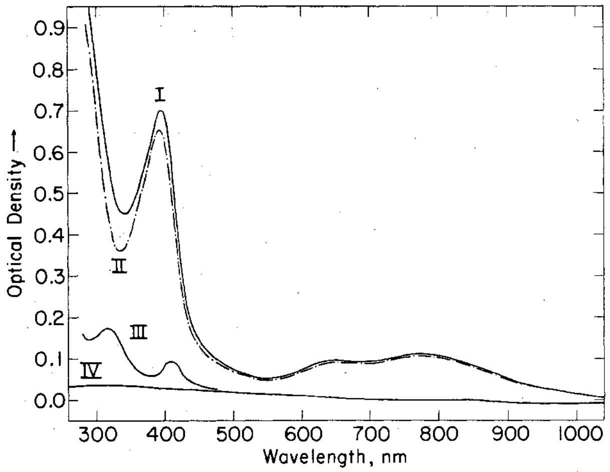

Figure 3. Optical spectra of 3.67×10^{-5} M $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ in CH_3CN–CCl_4 (1:9 by volume), curve I, and in pure CH_3CN, curve II, and the difference spectrum between I and II, curve III. Curve IV is the sample I vs. I, II vs. II, or air vs. air to demonstrate that a common baseline obtains. Thus, curve III clearly shows the spectral differences with CCl_4 present.

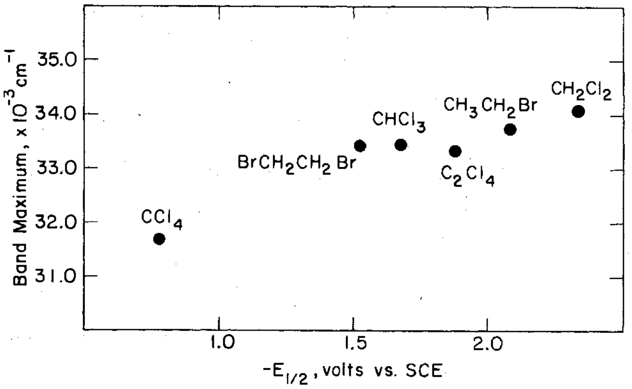

Figure 4. Correlation of CTTS absorption maximum with ease of reduction of the halocarbon solvent ($E_{1/2}$ values from C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, N.Y., 1970).

Table VI. Difference Spectral Data for $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$

Sample compartment[a]	λ,[b] nm	ΔOD[c]	$\Delta\epsilon$[d]
9:1 CCl_4-CH_3CN	316 (max)	0.22	4.0×10^3
	366	0.055	1.0×10^3
9:1 $CHCl_3$-CH_3CN	299 (max)	0.17	3.1×10^4
	313	0.13	2.4×10^3
	366	0.03	5.0×10^2
9:1 CH_2Cl_2-CH_3CN	294 (max)	0.12	2.2×10^3
	313	0.06	1.1×10^3
	366	0.02	4.0×10^2
9:1 EtBr-CH_3CN	296 (max)	0.085	1.6×10^3
9:1 C_2Cl_4-CH_3CN	300 (max)	0.20	3.7×10^3
9:1 1,2-$C_2H_4Br_2$-CH_3CN	299 (max)	0.22	4.0×10^3

[a] 5.50×10^{-5} M in solvent indicated; 1-cm pathlength; CH_3CN in reference compartment. [b] (max) indicates maximum of CTTS transition; cf. text and figures. [c] Observed optical density at λ. [d] Change in molar absorptivity associated with CTTS.

With respect to the photochemistry described above, the crucial result concerning the electronic spectrum of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ is that the near-UV spectrum is slightly perturbed in the presence of halocarbons. A comparison of the spectra of the neutral tetramer in CH_3CN and in CCl_4–CH_3CN 9:1 by volume is shown in Figure 3. In the difference spectrum maxima are observed at ~315 and ~400 nm. Generally, two maxima are found in the difference spectra involving other halocarbon–CH_3CN solvents. The higher energy peak maximum and its intensity depend on the halocarbon, while the lower energy maximum is constant in position but varies in intensity.

We propose that the increased absorptivity associated with the high-energy peak in the difference spectrum is due to charge-transfer-to-solvent (CTTS) excitation. Data in Table VI list the CTTS maximum and intensity for a number of

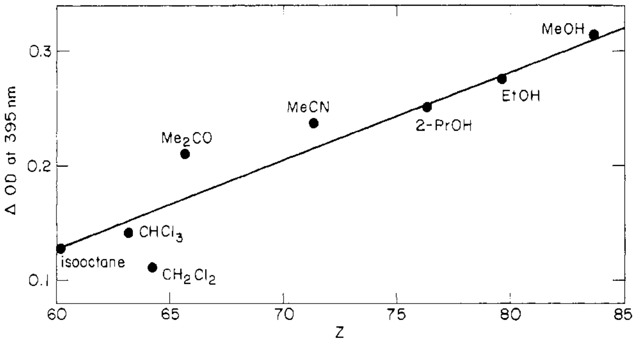

Figure 5. Correlation of low-energy difference peak intensity at 395 nm with Kosower[15] Z value. Difference spectra were recorded for 1.2×10^{-4} M tetramer in S–CCl_4 (9:1 by volume) in reference beam vs. 1.2×10^{-4} M tetramer in 100% CCl_4 in sample beam where S is the cosolvent.

halocarbons. The CTTS assignment gains support from the correlation of CTTS maximum and ease of reduction of the halocarbon, Figure 4. Consistently, we find that the more easily reduced halocarbon exhibits the lower energy CTTS maximum. The CTTS assignment is further substantiated by the wavelength dependence of the photooxidation efficiency (cf. Table II and Figure 3). Similar arguments have been used in interpreting both the spectra and photochemistry of Fe(η^5-C_5H_5)$_2$ in CCl_4.[13] Additionally, it is worth noting that the CTTS intensities found here for the tetramer are very similar to those for Fe(η^5-C_5H_5)$_2$.[13] Unfortunately, in the tetramer there exists a band of molar absorptivity of $\sim 2 \times 10^4$ in the vicinity of the CTTS which tends to obscure the CTTS band. In Fe(η^5-C_5H_5)$_2$ the nearby transitions have molar absorptivities of $<10^2$. We draw attention to one final similarity in the tetramer and Fe(η^5-C_5H_5)$_2$: the oxidation $E_{1/2}$ values for the two are very similar.[12] This fact is consistent with the comparable CTTS maximum for the two complexes.

The low-energy peak near 400 nm typically observed in the difference spectra is apparently not of the CTTS type. We draw this conclusion largely from the fact that we observe relatively little photooxidation at 405 nm. We ascribe the difference peak near 400 nm to "solvent effects". In fact, we find support for this interpretation from the intensity of the difference spectra of the neutral tetramer in various solvent–CCl_4 mixtures. The intensity of the maximum varies linearly with the empirical Kosower Z values[15] for a large number of solvents, Figure 5. The linear correlation coefficient for these data is 0.94. For the same set of data points the intensity is constant for the difference peak at ~315 nm associated with the CTTS transition. We offer no explanation for the lack of a solvent effect on the CTTS intensity, but the empirical result clearly distinguishes the high- and low-energy difference peaks. Importantly, the lack of a solvent dependence on the CT → CCl_4 band lends credence to the interpretation of the data in Table IV. That is, the difference in quantum efficiency cannot be ascribed to differences in the fraction of light giving rise to CTTS excitation.

Summary

The [(η^5-C_5H_5)Fe(CO)]$_4$ species can be photooxidized to [(η^5-C_5H_5)Fe(CO)]$_4^+$ by near-UV irradiation in the presence of halocarbons. Wavelength-dependent quantum yields can be correlated with a spectral feature attributed to a charge-transfer-to-solvent (halocarbon) excitation. These results parallel those for Fe(η^5-C_5H_5)$_2$. The photooxidation represents new photochemistry for clusters, but it is not clear whether the process offers any potential advantages compared to mononuclear complex photooxidations. Studies directed toward using the cluster as a photoassistance agent for driving redox processes are under way.

Experimental Section

Materials. All solvents used for spectroscopy and photochemistry are transparent over the wavelength range of interest and are commercially available in spectroscopic grade. The various halocarbons are commercially available and were either chromatographed or distilled prior to use. The (η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$ used in the synthesis of [(η^5-C_5H_5)Fe(CO)]$_4$ was used as received from commercial sources.

Preparation and Characterization of [(η^5-C_5H_5)Fe(CO)]$_4^{0,+}$. The [(η^5-C_5H_5)Fe(CO)]$_4$ was prepared according to the procedure of King.[11c] The complex was purified by recrystallization from CH_2Cl_2–hexane, and the resulting material has IR and UV-vis absorption spectral properties (tables and Figures) in accord with those in the literature,[11c,12] including molar absorptivites within 10%. The cationic cluster was prepared by passing Cl_2 through a CH_2Cl_2 solution of [(η^5-C_5H_5)Fe(CO)]$_4$. The [(η^5-C_5H_5)Fe(CO)]$_4$Cl salt precipitated, and the PF_6^- salt was prepared by dropwise addition of a saturated aqueous solution of NH_4PF_6 to an aqueous solution of the [(η^5-C_5H_5)Fe(CO)]$_4$Cl. The [(η^5-C_5H_5)Fe(CO)]$_4$PF$_6$ precipitated and was collected by filtration. The solid was washed with cold water and cold EtOH and then dried. Spectral properties (tables and figures) are in accord with literature values.[12]

Spectra. All UV-vis-near-IR spectra were obtained with a Cary 17 UV-vis-near-IR spectrophotometer. IR spectra were recorded on a Perkin-Elmer 180 grating infrared spectrometer using matched 1.0-mm path length cells.

Difference spectra were accurately recorded with the following illustrative procedure. Solutions of the tetramer in 9:1 halocarbon–CH_3CN mixture were obtained by halocarbon dilution of 1.0-mL aliquots of a stock CH_3CN solution containing 5×10^{-4} M tetramer. A reference solution was made by similarly diluting the stock solution with CH_3CN. By using matched 1.0-cm path length quartz cells and scanning slowly to allow for slit width equilibration, the difference spectra were recorded with the halocarbon solution in the sample beam and the CH_3CN solution in the reference beam. Baselines were also recorded by scanning mixed solvent vs. CH_3CN. When the solvent mixture absorbed appreciably in the region of interest, this could be automatically subtracted out by placing a second cell containing pure mixed solvent in the reference beam. In these cases the spectra and baselines were recorded with the additional cell in the reference beam. In all cases we were certain to assure that the optical density did not exceed 2.0 in either the reference or sample compartment.

Photolyses. In a typical experiment, 3.0-mL samples of a solution containing 2×10^{-4} M complex were placed in 13 × 100 mm Pyrex test tubes with constrictions. These were degassed in at least three freeze–pump–thaw cycles and were then hermetically sealed. Photolyses were performed with a merry-go-round[16] apparatus equipped with either a 450- or a 550-W Hanovia medium-pressure mercury lamp and appropriate Corning glass filters and filter solutions to isolate the 313-, 366-, 405-, and 436-nm Hg emissions. Spectra-Physics He–Ne and Ar ion lasers equipped with 6× beam expanders were used for the 632.8- and 514.5-nm irradiations, respectively. Actinometry was accomplished with ferrioxalate[17] or Reinecke's salt.[18] Progress of the photooxidation was monitored by UV-vis-near-IR or IR spectral measurements. For the quantum yield determinations, the conversions were kept below 10%, and over this period plots of conversion against irradiation time are linear.

Acknowledgment. We thank the Office of Naval Research for support of this work.

Registry No. [(η^5-C_5H_5)Fe(CO)]$_4$, 12203-87-1; [(η^5-C_5H_5)Fe(CO)]$_4^+$, 51923-54-7.

References and Notes

(1) Fellow of the Alfred P. Sloan Foundation, 1974–1976, and Dreyfus Teacher-Scholar Grant recipient, 1975–1980.
(2) (a) M. Wrighton and D. Bredesen, *J. Organomet. Chem.*, **50**, C35 (1973); (b) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 2065, 4246 (1975); (c) D. S. Ginley and M. S. Wrighton; *ibid.*, **97**, 3533, 4908 (1975); (d) D. L. Morse and M. S. Wrighton, *ibid.*, **98**, 3931 (1976).
(3) (a) A. R. Burkett, T. J. Meyer, and D. G. Whitten, *J. Organomet. Chem.*, **67**, 67 (1974); (b) J. L. Hughey, IV, C. R. Bock, and T. J. Meyer, *J. Am. Chem. Soc.*, **97**, 4440 (1975); (c) J. L. Hughey, IV, and T. J. Meyer, *Inorg. Chem.*, **14**, 947 (1975).
(4) (a) G. L. Geoffroy, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **96**, 5565 (1974); (b) R. H. Fleming, G. L. Geoffroy, H. B. Gray, A. Guputa, G. S. Hammond, D. S. Kliger, and V. M. Miskowski, *ibid.*, **98**, 48 (1976).

(5) D. M. Allen, A. Cox, T. J. Kemp, Q. Sultana, and R. B. Pitts, *J. Chem. Soc., Dalton Trans.*, 1189 (1976).
(6) (a) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974); (b) M. S. Wrighton, *Top. Curr. Chem.*, **65**, 37 (1976).
(7) B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Organomet. Chem.*, **67**, C75 (1974).
(8) (a) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 2874 (1974); *J. Chem. Soc. A*, 3147 (1970); 2559 (1969); (b) A. Brockes, S. A. R. Knox, and F. G. A. Stone, *ibid.*, 3469 (1971).
(9) F. A. Cotton, A. J. Deeming, P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Am. Chem. Soc.*, **93**, 4624 (1971).
(10) W. R. Cullen and D. A. Harbourne, *Inorg. Chem.*, **9**, 1839 (1970).
(11) (a) M. A. Newman, Trinh-Toan, and L. F. Dahl, *J. Am. Chem. Soc.*, **94**, 3383 (1972); (b) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, *ibid.*, **94**, 3385 (1972); (c) R. B. King, *Inorg. Chem.*, **5**, 2227 (1966).
(12) J. A. Ferguson and T. J. Meyer, *Chem. Commun.*, 623 (1971); *J. Am. Chem. Soc.*, **94**, 3409 (1972).
(13) (a) O. Traverso and F. Scandola, *Inorg. Chim. Acta*, **4**, 493 (1970); (b) J. C. D. Brand and W. Snedden, *Trans. Faraday Soc.*, **53**, 894 (1957).
(14) (a) Y. Hoshi, T. Akiyama, and A. Sugimori, *Tetrahedron Lett.*, 1485 (1970); (b) T. Akiyama, Y. Hoshi, S. Goto, and A. Sugimori, *Bull. Chem. Soc. Jpn.*, **46**, 1851, 1855 (1973).
(15) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3261 (1958).
(16) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).
(17) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(18) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).

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Reactions of the Zerovalent Complex Ni[HP(C_6H_5)$_2$]$_4$[1]

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Received September 20, 1976 AIC60685L

Ligand substitution and oxidative addition reactions of the complex Ni[HP(C_6H_5)$_2$]$_4$ have been investigated. Complete substitution of diphenylphosphine occurs upon reacting Ni[HP(C_6H_5)$_2$]$_4$ with phosphites, L, resulting in the production of NiL_4 in reasonable yields. Reactions of Ni[HP(C_6H_5)$_2$]$_4$ with organic halides and with HgX_2 (X = Cl, Br, I, SCN) produce the pentacoordinate species Ni[HP(C_6H_5)$_2$]$_3$$X_2$, while reactions with $Hg(CN)_2$ form polymeric {Ni[HP(C_6H_5)$_2$]$(CN)_2 \cdot H_2O$}$_n$, with benzoyl cyanide form square-planar Ni[HP(C_6H_5)$_2$]$_2$$(CN)_2 \cdot 2C_6H_6$, and with phenyl isothiocyanate form Ni[HP(C_6H_5)$_2$]$_2$(C_6H_5NCS)$_2$. Oxidative additions with HgX_2 produce, in most cases, Hg_2X_2 rather than elemental mercury suggesting that these reactions occur by sequential one-electron oxidations rather than simultaneous two-electron oxidations. The relative ease of these oxidations Cl > Br > I suggests that these oxidations occur by atom transfer without the intermediate formation of Ni–Hg bonds. The organic products of some of the oxidative additions of RX have been isolated and characterized. The nature of the organic products suggests that oxidative addition reactions of Ni[HP(C_6H_5)$_2$]$_4$ with RX proceed by radical pathways involving sequential oxidative addition and reductive elimination steps.

Introduction

There has been considerable interest in recent years in the reactions of zerovalent transition metal complexes[3] since they have been suggested as model systems for the study of relations between homogeneous and heterogeneous catalysts.[4] This idea rests upon the tenet that coordination and chemisorption can be related by similar electronic interactions and that the behavior in solution of some zerovalent metal complexes is essentially that of solvated metal atoms. The mechanisms of oxidative additions have been studied with the hope of explaining the homogeneous catalytic activity of these species.[5] Proposals involving carbonium ions, free radicals, and concerted three-center intermediates have evolved from various kinetic investigations.[5b,c,6]

To date only tertiary phosphine and di(tertiary phosphine) complexes of nickel(0), palladium(0), and platinum(0) have been extensively investigated[3] but no detailed investigations of all the products of these reactions have been reported. All of these complexes have two features in common: they are or they can become coordinatively unsaturated[7] in solution, and the metal is coordinated to "soft" ligands such as phosphines or arsines.

Since the small steric requirements of diphenylphosphine might be expected to enhance the stability of its complexes,[7] an investigation of the reactions of Ni[HP(C_6H_5)$_2$]$_4$ was undertaken especially because the complex Ni[HP(C_6H_5)$_2$]$_4$ is readily obtained[8] and easily handled.

Experimental Section

The complex Ni[HP(C_6H_5)$_2$]$_4$ was prepared by the literature method.[8] It is moderately air sensitive but may be handled briefly in the air and can be kept in a desiccator under vacuum for approximately 2 days before decomposing. Decomposition is accompanied by a color change from lemon yellow to brown.

A. Oxidative Additions of Alkyl and Aryl Halides. These reactions were all run similarly either by suspending Ni[HP(C_6H_5)$_2$]$_4$ in anhydrous benzene under dry nitrogen and adding an excess of the organic reagent or by suspending Ni[HP(C_6H_5)$_2$]$_4$ in the neat reactant in a dry nitrogen atmosphere. The following are typical.

(1) To 4.44 g (5.5×10^{-3} mol) of Ni[HP(C_6H_5)$_2$]$_4$ suspended in 100 mL of dry benzene under a stream of dry nitrogen was added 1.12 mL (1.236 g, 1.1×10^{-2} mol) of chlorobenzene. The suspension was refluxed for approximately 24 h (until nearly all of the Ni[HP(C_6H_5)$_2$]$_4$ dissolved) with a color change from bright yellow to yellow-brown. Unreacted Ni[HP(C_6H_5)$_2$]$_4$ was removed by filtration and anhydrous diethyl ether was added to the filtrate to precipitate [HP(C_6H_5)$_2$]$_3$$NiCl_2$ as brown crystals (mp 94 °C) which were removed by filtration under a stream of nitrogen. The resultant filtrate was concentrated on a rotary evaporator at 40–50 °C. White crystals were recovered from the filtrate (0.124 g; 10%; mp 70–71 °C) and identified as biphenyl on the basis of melting point, GC analysis, and NMR.

(2) To 4.44 g (5.5×10^{-3} mol) of Ni[HP(C_6H_5)$_2$]$_4$ was added 50 mL of freshly distilled chlorobenzene and the suspension was refluxed under nitrogen until most of the Ni[HP(C_6H_5)$_2$]$_4$ dissolved (~24 h). The solution changed color from yellow to yellow-brown as the Ni[HP(C_6H_5)$_2$]$_4$ dissolved. A minor amount of gelatinous material was removed by filtration and the filtrate was triturated with diethyl ether to yield 0.99 g (26%) of Ni[HP(C_6H_5)$_2$]$_3$$Cl_2$. The filtrate was concentrated to 10 mL by distillation and treated with a trace of water to yield 0.13 g of white crystals, mp 71 °C, identified as biphenyl.

(3) Excess cyclohexyl iodide was reacted as in part 2. After filtration of the reaction mixture, addition of dry acetone, and isolation of Ni[HP(C_6H_5)$_2$]$_3$$I_2$ by filtration, the filtrate was distilled. The distillation products were identified as cyclohexane, cyclohexene, and dicyclohexyl by their boiling points and infrared and NMR spectra.

(4) *d*-Bromocamphor was reacted as in part 1. After separation of the crystalline precipitate of Ni[HP(C_6H_5)$_2$]$_3$$Br_2$, the solution was treated with 50 mL of hexane and filtered. Excess 2,4-dinitrophenylhydrazine reagent was then added to the filtrate and it was allowed to stand for 12 h. The crystalline product thus formed melted sharply at 168 °C. Though this product was not completely characterized, its infrared spectrum confirmed that it was a 2,3-dinitrophenylhydrazone and the integrated NMR spectrum indicated the presence of two camphoric fragments for every hydrazone group in the molecule, indicating that the camphor had dimerized. The