2792 *Inorg. Chem.* **1985**, *24*, 2792-2796

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Photochemistry of (Alkene)pentacarbonyltungsten(0) Complexes in Rigid Alkane at Low Temperature: Relative Importance of Dissociative Loss of Alkene and Carbon Monoxide

KEITH R. POPE and MARK S. WRIGHTON*

Received November 15, 1984

UV irradiation (254 or 313 nm) of $W(CO)_5$(alkene) (alkene = C_2H_4, C_3H_6, 1-C_5H_{10}) in methylcyclohexane at 77 K yields two primary photoprocesses, CO and alkene loss. The relative loss of alkene is approximately 2 times more important upon 313-nm irradiation than when irradiation is at 254 nm. Further, the relative importance of alkene loss increases approximately threefold: $C_2H_4 < C_3H_6 <$ 1-C_5H_{10}. The loss of alkene is accompanied by the formation of $W(CO)_5$, while loss of CO gives the 16e $W(CO)_4$(alkene) species. Since the spectrum of the CO-loss product from $W(CO)_5(C_2H_4)$ is nearly the same as that from $W(CO)_5(C_3H_6)$ or $W(CO)_5$(1-C_5H_{10}), no evidence for $W(CO)_4(H)(\pi\text{-allyl})$ complexes is found. Even $W(CO)_5(\eta^2$-1,4-pentadiene) and $W(CO)_5(\eta^2$-cyclopentadiene), having doubly allylic C–H bonds, do not yield a hydride upon light-induced loss of CO. The measurement of the quantitative ratio of alkene:CO loss has been made possible by a quantitative determination of the extinction coefficient, ϵ, for free CO at 2132 cm^{-1} in methylcyclohexane at 77 K. The values of ϵ_{CO} were determined by measuring the absorptivity at 2132 cm^{-1} for known fractional light-induced conversion of $Cr(CO)_6$, $W(CO)_6$, and $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ to CO and the appropriate 16e metal carbonyl; the values of ϵ_{CO} from these precursors are 420 ± 40, 390 ± 20, and 420 ± 20 M^{-1} cm^{-1}, respectively. In a 2-methyltetrahydrofuran glass the value of ϵ_{CO} is lower, 350 ± 20 M^{-1} cm^{-1}.

We wish to report on the relative importance of light-induced loss of CO and alkene from $W(CO)_5$(alkene) upon UV irradiation in methylcyclohexane (MCH) at 77 K (eq 1 and 2). Part of the

$$W(CO)_5(\text{alkene}) \xrightarrow{h\nu} W(CO)_4(\text{alkene}) + CO \tag{1}$$

$$W(CO)_5(\text{alkene}) \xrightarrow{h\nu} W(CO)_5 + \text{alkene} \tag{2}$$

motivation for this work stems from the recent observation that irradiation of $Fe(CO)_4$(alkene) in low-temperature matrices allows the observation[1] of important intermediates in the catalytic cycle for $Fe(CO)_5$-photocatalyzed reaction of alkenes.[2] It is also known that UV irradiation of $W(CO)_6$ in the presences of olefins yields catalytic reactions.[3,4] The $W(CO)_5$(alkene) species are known to be photosensitive,[4] but a quantitative investigation of their reactivity has not been reported.

In the present work we show that the two processes represented by eq 1 and 2 can be quantitatively evaluated at 77 K. Much effort has been directed toward characterizing the relative importance of various photoprocesses of metal carbonyls in solution,[4,5] but there is little quantitative information concerning competing processes in low-temperature glasses. The relative importance of chemistry according to eq 1 and 2 depends on both wavelength and the alkene, with shorter wavelengths and smaller alkene (alkene = C_2H_4, C_3H_6, 1-C_5H_{10}) favoring CO loss. The key to being able to assess the relative importance of CO vs. alkene loss is the ability to measure the absorptivity of uncomplexed CO in the matrix at 77 K. The absorptivity of CO, ~400 M^{-1} cm^{-1} in MCH at 77 K, is important in general in assessing the importance of CO loss from metal carbonyls at 77 K.[6]

Experimental Section

Instrumentation. UV–vis absorption spectra were recorded by using a Cary 17 spectrophotometer or a Hewlett-Packard 8451-A diode array spectrometer. Infrared spectra were recorded with a Nicolet 60-SX or a 7199 Fourier transform spectrometer or a Perkin-Elmer Model 180 spectrometer.

Low-temperature spectra were obtained with a Precision Cell, Inc., Model P/N 21000 variable-temperature cell with CaF_2 outer and inner windows, with liquid N_2 as the coolant. The temperature of the alkane glass was monitored with a copper–constantan thermocouple in contact with the inner window of the cell. Temperatures are accurate to ±5 K.

Chemicals. Methylcyclohexane (MCH) was purchased ("Photorex" grade, J. T. Baker) and distilled from Na under Ar prior to use. 2-Methyltetrahydrofuran (Aldrich) was twice distilled from Na under Ar prior to use.

The purity of glassing solvents was checked by UV–vis spectroscopy prior to use. Isooctane ("Photorex" grade, J. T. Baker) was used without further purification for the synthesis of $W(CO)_5NH_3$. Ammonia gas (99.99%, anhydrous, Matheson) was used without further purification. Tungsten and chromium hexacarbonyls (Alfa) were twice sublimed in the dark prior to use.

$W(CO)_5NH_3$ was prepared by near-UV irradiation of $W(CO)_6$ in isooctane purged with NH_3, according to a previously reported method.[7] The $W(CO)_5NH_3$ precipitates from the irradiated solution, and the solid was repeatedly washed with isooctane to remove traces of $W(CO)_6$.

The $W(CO)_5$(olefin) complexes were prepared by 436-nm irradiation of a solution of $W(CO)_5NH_3$ in the appropriate solvent in the presence of an excess of the olefin. In the case of ethylene and propylene, the alkene was rapidly purged through the solution during irradiation, and the excess alkene was subsequently removed by an Ar purge. The quantitative formation of the olefin complex was verified by infrared analysis.[8] The $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ was available from previous work[9] and was twice sublimed before use.

Irradiations. Irradiations at 313 nm were carried out with a Bausch and Lomb SP250 high-pressure Hg lamp filtered by a 10-cm H_2O filter with Pyrex windows followed by a 1-cm cell containing a K_2CrO_4–K_2CO_3 solution to give 313 ± 20 nm. Irradiations at 254 nm were carried out with an unfiltered Ultraviolet Products Inc. Model PCQ-X1 low-pressure Hg lamp.

Results and Discussion

Absorptivity of Uncomplexed CO in Low-Temperature Organic Glasses. Work in this laboratory[5] has concerned the irradiation of metal carbonyls in low-temperature (~77 K) organic glasses. Part of this effort has been to quantitatively measure the molar amount of CO ejected from the coordination sphere of a complex compared to the molar amount of the complex consumed. Such studies are valuable when reactions other than CO loss can occur, such as H–X elimination, radical formation, and loss of other ligands. The ability to make a quantitative assessment of the importance of CO loss using IR spectroscopy requires knowing the absorbance changes for at least one characteristic band of the

---

(1) Mitchener, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1065.

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

(3) Wrighton, M. S.; Hammond, G. S.; Gray, H. B. *J. Organomet. Chem.* **1974**, *70*, 283.

(4) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(5) (a) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1977**, *16*(2), 3154. (b) Dahlgren, R. M.; Zink, J. I. *J. Chem. Soc., Chem. Commun.* **1978**, *20*, 863. (c) Dahlgren, R. M.; Zink, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 1448. (d) Geoffroy, G. L. *J. Chem. Educ.* **1983**, *60*, 861.

(6) (a) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5934. (b) Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 995. (c) Bentsen, J. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 4041. (d) Liu, D. K.; Brinkley, C. G.; Wrighton, M. S. *Organometallics* **1984**, *3*, 1449. (e) Liu, D. K.; Wrighton, M. S.; McKay, D. R.; Maciel, G. E. *Inorg. Chem.* **1984**, *23*, 212. (f) Lewis, C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 7768. (g) Hepp, A. F.; Blaha, J. P.; Lewis, C.; Wrighton, M. S. *Organometallics*, **1984**, *3*, 174. (h) Bentsen, J. G.; Wrighton, M. S. *Inorg. Chem.* **1984**, *23*, 512.

(7) Wrighton, M. S. *Inorg. Chem.* **1974**, *13*, 905.

(8) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *Inorg. Chem.* **1963**, *2*, 1264.

(9) Kazlaukas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 1727.

0020-1669/85/1324-2792$01.50/0 © 1985 American Chemical Society

Table I. Spectroscopic Data for Relevant Compounds

compd[c]	IR[a] ν_{CO} (ϵ or rel OD)	UV–vis[b] λ_{max} (ϵ)
CO	2132 (4.0×10^2)	
$W(CO)_6$	1980 (6.8×10^4)	340 (1×10^3), 280 (1×10^4)
$W(CO)_5$	2087 (6.0×10^2), 1951 (4.1×10^4), 1921 (7.8×10^3)	415, 242
$W(CO)_5$-(η^2-C_2H_4)	2085 (2.0×10^3), 1968 (1.6×10^4), 1947 (1.9×10^4)	360
$W(CO)_4$-(η^2-C_2H_4)	2047 (3.0×10^3), 1883 (8.1×10^3)	
$W(CO)_5$-(η^2-C_3H_6)	2082 (2.0×10^3), 1961 (1.5×10^4), 1944 (1.8×10^4)	355
$W(CO)_4$-(η^2-C_3H_6)	2044 (3.0×10^3), 1885 (3.3×10^3)	
cis-$W(CO)_4$-(η^2-C_3H_6)$_2$	2039 (1.0), 1890 (1.5)	
$W(CO)_5$-(η^2-1-C_5H_{10})	2082 (2.0×10^3), 1961 (1.5×10^4), 1944 (1.9×10^4)	
$W(CO)_4$-(η^2-1-C_5H_{10})	2044 (3.0×10^3), 1881 (7.4×10^3)	
$W(CO)_5$-(η^2-1,4-pent)	2082 (1.00), 1963 (6.13), 1944 (7.80)	
cis-$W(CO)_4$-(η^2-1-C_5H_{10})$_2$	2037 (1), 1885 (2.5)	
trans-$W(CO)_4$-(η^2-1-C_5H_{10})$_2$	1950	
$W(CO)_5$-(η^2-C_5H_6)	2078 (1.00), 1957 (8.82), 1946 (10.9)	
$W(CO)_4$(nor)	2042 (1.0), 1952 (2.3), 1989 (1.7)	
$Cr(CO)_6$	1983 (5.49×10^4)	
$Cr(CO)_5$	2082 (9.30×10^2), 1954 (3.34×10^4), 1927 (6.62×10^3)	
(η^5-C_5H_5)-$W(CO)_3CH_3$	2018 (6.58×10^3), 1925 (1.00×10^4)	

[a] ν is in units of cm^{-1} and ϵ in units of M^{-1} cm^{-1} at 77 K in MCH; error is ±15%. [b] UV–VIS spectra were recorded in MCH glass at 77 K. λ is in units of nm and ϵ in units of M^{-1} cm^{-1}. [c] Abbreviations: nor = norbornadiene; 1,4-pent = 1,4-pentadiene.

starting complex (present at a known initial concentration) and the absorptivity, ϵ, of the characteristic feature of uncomplexed CO at 2132 cm^{-1}.[10] Our strategy for determining the absorptivity of uncomplexed CO in low-temperature glasses has been to examine the initial IR absorbance changes upon photolysis of $Cr(CO)_6$ and $W(CO)_6$ in low-temperature matrices.[11] The key is that these materials only undergo dissociative loss of CO upon near-UV irradiation; thus, the stoichiometry is given by eq 3 at

$$M(CO)_6 \xrightarrow[\sim 77\ K]{h\nu} M(CO)_5 + CO \qquad (3)$$

low absorbance changes upon photolysis of $Cr(CO)_6$ and $W(CO)_6$ in low-temperature matrices. The $M(CO)_6$ species are easy to purify and handle, and solutions of known concentration are easily prepared. The disadvantage with using $M(CO)_6$ to generate known concentrations of CO for the purpose of determining ϵ_{CO} is that $\epsilon_{M(CO)_6}$ is more than 2 orders of magnitude larger than ϵ_{CO}. Accordingly, we have made numerous independent measurements in order to define a good value for ϵ_{CO}. Additionally, we have used (η^5-C_5H_5)$W(CO)_3CH_3$ *assuming* that chemistry according to eq 4 accounts for all (η^5-C_5H_5)$W(CO)_3CH_3$ consumed upon near-UV irradiation.[9]

$$(\eta^5\text{-}C_5H_5)W(CO)_3CH_3 \xrightarrow[\sim 77\ K]{h\nu} (\eta^5\text{-}C_5H_5)W(CO)_2CH_3 + CO \qquad (4)$$

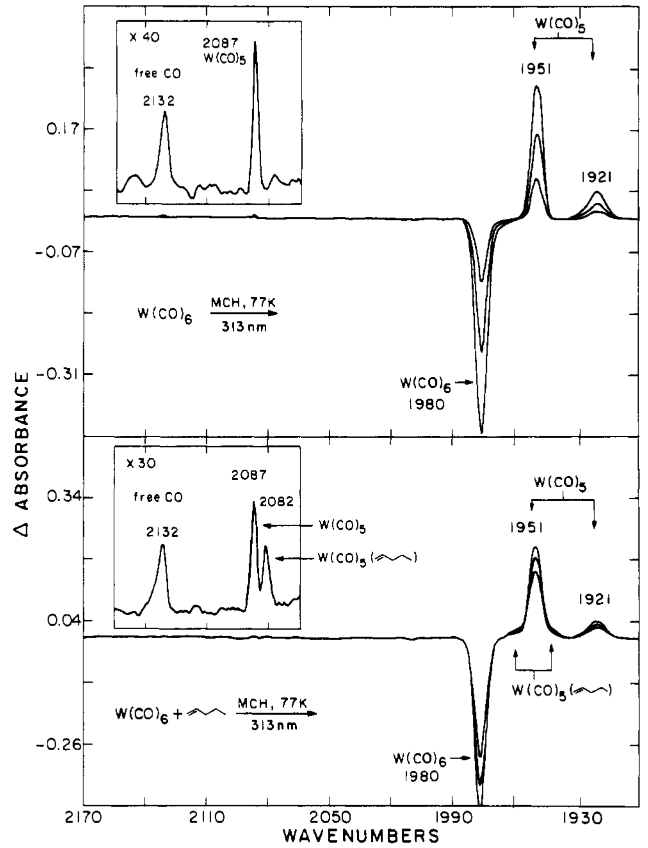


Figure 1. (Top) IR difference spectrum upon photolysis of $W(CO)_6$ in rigid MCH at 77 K. (Bottom) IR difference spectrum upon photolysis of $W(CO)_6$ in rigid MCH-1-pentene (~1% alkene) at 77 K. Spectra at three irradiation times are shown. The maximum extent of conversion is <25%. Insets show a vertical scale magnification for the longest irradiation time.

Table II. Molar Absorptivity, ϵ, of Uncomplexed CO in Organic Gases[a]

CO source	solvent	no. of determns	$\epsilon \pm \sigma$, M^{-1} cm^{-1}
$Cr(CO)_6$	MCH	13	420 ± 40
$W(CO)_6$	MCH	5	390 ± 20
(η^5-C_5H_5)$W(CO)_3CH_3$	MCH	2	420 ± 20
$W(CO)_6$	2-MeTHF	4	350 ± 20

[a] All measurements made at <25% conversion with 313-nm light. The temperature was maintained at 77 ± 10 K.

The procedure used to determine ϵ_{CO} is as follows. A solution of known metal carbonyl ($M(CO)_6$ or (η^5-C_5H_5)$W(CO)_3CH_3$) concentration at 298 K in an IR cell of known path length is cooled to 77 K. The absorbance(s) of the metal carbonyl is recorded, and ϵ for the metal carbonyl is calculated, (Table I). The sample is then irradiated for a short period of time with near-UV light to effect less than 25% consumption of the metal carbonyl. The IR spectrum of the irradiated sample at 77 K is then subtracted from that for the starting material. The growth of absorbance at 2132 cm^{-1} is attributed to the production of uncomplexed CO.[10] The decline in absorbance due to the photoreaction represented by eq 3 or 4 thus gives the concentration of CO generated. Figure 1 illustrates representative IR spectral changes for the irradiation of $W(CO)_6$ in MCH at 77 K showing the quality of the data that can be obtained. Table II gives a summary of the data relating to the determination of ϵ_{CO}. As can be seen from the data, each of the three metal carbonyls gives the same value of ϵ_{CO}, consistent with the conclusion that the stoichiometry of the photochemistry is given by eq 3 or 4 and that the ejected CO has negligible residual interaction with the accompanying 16e metal carbonyl fragment. In the coordinating organic glass 2-methyltetrahydrofuran the value of ϵ_{CO} is somewhat lower than in the MCH glass. The use of 2-methyltetrahydrofuran generally broadens metal carbonyl absorptions in the IR compared to the case for alkane solvents.

---

(10) Leroi, G. E.; Ewing, G. E.; Pimentel, G. C. *J. Chem. Phys.* **1964**, *40*, 2298.

(11) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791, 4800.

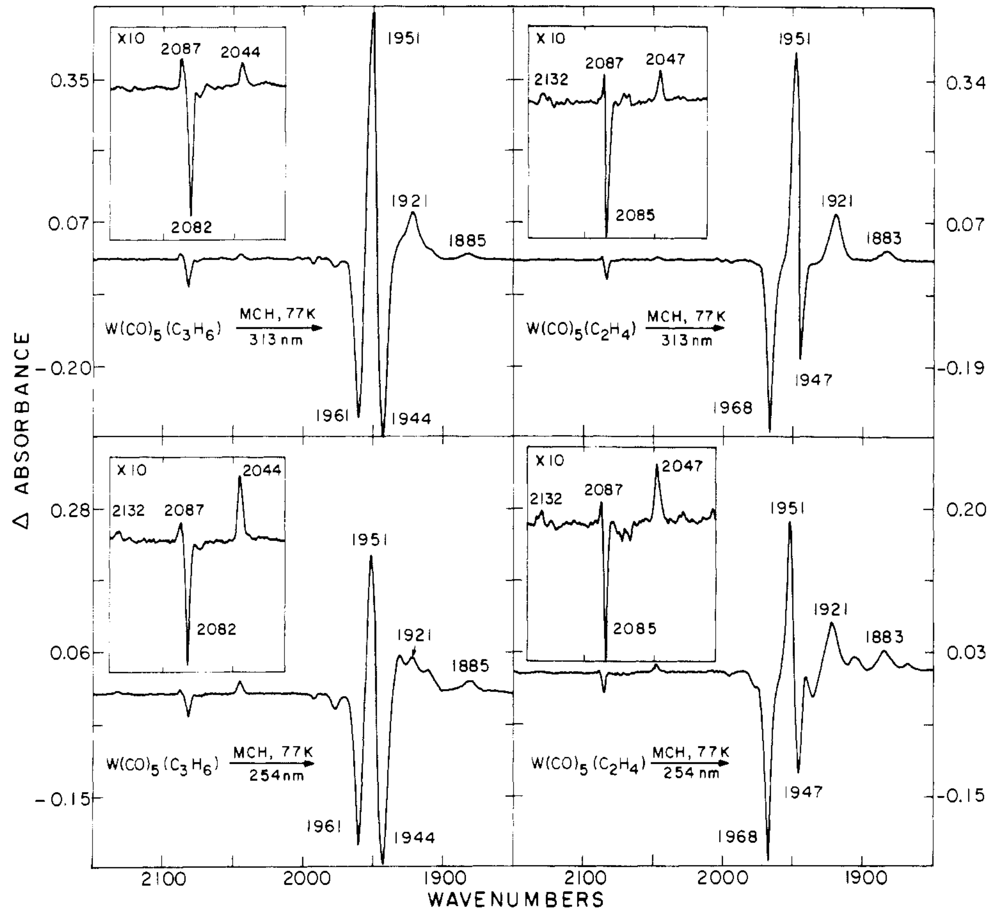


Figure 2. (Top) IR difference spectra upon 313-nm irradiation of $W(CO)_5(C_3H_6)$ (left) and $W(CO)_5(C_2H_4)$ (right) in rigid MCH at 77 K. (Bottom) IR difference spectra upon 254-nm irradiation of $W(CO)_5(C_3H_6)$ (left) and $W(CO)_5(C_2H_4)$ (right). The maximum extent of conversion is <25%. Insets show a vertical scale magnification. Experiments performed at different wavelengths involved use of two aliquots of the same sample.

In the study of $W(CO)_5$(alkene) the matrix material used was MCH. Thus, we use the value $\epsilon_{CO} = 400\ M^{-1}\ cm^{-1}$ in the calculations of alkene vs. CO loss.

Note that in assessing ϵ_{CO} we have also obtained the data necessary to calculate the absorptivities of the bands for the metal carbonyl fragments. These values are included in the appropriate entries in Table I. The values of ϵ reported have not been corrected for solvent contraction upon cooling from 298 to 77 K. All ϵ values reported have an estimated error of ±15%.

Relative Importance of CO and Alkene Loss from $W(CO)_5$(alkene). Irradiation of $W(CO)_5$(alkene) (alkene = C_2H_4, C_3H_4, C_3H_6, 1-C_5H_{10}) has been carried out at 77 K in MCH to assess the relative importance of CO vs. alkene loss from the lowest excited states. Data have been collected for all three complexes at two excitation wavelengths, 254 and 313 nm. IR spectroscopy allows quantitative assessment of the ratio of products at 77 K. To demonstrate, for example, that $W(CO)_5$ and $W(CO)_5$(alkene) can be distinguished, consider the bottom portion of Figure 1, which illustrates the spectral changes that occur upon irradiation of $W(CO)_6$ in an MCH glass containing 1-C_5H_{10}. In particular, note the differences in the vicinity of 2080–2090 cm^{-1}. The 16e C_{4v} species exhibits a weak absorption, a_1, at 2087 cm^{-1}, whereas $C_{4v}W(CO)_5(1\text{-}C_5H_{10})$ exhibits a_1 at a slightly lower energy, 2082 cm^{-1}. These a_1 bands are characteristic, have about the same absorptivity as uncomplexed CO, and are not obscured by other bands. Thus, the growth of CO monitored at 2132 cm^{-1} and the growth of $W(CO)_5$ monitored at 2087 cm^{-1} allows a quantitative assessment of the relative importance of CO loss and alkene loss, respectively, from photoexcited $W(CO)_5$(alkene).

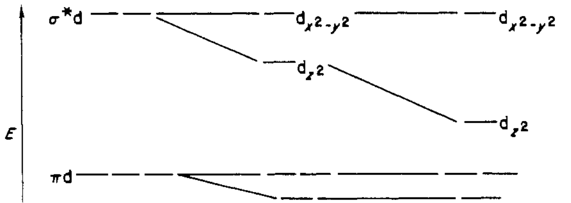
Figure 2 illustrates the spectral changes accompanying 313- or 254-nm excitation of $W(CO)_5(C_2H_4)$ and $W(CO)_5(C_3H_6)$ at 77 K in MCH containing no added alkene. The data show both formation of $W(CO)_5$, 2087 cm^{-1}, and uncomplexed CO, 2132 cm^{-1}, at both wavelengths, relatively more CO at 254-nm compared to 313-nm excitation for both complexes, and relatively more CO for the C_2H_4 complex than for the C_3H_6 complex at both wavelengths. Table III summarizes the quantitative data for all three complexes. The ratios given are the average of at least three independent determinations at <25% conversion (typically ~10%). Clearly, the longer excitation wavelength and larger alkene favor loss of alkene.

Table III. Molar Ratio of Alkene:CO Loss[a]

alkene	irradn wavelength 313 nm	irradn wavelength 254 nm
C_2H_4	3.5	1.7
C_3H_6	7.0	3.5
1-C_5H_{10}	10	5

[a] All values are measured at 77 K in MCH glass at ~1.0 mM initial concentration of $W(CO)_5$(alkene).

Scheme I. One-Electron Diagrams for $W(CO)_6$, $W(CO)_5$(alkene), and $W(CO)_5NH_3$



The rationale for the trends in the ratio of alkene to CO loss is not obvious. That the longer wavelength favors alkene loss correlates with the fact that the alkenes are somewhat weaker field ligands than CO and the lowest excited state has more d_{z^2}

character (Scheme I). However, in many respects CO and alkene are similar ligands (σ-donor, π-acceptor). It would seem that the splitting of the d_{z^2} and $d_{x^2-y^2}$ orbitals in $W(CO)_5$(alkene) is not really great enough to invoke the specific axis labilization characteristic of complexes like $W(CO)_5NH_3$, where NH_3 is much weaker in ligand field strength than CO and d_{z^2} and $d_{x^2-y^2}$ are significantly split.[7,12] The point is that there are strong similarities between CO and alkene ligands and little difference in the electronic structural features among the three $W(CO)_5$(alkene) complexes studied. The general tendency to lose the alkene correlates well with the fact that the alkene is more weakly held in the ground state than is CO. Photoexcitation corresponding to a $\pi d \rightarrow \sigma^* d$ transition (Scheme I) labilizes all of the ligands, since both the CO and alkene are π-acceptor, σ-donor ligands. Loss of alkene dominates presumably because the degree of CO labilization is insufficient to overcome the lability of the alkene. The wavelength dependence is, however, consistent with reactivity from different one-electron excited states, the lower one having more d_{z^2} character and the upper one having more $d_{x^2-y^2}$ character. Thus, despite the similarity of CO and alkene we favor the interpretation of the wavelength dependence invoked for $W(CO)_5NH_3$ and related complexes.

The trend in alkene to CO loss among the three alkenes correlates with the thermal lability of the complexes $C_2H_2 < C_3H_6 < 1\text{-}C_5H_{10}$. The difference in relative importance for alkene loss in the rigid matrix is especially interesting inasmuch as the most massive ligand, $1\text{-}C_5H_{10}$, is the most labile and the least massive ligand, C_2H_4, is the least labile. Note that the mass of CO is the same as that of C_2H_4. The fact that there is a difference between C_2H_4 and CO lability upon photoexcitation illustrates the unsurprising fact that even though both CO and C_2H_4 are π-acceptor, σ-donor ligands there can be major differences in their lability upon photoexcitation of a metal carbonyl–alkene complex. The effects of ligand mass on the photochemistry of complexes in rigid matrices may be important, due to the large cage effect. However, the differences in binding strength appear to dominate the relative photolability of CO vs. alkene in $W(CO)_5$(alkene).

The relative importance of net CO loss compared to alkene loss may not be a result that can be extended to a general conclusion regarding excited-state reactivity. Matrix effects may be very important both in controlling the primary loss of the ligands and in back-reaction with the 16e metal-containing fragment. More work on gas-phase photochemistry will be required to establish a complete picture of excited-state reactivity in these systems.

Nature of the CO-Loss Product from $W(CO)_5$(alkene). Photoexcitation of $W(CO)_5$(alkene) does lead to CO loss as an important, though not dominant, chemical process. This reaction is presumably important in $W(CO)_6$ photocatalyzed reactions, since $W(CO)_5$(alkene) is not an effective thermal catalyst for alkene isomerization.[3] It would seem that CO loss from $W(CO)_5$(alkene) is the minimum chemistry necessary to effect the catalytic alkene isomerization via a π allyl hydride mechanism.[3,4] Figure 2 shows a comparison of the IR spectral changes accompanying UV irradiation of $W(CO)_5(C_2H_4)$ and $W(CO)_5(C_3H_6)$. Both species give CO loss as evidenced by the appearance of the feature at 2132 cm^{-1}, and other features appear that cannot be attributed to $W(CO)_5$ from the loss of alkene. Since the appearance of $W(CO)_5$ (2087 cm^{-1}) and CO (2132 cm^{-1}) accounts for all $W(CO)_5$(alkene) consumed, the new metal carbonyl absorptions must be associated with $W(CO)_4$(alkene) or rearrangement products from $W(CO)_4$(alkene).

The features for $W(CO)_4(C_2H_4)$ and $W(CO)_4(C_3H_6)$ are very similar, unlike the comparison for the CO-loss products from $Fe(CO)_4(C_2H_4)$ and $Fe(CO)_4(C_3H_6)$. The significant difference between C_2H_4 and C_3H_6 is that the C_3H_6 has allylic hydrogens and the C_2H_4 does not. The photolysis of $Fe(CO)_4(C_3H_6)$ at 77 K in a rigid alkane yields the 18e $HFe(CO)_3(\eta^3\text{-}C_3H_5)$ whereas the photolysis of $Fe(CO)_4(C_2H_4)$ under the same conditions yields the 16e $Fe(CO)_3(C_2H_4)$.[1,13] For CO loss from $W(CO)_5$(alkene) there is no evidence for the formation of a π allyl hydride when the alkene is C_3H_6, since nearly identical spectral changes occur for alkene = C_2H_4 and C_3H_6 (Figure 2). Moreover, we find that 313-nm irradiation of $W(CO)_5$(1,4-pent)(1,4-pent = 1,4-pentadiene) yields spectral changes that are very similar to those for $W(CO)_5(1\text{-}C_5H_{10})$. The crucial feature is the band that appears at ~2045 cm^{-1}. The other band of note is at ~1885 cm^{-1}. These features are common to each $W(CO)_4$(alkene) species and appear at nearly the same position and relative intensity in each case. There are likely other features in the 1960–1900-cm^{-1} region, but these are obscured by bands of $W(CO)_5$. The similarity of the absorptions attributable to $W(CO)_4$(alkene) indicate that this species is a 16e compound and not a π allyl hydride.

The structure of the $W(CO)_4$ portion of the 16e $W(CO)_4$(alkene) is remarkably similar to that for *cis*-$W(CO)_4$(alkene)$_2$ complexes, based on the positions and relative intensities of the absorptions in the CO-stretching region. The *cis*-$W(CO)_4$(alkene)$_2$ complexes can be generated by photolysis of $W(CO)_5$(alkene) in an MCH matrix containing a large concentration of alkene. Under such circumstances the yield of $W(CO)_5$ is suppressed, consistent with back-reaction (eq 5), in the presence of excess alkene. The

$$W(CO)_5 + \text{alkene} \rightarrow W(CO)_5(\text{alkene}) \qquad (5)$$

irradiation of $W(CO)_5$(alkene) in an MCH matrix containing a modest concentration of alkene yields IR spectral changes consistent with formation of $W(CO)_5$, $W(CO)_4$(alkene), *cis*-$W(CO)_4$(alkene)$_2$, and CO. The assignments of the bands for *cis*-$W(CO)_4$(alkene)$_2$ are based on the similarity of the bands to those of the model cis species $W(CO)_4$(nor) (nor = norbornadiene)[14] (Table I). The high-energy feature in the CO region of the spectrum is at ~2042 cm^{-1} for $W(CO)_4$(nor) in an MCH matrix at 77 K. The main point is that the IR spectra of the 16e $W(CO)_4$(alkene) species in the CO-stretching region show a strong resemblance to those of *cis*-$W(CO)_4$(alkene)$_2$. This suggests that the open site in the 16e species is cis to the alkene. Calculations[15] show that $W(CO)_4$(alkene) with a vacant site cis to the alkene should show a feature near 2040 cm^{-1}, as observed.

Summary

Low-temperature (~77 K) irradiation of the binary carbonyls $M(CO)_6$ (M = Cr, W) in organic glasses can be monitored quantitatively to determine a molar absorptivity of 400 M^{-1} cm^{-1} for uncomplexed CO in the glass. This value is important in quantitative assessments of the relative importance of CO loss and other photoreactions of mixed carbonyl complexes at ~77 K in organic glasses.

The complexes $W(CO)_5$(alkene) (alkene = C_2H_4, C_3H_6, $1\text{-}C_5H_{10}$) are photosensitive at ~77 K in MCH glasses. The use of ϵ_{CO} = 400 M^{-1} cm^{-1} and quantitative measures of the absorption spectral changes upon 254- or 313-nm irradiation of glasses (~77 K) containing a known concentration of $W(CO)_5$(alkene) establish the loss of alkene to dominate in all cases with alkene loss being more important at 313-nm compared to 254-nm excitation and alkene loss being relatively more important in the order $1\text{-}C_5H_{10} > C_3H_6 > C_2H_4$. The wavelength dependence of alkene vs. CO loss is attributed to differences in the reactivity of the lowest ligand field excited state (greater d_{z^2} character) and an upper excited state (greater $d_{x^2-y^2}$ character). The general tendency to lose alkene vs. CO and the alkene dependence appear to correlate with the binding strength of the ligands in the ground state. The CO-loss product from $W(CO)_5$(alkene) is a 16e $W(CO)_4$(alkene) with a vacant site cis to the alkene. There does not appear to be evidence for the formation of a π allyl hydride from the C_3H_6 or $1\text{-}C_5H_{10}$ species, in contrast to results[1] for related $Fe(CO)_4$(alkene) complexes. Further studies are required to identify intermediates in

---

(12) (a) Murphy, M. A.; Darensbourg, D. J. *Inorg. Chem.* **1978**, *17*, 884. (b) Murphy, M. A.; Darensbourg, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 463.

(13) Grevels, F.-W.; Schultz, D.; Koerner von Gustorf, E. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 534.

(14) Tappan, J. E.; Nelson, H. H.; Darensbourg, D. J. *Inorg. Chem.* **1977**, *16*, 534.

(15) (a) Timney, J. A. *Inorg. Chem.* **1979**, *18*, 2502. (b) Haas, H.; Sheline, R. K. *J. Chem. Phys.* **1967**, *47*, 2996.

$W(CO)_6$-photocatalyzed reactions of olefins.[3,4]

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. $W(CO)_6$, 14040-11-0; $W(CO)_5$, 30395-19-8; $W(CO)_5(\eta^2\text{-}C_2H_4)$, 93117-80-7; $W(CO)_4(\eta^2\text{-}C_2H_4)$, 97073-99-9; $W(CO)_5(\eta^2\text{-}C_3H_6)$, 93223-97-3; $W(CO)_4(\eta^2\text{-}C_3H_6)$, 97074-00-5; *cis*-$W(CO)_4(\eta^2\text{-}C_3H_6)_2$, 94920-28-2; $W(CO)_5(\eta^2\text{-}1\text{-}C_5H_{10})$, 53261-74-8; $W(CO)_4(\eta^2\text{-}1\text{-}C_5H_{10})$, 97074-01-6; $W(CO)_5(\eta^2\text{-}1,4\text{-pent})$, 97074-02-7; *cis*-$W(CO)_4(\eta^2\text{-}1\text{-}C_5H_{10})_2$, 97074-03-8; *trans*-$W(CO)_4(\eta^2\text{-}C_5H_{10})_2$, 97133-84-1; $W(CO)_5(\eta^2\text{-}C_5H_6)$, 97102-14-2; $W(CO)_4(\text{nor})$, 12129-25-8; $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5$, 26319-33-5; $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$, 12082-27-8; $W(CO)_5NH_3$, 15133-64-9; CO, 630-08-0; ethylene, 74-85-1; propylene, 115-07-1; 1-pentene, 109-67-1.

Contribution from the Department of Chemistry, City University of New York, Hunter College,
New York, New York 10021, and Exxon Research and Engineering, Annandale, New Jersey 08801

Transport of Hydrogen Ions by a 4Fe–4S Model Compound in a Directional Electron-Transport System[†]

H. TSAI,[‡] W. V. SWEENEY,*[‡] and C. L. COYLE[§]

Received February 6, 1985

The ability of $Fe_4S_4(SC_6H_5)_4^{2-/3-}$ to cotransport electrons and hydrogen ions in a directional electron-transport system has been examined. A sequential electron-transport system was used, where aqueous Cr^{II}edta was the electron donor, and $(CH_3N((CH_2)_7CH_3)_3)_2Fe_4S_4(SC_6H_5)_4$ in toluene solution mediated the terminal reduction of methylviologen in aqueous solution. That $Fe_4S_4(SC_6H_5)_4^{2-/3-}$ mediated the electron transfer was demonstrated by using optical and EPR spectroscopies. The average molar ratio of electrons/hydrogen ions transported for 11 trials was found to be 1.18 ± 0.24. Valinomycin, a potassium ionophore, did not diminish the cotransport of hydrogen ions.

Iron–sulfur proteins are found in plants, bacteria, and mammals. They function in a wide range of reactions, including electron transport, enzymatic functions, and perhaps in regulation as well. Iron–sulfur proteins may be involved in proton translocation in energy-transducing membranes.[1,2] This possible energy conservation role, with consideration that some hydrogenases contain 4Fe–4S centers, suggests that reduction-linked hydrogen ion binding may be a functionally important property for some iron–sulfur proteins.

Soluble low-molecular-weight iron–sulfur proteins generally exhibit some pH dependence in their midpoint reduction potentials.[3,4] Previous studies[5] have shown that *Clostridium pasteurianum* ferredoxin can exhibit reduction-linked hydrogen ion binding in a manner consistent with two equivalent proton binding sites with $pK_{ox} = 7.4$ and $pK_{rd} = 8.9$. Whether the peptide or the $Fe_4S_4Cys_4$ cluster provides the site(s) of proton binding in this protein has not yet been established.

pH-dependent behavior of several $Fe_4S_4(SR)_4^{n-}$ model complexes has been reported. Job and Bruice[6] have reported an optically detected pK_a of 7.4 for the water-soluble complex $Na_5(n\text{-}C_4H_9)_4NFe_4S_4(SCH_2CH_2COO)_4$. Additionally, Bruice et al.[7] have reported a kinetically determined pK_a of 3.92 for $((n\text{-}C_4H_9)_4N)_2Fe_4S_4(SCH_2CH(CH_3)_2)_4$ in 60/40 (v/v) *N*-methylpyrrolidinone/H_2O. A pH dependence of approximately 60 mV/pH unit has been reported[8] for the reduction potential of $((n\text{-}C_4H_9)_4N)_2Fe_4S_4(SC_6H_4(n\text{-}C_8H_{17})\text{-}p)_4$ and two related complexes in aqueous micellar solution, although a species adsorbed onto the mercury electrode may actually have been observed.

Studies are described here which demonstrate that the model compound $(CH_3N((CH_2)_7CH_3)_3)_2Fe_4S_4(SC_6H_5)_4$ in toluene solution can mediate electron transfer between two aqueous phases and in concert translocate hydrogen ions stoichiometrically.

Experimental Section

Cr^{II}edta Solution. Solid $CrCl_2 \cdot 4H_2O$ was prepared according to Holah and Fackler,[9] with use of pure Cr metal obtained from Alfa Inorganics. Because of the tendency of Cr(II) to polymerize in solution near neutrality, Cr^{II}edta was prepared for each experiment from a stock 0.5 M solution of $CrCl_2$ in 0.1 M HCl. A typical solution of Cr^{II}edta was prepared by adding 750 μL of 0.2 M edta (pH 5.1) to 300 μL of 0.5 M $CrCl_2$, followed by addition of 3.0 mL of 0.1 M Tris-Cl/0.1 M KCl buffer, pH 8.5. The final solution contained 37 mM Cr^{II}edta, pH 7.5.

Synthesis of the Iron–Sulfur Complex. A methanolic solution of $Na_2Fe_4S_4(SC_6H_5)_4$ was prepared as previously described.[10] $(CH_3N((CH_2)_7CH_3)_3)_2Fe_4S_4(SC_6H_5)_4$ was prepared by the addition of 2 mol of $(CH_3N((CH_2)_7CH_3)_3)Cl$ (Aldrich)[11] per mole of cluster in methanol. The complex was isolated after storage at −40 °C. The resulting black solid was recrystallized twice from warm CH_3CN/MeOH and dried in vacuo.[12] The complex is freely soluble in toluene, and as such is the first reported $Fe_4S_4(SR)_4^{n-}$ complex soluble in a non-water-miscible solvent.

Spectral Studies. Electron paramagnetic resonance (EPR) spectra were recorded with a Varian V-4500 X-band spectrometer equipped with a Heli-Tran liquid helium transfer system (Air Products). The frequency was measured with a Hewlett-Packard 532A frequency meter, and α,α′-diphenyl-β-picrylhydrazyl (DPPH) was used as a *g* marker.

Optical spectra were obtained with use of quartz cells of 1-, 2-, or 10-mm path length fitted with cotton plugs containing aqueous $CrCl_2$ and sealed from the atmosphere with rubber septums. Spectra were recorded with a Cary 219 recording UV–visible spectrometer.

The Electron-Transport System

In these experiments a sequential system for electron transfer was used, where aqueous Cr^{II}edta was the electron donor, and $(CH_3N((CH_2)_7CH_3)_3)_2Fe_4S_4(SC_6H_5)_4$ (Fe–S complex) in toluene solution mediated the terminal reduction of methylviologen in aqueous solution. Because of the air sensitivity of these species, all reactions and transfers were conducted in a glovebox fitted

---

[†] This work has been supported in part by a grant from the City University of New York Professional Staff Congress-Board of Higher Education Research Award Program.

[‡] Hunter College.

[§] Exxon Research and Engineering.

(1) Ingledew, W. J.; Ohnishi, T. *Biochem. J.* **1980**, *186*, 111–117.
(2) Ohnishi, T. *Eur. J. Biochem.* **1976**, *64*, 91–103.
(3) Lode, E. T.; Murray, C. L.; Rabinowitz, J. C. *J. Biol. Chem.* **1976**, *251*, 1683–1687.
(4) Stombaugh, N. A.; Sundquist, J. E.; Burris, R. H.; Orme-Johnson, W. H. *Biochemistry* **1976**, *15*, 2633–2641.
(5) Magliozzo, R. S.; McIntosh, B. A.; Sweeney, W. V. *J. Biol. Chem.* **1982**, *257*, 3506.
(6) Job, R. C.; Bruice, T. C. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2478–2482.
(7) Bruice T. C.; Maskiewicz, R.; Job, R. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 231–234.
(8) Tanaka, K.; Tanaka, T.; Kawafure, I. *Inorg. Chem.* **1984**, *23*, 516–518.
(9) Holah, D. G.; Fackler, J. P., Jr. *Inorg. Synth.* **1967**, *10*, 26–35.
(10) (a) Averill, B. A.; Herskovitz, T.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3523–3534. (b) Christou, G.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1093–1094.
(11) The cation is a mixture of C_8–C_{10} chains, with C_8 predominating.
(12) Anal. Calcd. for $C_{74}H_{128}Fe_4N_2S_8$: Fe, 14.64; N, 1.84; S, 16.81. Found: Fe, 13.56; N, 1.82; S, 15.69.[11]

0020-1669/85/1324-2796$01.50/0