Time-Resolved IR Study of the Photobehavior of W(CO)₅(4-Acpy) (4-Acpy = 4-Acetylpyridine)

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Received February 25, 1993®

Fast time-resolved infrared spectroscopy (TRIR) is used to probe the photochemistry of $W(CO)_5$(4-acetylpyridine) in *n*-heptane. Visible irradiation (510 nm) populates the lowest MLCT state, which is monitored by TRIR. Subsequent dissociation to $W(CO)_5 \cdots n$-heptane, via equilibrium with the ^{3}LF state, is also followed. On UV irradiation (308 nm), the LF state is populated directly and $W(CO)_5 \cdots n$-heptane appears immediately. With 510-nm irradiation, the yield of $W(CO)_5 \cdots n$-heptane as a function of temperature is measured to give a value for the energy gap between the lowest MLCT state and the ^{3}LF state, $\sim$4000 cm^{-1}.

Introduction

There has been great interest in the photophysical and photochemical behavior of compounds of the type M(CO)₅L (M is a group 6 metal), particularly where M = W and L is a pyridine type ligand.[1–9] It has been clearly demonstrated, by both absorption and emission spectroscopy, that when L is pyridine itself, or a similar ligand such as piperidine, the lowest excited state is of ligand field character and that dissociative photochemistry occurs via this state with high quantum yield according to the scheme

$$W(CO)_5L + Q \xrightarrow{h\nu} W(CO)_5Q + L$$
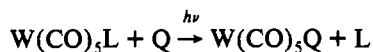
In contrast, when L is a substituted pyridine ligand, containing an electron-withdrawing group, such as 4-cyanopyridine (4-CNpy) or 4-acetylpyridine (4-Acpy), then the lowest excited state is charge transfer in character. The photobehavior of these complexes is very different; if the irradiation is not energetic enough to populate directly the LF state, then dissociation is much less efficient since this now depends on the equilibrium between the LF and CT states. The important energy levels can be represented as shown in Figure 1.

Both of the CT states of W(CO)₅(4-CNpy) are emissive,[7] with λ_{max} at 613 and 545 nm, and, since in fluid solution the lifetimes are equal, the two states are in rapid equilibrium. From the temperature variation of the intensities at 613 and 545 nm, it has been possible[7] to estimate the energy gap between CT₁ and CT₂: $\sim$1000 cm^{-1}. With irradiation at 465 nm, which is too low in energy to directly populate the lowest LF level, the quantum yield (ϕ) for substitution is very low.[1,6] A plot of ln(ϕ) versus $1/T$ yields[6] a value for both the cyano and acetyl complexes of $\sim$7.9 kcal mol^{-1} (but see Appendix). This was originally[6] assigned to the energy gap between CT₂ and ^{3}LF; more recent experiments[7,9] however suggest it is relevant to the CT₁/^{3}LF gap.

It was recently shown[9] that time-resolved infrared spectroscopy (TRIR) in the ν(CO) region can probe the complete photo-
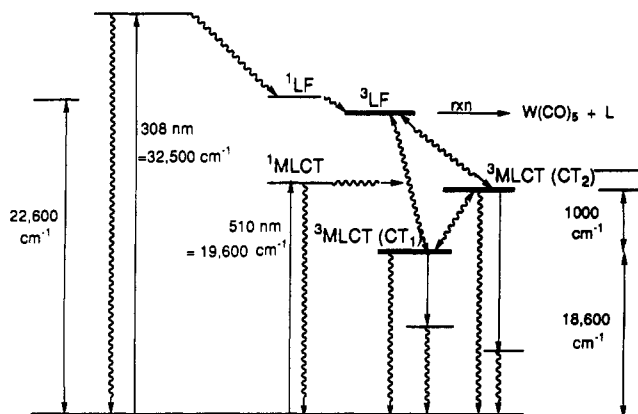

Figure 1. Schematic representation of important energy levels involved in the photochemistry of W(CO)₅L complexes, where L is an electron-withdrawing group such as 4-cyanopyridine or 4-acetylpyridine. CT₁ and CT₂ are the lowest MLCT levels. They are populated via the ^{1}MLCT state or from higher levels. The ^{3}LF state is populated directly via the ^{1}LF state or indirectly via the equilibrium with the MLCT states. Although W is a heavy metal, the spin designations have been left in for convenience.

chemistry of W(CO)₅(4-CNpy); it proved possible to monitor directly the generation of the lowest MLCT state, to observe it partially decay back to the ground state and partially dissociate via the LF state to W(CO)₅, and, in the presence of excess CO, to monitor the formation of W(CO)₆. This helped to unravel some of the features of the photochemistry, in particular the nature of the excited state and the kinetics of the reactions. The 4-CNpy complex is not particularly soluble in hydrocarbon solvents, and the ν(CO) bands are much broader in polar solvents and therefore more difficult to study. Fortunately the 4-acetyl complex is more soluble, and we have carried out TRIR experiments, particularly as a function of temperature, to probe its photochemistry and compare the results with the earlier emission and quantum yield measurements.

Experimental Section

Materials. W(CO)₅(4-acetylpyridine) was prepared photochemically[1] via W(CO)₅(thf) (thf = tetrahydrofuran). The complex is moderately stable, especially when stored in the dark, under argon, at –10 °C; it was recrystallized frequently from 2:1 cyclohexane/CH₂Cl₂. The 4-acetylpyridine ligand (Aldrich) and argon and CO (BOC) were used without further purification. Methylcyclohexane (mch; Aldrich 99+%) and *n*-heptane (Aldrich HPLC grade) were distilled over CaH₂. All solutions for the TRIR measurements were pump-degassed and then overpressured at 2 atm with the desired gas (Ar or CO).

Spectroscopic Measurements. Standard infrared spectra were obtained in *n*-heptane or mch with a Nicolet 730 FTIR instrument using 2-cm^{-1}

® Abstract published in *Advance ACS Abstracts*, August 15, 1993.

(1) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105.

(2) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1977**, *16*, 3154.

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

(4) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.

(5) Moralejo, C.; Langford, C. H.; Sharma, D. K. *Inorg. Chem.* **1989**, *28*, 2205.

(6) Lees, A. J.; Adamson, A. W. *J. Am. Chem. Soc.* **1982**, *104*, 3804.

(7) Rawlins, K. A.; Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1990**, *29*, 3866.

(8) Wieland, S.; van Eldick, R.; Crane, D. R.; Ford, P. C. *Inorg. Chem.* **1989**, *28*, 3663.

(9) Glyn, P.; Johnson, F. P. A.; George, M. W.; Lees, A. J.; Turner, J. J. *Inorg. Chem.* **1991**, *30*, 3543.

resolution. The time-resolved IR apparatus[9,10] uses a pulsed excimer laser (Lumonics HyperEX 440; 308 nm; ~100 mJ per pulse) or a dye laser (Oxford Instruments EDL 1; coumarin dye, 510 nm; ~10 mJ per pulse) pumped by the excimer laser. The changes in IR absorption at particular wavelengths are monitored by a CW CO infrared laser (modified Edinburgh Instruments PL3) which is tunable in steps of 4 cm^{-1} between 2010 and 1700 cm^{-1}. The CO laser beam is restricted to approximately 1-mm diameter with an iris. The two laser beams, CO and excimer/dye, are almost collinear and impinge on the same area of the solution cell. In these experiments the rise time was ~1–2 μs with a photoconductive 77 K HgCdTe detector (Infrared Associates HCT-100) and ~100 ns with a photovoltaic 77 K detector (Laser Monitoring Systems S-0025). IR spectra are built up "point-by-point" by repeating the UV or visible flash photolysis with the IR laser tuned to a different wavenumber for each UV shot. The spectra are **difference** spectra; i.e., they compare the intensity of IR bands before and after the flash. In the spectra reported here new species formed by the flash have **positive** absorptions (i.e., plotted upward) and those destroyed by the flash (e.g., the ground-state bands) have **negative** absorptions and are plotted downward. Each experiment was repeated between 5 and 10 times, and the figures show typical results. The IR cell is a conventional solution cell with facilities for flowing through the solution. For the variable-temperature experiments a special cell, cooled by liquid nitrogen, was constructed.[11] In these temperature variation experiments it was particularly important to eliminate heating effects due to the CO laser. With the configuration of the cell and the laser power, this was approximately 1 K min^{-1}. With the low-temperature experiments the cell was left for several minutes to equilibrate. Thus the CO laser beam was blocked and only unblocked a few seconds before the TRIR measurements. The local heating effect of the excimer or dye laser was no more than ~0.1 K.

Results and Discussion

Figure 2 shows TRIR spectra obtained for W(CO)₅(4-Acpy) using both 308- and 510-nm excitation. The spectroscopic and kinetic data are summarized in Tables I and II, respectively; these include, for completeness, the results[9] for W(CO)₅(4-CNpy). Partly by comparison with this earlier data for W(CO)₅(4-CNpy), the interpretation is as follows.

(i) The spectrum recorded at 125 ns, following 510-nm photolysis (b), shows loss of parent and generation of the ν(CO) bands (arrowed) of the lowest excited state, CT₁. At 510 nm there is no direct population of the LF state. We make the reasonable assumption, based on their absorption and emission spectra,[1,6,7] that for W(CO)₅(4-CNpy) and W(CO)₅(4-Acpy) the CT₁/CT₂ gaps are approximately equal at ~1000 cm^{-1}. Since the two MLCT states are in rapid equilibrium, the contribution to the ν(CO) spectrum from molecules in CT₂ is negligible. There is an upward shift in ν(CO) frequency from the ground state, because in the MLCT state there is charge transfer from the metal to the 4-acetylpyridine ligand, leaving the CO groups coordinated to a metal in a higher oxidation state. The shift is very similar to that observed for W(CO)₅(4-CNpy) and can be similarly explained.[9] [Such shifts to high frequency have been observed in the TRIR spectrum[12] of ClRe(CO)₃(4,4'-bipyridyl)₂ and in the TR[3] spectrum[13] of W(CO)₄(diimine).] The anticipated shift in the high-frequency band cannot presently be followed since it is outside the range of the CO-laser-based apparatus.

(ii) After 2.5 μs (c), the excited-state bands have vanished, there has been partial recovery of parent, and, in addition, generation of W(CO)₅···n-heptane. This shows only one ν(CO) band since the band at lower frequency overlaps with the parent band. At longer time scales (not shown), the W(CO)₅···n-heptane either reverts back to parent, dimerizes, or, in the presence of excess CO, reacts to form W(CO)₆. The photoscheme is outlined in Figure 3.

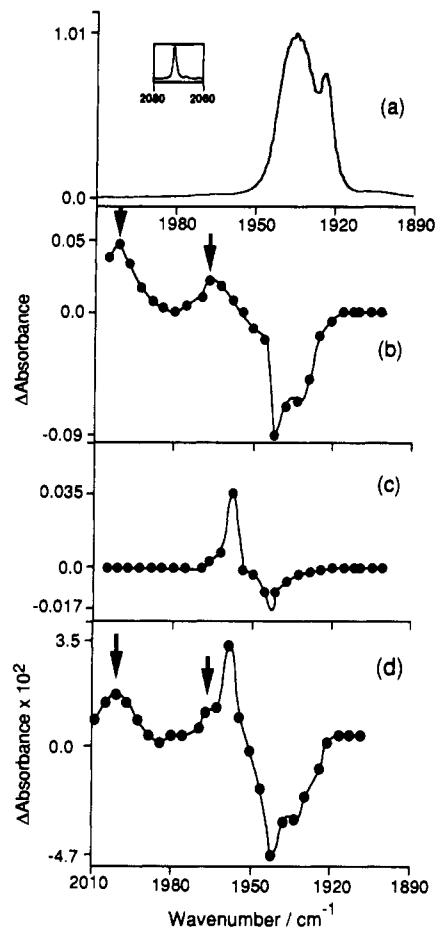(10) Dixon, A. J.; Healy, M. A.; Hodges, P. M.; Moore, B. D.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; West, M. A. *J. Chem. Soc., Faraday Trans.* **1986,** *82,* 2083.
(11) George, M. W. Ph.D. Thesis, University of Nottingham, 1990.
(12) Glyn, P.; George, M. W.; Hodges, P. M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1989,** 655.
(13) Perng, J.-H.; Zink, J. I. *Inorg. Chem.* **1990,** *29,* 1158.

Figure 2. ν(CO) IR spectra of W(CO)₅(4-Acpy) in *n*-heptane (~5 × 10^{-4} M; path length 4 mm): (a) FTIR spectrum of the complex in its ground state, with the inset showing the high-frequency a₁ mode; (b, c) TRIR spectra recorded under Ar at 125 ns and 2.5 μs, respectively, following a dye laser flash at 510 nm; (d) TRIR spectrum recorded at 125 ns after excimer laser flash at 308 nm. In (b) and (d), the arrows highlight the bands assigned to the excited MLCT state CT₁. The band at ~1960 cm^{-1} is assigned to W(CO)₅ weakly interacting with solvent,[9] i.e., W(CO)₅···n-heptane.

Table I. Frequencies (cm^{-1}) and Assignments, Based on C_{4v} Symmetry, in the ν(CO) Region, of Species Involved in the Photochemistry of W(CO)₅(4-X-py) Complexes (X = C(O)CH₃ or CN)

complex	a₁	e	a₁	
W(CO)₅(4-Acpy)^{a,b}	2072.0	1936.5	1924.7 (sh)	1710^c
[W(CO)₅(4-Acpy)]*^{b}	d	2000	1966	
W(CO)₅(4-CNpy)^{a,e}	2072.5	1936.4	1929.5 (sh)	
[W(CO)₅(4-CNpy)]*^{e}	d	2000	1966	
W(CO)₅···n-heptane	d	1957	f	
W[CO)₅···mch^e	d	1954	f	
W(CO)₆^e	1984 (t₁ᵤ)			

^{a} FTIR spectrum. ^{b} *n*-Heptane solution. ^{c} ν(CO) of the acetyl group; attempts to monitor the behavior of this band by TRIR were unsuccessful. ^{d} Outside CO laser range. ^{e} Methylcyclohexane solution. ^{f} Obscured by parent band.

(iii) Following 308-nm photolysis (d), which **can** directly populate the LF state, at 125 ns, there is, in addition to the CT₁ state, **immediate** formation of W(CO)₅···n-heptane. Thus W(CO)₅···n-heptane is formed **directly** from the LF state.

This experiment thus provides direct proof of the role of the equilibrium between the MLCT and LF states in the dissociation photolysis of W(CO)₅(4-Acpy). We can probe this equilibrium further by investigating the photolysis as a function of temperature.

Figure 4 shows an experiment in which the yield of W(CO)₅···n-heptane is measured at different temperatures following 510-nm photolysis. At each of these temperatures we have also measured

Table II. Rate Constants (±10%) [Lifetimes (μs)] for Reactions Involved in the Photochemistry of $W(CO)_5(4\text{-X-py})$ (X = $C(O)CH_3{}^a$ or CN^b) at 298 K (Figure 3)

X		under Ar	under CO (2.4 × 10⁻² M)
$C(O)CH_3$	$k_1{}^c$ (×10⁻⁶ s⁻¹)	2.6 [0.38]	2.3 [0.44]
$C(O)CH_3$	$k_2{}^{d,e}$ (×10⁻⁶ s⁻¹)	2.6 [0.39]	
$C(O)CH_3$	decay (×10⁻⁶ s⁻¹) of $[W(CO)_5(4\text{-X-py})]^*$	2.5^f [0.42]	2.3 [0.44]
$C(O)CH_3$	$k_4{}^g$ (×10⁻⁶ M⁻¹ s⁻¹)		0.83
CN	$k_1{}^c$ (×10⁻⁶ s⁻¹)	3.8 [0.26]	3.6 [0.28]
CN	$k_2{}^d$ (×10⁻⁶ s⁻¹)	4.0 [0.25]	4.2 [0.24]
CN	decay (×10⁻⁶ s⁻¹) of $[W(CO)_5(4\text{-X-py})]^*$	4.0^f [0.25]	3.9 [0.26]
CN	$k_3{}^h$ (×10⁻⁶ M⁻¹ s⁻¹)	4.6	
CN	$k_4{}^g$ (×10⁻⁶ M⁻¹ s⁻¹)		0.32

^{a} All measurements in n-heptane. ^{b} All measurements in methylcyclohexane. ^{c} From regeneration of the ground state. ^{d} From generation of $W(CO)_5\cdots$sol. ^{e} After excimer flash photolysis, this lifetime is <0.125 μs due to immediate population of the LF state. ^{f} This lifetime decreases to <0.125 μs under O_2. ^{g} From loss of $W(CO)_5\cdots$sol. ^{h} From loss of $W(CO)_5\cdots$sol and growth of $W(CO)_6$.
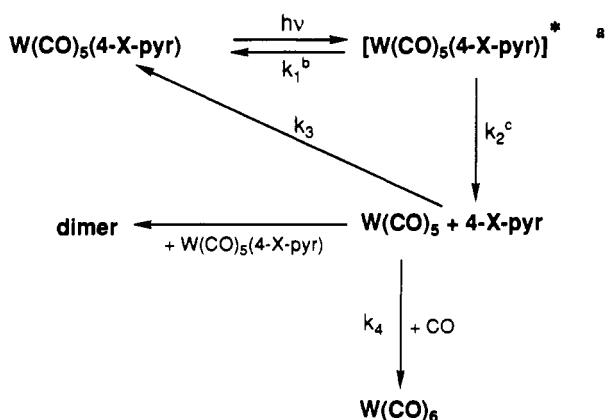
Figure 3. Schematic representation of the overall photochemistry of $W(CO)_5(4\text{-X-py})$ (X = $C(O)CH_3$, CN): (a) $[W(CO)_5(4\text{-X-py})]^*$ represents the three equilibrating states; (b) k_1 is the rate constant for all routes back to the ground state except the initial very fast prompt process (see text); (c) k_2 is the rate of dissociation from the ³LF state.
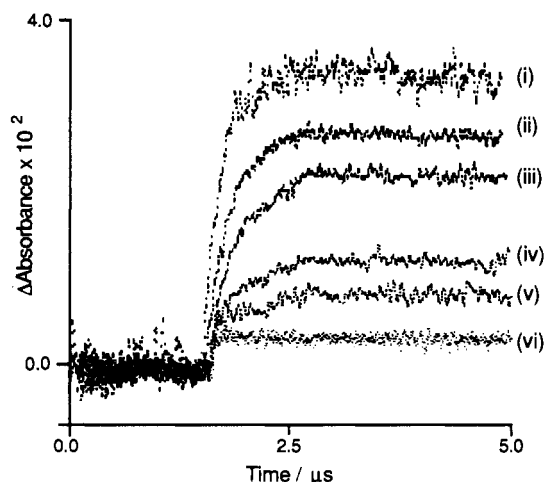
Figure 4. Kinetic traces recorded after dye laser flash photolysis (510 nm) of $W(CO)_5(4\text{-Acpy})$ in n-heptane. All the traces are taken at 1957 cm⁻¹ and monitor the yield of $W(CO)_5\cdots n$-heptane, produced at different temperatures: (i) 311 K; (ii) 303 K; (iii) 296 K; (iv) 284 K; (v) 276 K; (vi) 263 K. The trace at 268 K is not shown.

(not shown) the lifetime of the excited state which precedes the formation of $W(CO)_5\cdots$solvent. The results are shown in Table III. The measurement of yield is reasonably accurate, but the measurement of lifetime is very difficult and this is reflected in

Table III. Yield of $W(CO)_5\cdots n$-heptane, from 510-nm Photolysis of $W(CO)_5(4\text{-Acpy})$ in n-Heptane, at Different Temperatures

T, K	lifetime (τ) in CT_1 level, ns	absorbance A (×10²) of $W(CO)_5\cdots n$-heptane band
311	161	3.49
303	267	2.86
296	357	2.35
284	416	1.25
275	357	0.79
268	700	0.60
263	666	0.40

the scatter of the lifetime data; nontheless it is clear that, overall, the lifetime increases as the temperature decreases. Assuming a relationship among temperature (T), lifetime (τ), and yield (A) of the form

$$\ln(A/\tau) \propto 1/T$$

(see Appendix for derivation) a plot of $\ln(A/\tau)$ versus $1/T$ should yield a straight line of slope $\Delta G^\circ/R$; Figure 5 shows a plot, which yields a value of ~-11.6 kcal mol⁻¹ (~ 4060 cm⁻¹) for ΔG°. This should be compared with the value obtained[6] from quantum yield measurements, ~-10.7 kcal mol⁻¹ (3740 cm⁻¹) (see Appendix). Given the difficulties of these measurements, this agreement is very pleasing.

One interesting feature of these experiments is that, in spite of very low continuous photolysis quantum yields, pulsed irradiation leads to substantial conversion of parent to $W(CO)_5\cdots$solvent. We have previously argued[9] that this occurs because there is multiple excitation and reexcitation during the lifetime of the pulse. It is conceivable that the apparent high yield arises from **direct** population of the LF levels via a two-photon process. The variable-wavelength and -temperature experiments demonstrate that this is not true. However a final check is to observe the yield of $W(CO)_5\cdots$solvent as a function of laser energy. The 4-Acpy complex is less photosensitive than the 4-CNpy, so that experiments with variable laser energy were very difficult. However Figure 6 shows an experiment with $W(CO)_5(4\text{-CNpy})$; this clearly shows a linear yield with energy, so the process cannot be two-photon and hence it confirms the original proposal that multiple excitation is responsible for the high yield.

Conclusions

We have shown that time-resolved infrared spectroscopy (TRIR) can probe the photochemical and photophysical process in $W(CO)_5(4\text{-acetylpyridine})$, where the lowest excited state is MLCT. In particular, it has been possible (i) to demonstrate the formation of this lowest lying state on irradiation with 510-nm light, (ii) to monitor the conversion to $W(CO)_5\cdots$solvent, (iii) to show that this conversion depends on an equilibrium with a LF state approximately 4000 cm⁻¹ higher in energy, and (iv) to demonstrate that, at higher energy irradiation (308 nm), the LF state is directly populated and immediately leads to the formation of $W(CO)_5\cdots$solvent. Compounds such as $W(CO)_5(\text{pyridine})$, where the lowest excited state is LF, have been studied by resonance Raman spectroscopy[14] employing the time-dependent formulation[15] to measure the structural distortion in this LF state. Preliminary experiments[16] using TRIR suggest large $\nu(CO)$ band shifts in this state, consistent with a substantial distortion. In future experiments we hope to determine the complete force field in this excited state, which will provide accurate values for the

(14) Zink, J. I.; Shin, K.-S. K. *Adv. Photochem.* **1991**, *16*, 119 and references therein.
(15) Heller, E. J.; Sundberg, R. L.; Tannor, D. J. *J. Phys. Chem.* **1982**, *86*, 1822.
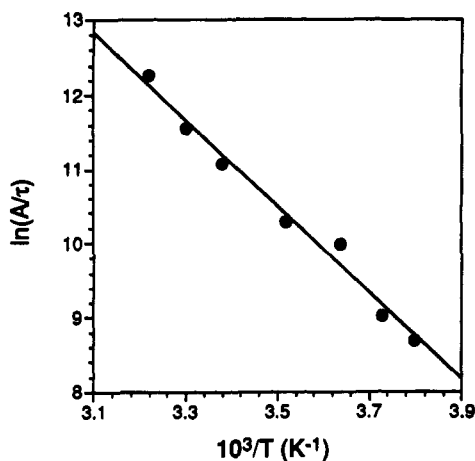(16) Johnson, F. P. A. Ph.D. Thesis, University of Nottingham, 1992.

Figure 5. Plot of $\ln(A/\tau)$ versus $1/T$, where A is the absorbance of W(CO)₅···n-heptane produced from W(CO)₅(4-Acpy) (see Figure 3) and τ is the excited-state lifetime.

changes in C–O bond lengths. Thus TRIR experiments will continue to provide a novel method of probing the excited-state behavior of complexes of type W(CO)₅L.

Appendix

Since the two CT states are in very rapid equilibrium, we can ignore the upper level in the derivation and simplify the photosystem as
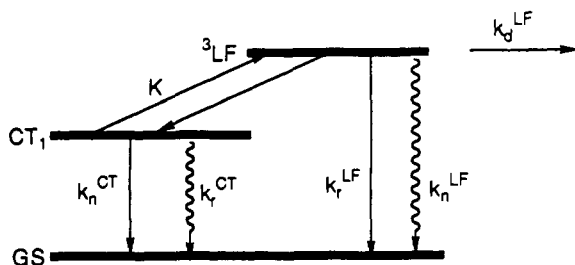
k_n, k_r, and k_d represent nonradiative, radiative, and dissociative rate constants, respectively; K is the equilibrium constant between the lowest CT and LF states (i.e., [CT]/[LF]). (The convention $K = [CT]/[LF]$ is retained, even though in this case K is clearly much greater than unity.)

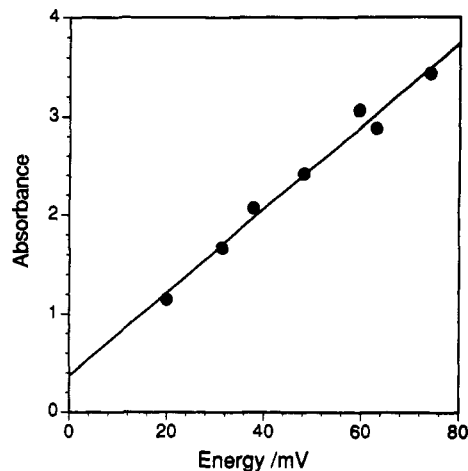**Figure 6.** Plot of absorbance of W(CO)₅···mch in methylcyclohexane versus the energy of the 510-nm dye laser pulse (measured in millivolts of detector signal).

The quantum yield of dissociative products (ϕ) and lifetime (τ) are given by[8,17]

$$\phi = \frac{k_d^{LF}}{k_d^{LF} + k_n^{LF} + k_r^{LF} + K(k_n^{CT} + k_r^{CT})}$$

$$\tau = \frac{1 + K}{k_d^{LF} + k_n^{LF} + k_r^{LF} + K(k_n^{CT} + k_r^{CT})}$$

Since CT is much lower than LF, $K \gg 1$ and

$$\tau = \frac{K}{k_d^{LF} + k_n^{LF} + k_r^{LF} + K(k_n^{CT} + k_r^{CT})}$$

Hence

$$\phi = k_d^{LF}\tau/K$$

Since $K = \exp(-\Delta G^\circ/RT)$ (where ΔG° is the energy gap between CT₁ and LF)

$$\phi = k_d^{LF}\tau/[\exp(-\Delta G^\circ/RT)]$$

The quantum yield of dissociation is proportional to the absorbance (A) of W(CO)₅···n-heptane, so, assuming k_d^{LF} is not sensitive to temperature, a plot of $\ln(A/\tau)$ versus $1/T$ will give a straight line of slope $\Delta G^\circ/R$. If τ is relatively invariant to temperature then a plot of $\ln(A)$ versus $1/T$ will also give a straight line of slope $\Delta G^\circ/R$. Lees and Adamson[6] plotted this latter quantity; however they also quoted lifetimes, so, using this data, a plot of $\ln(\phi/\tau)$ versus $1/T$ gives an energy gap of 10.7 kcal mol⁻¹ (3740 cm⁻¹) rather than 7.9 kcal mol⁻¹ (2760 cm⁻¹).

(17) Kemp, T. J. *Prog. React. Kinet.* **1980**, *10*, 302.