in terms of the nature of the transition state.

Conclusions

Rate constants for the hypohalite and hypohalous acid reactions with iodide and sulfite ions are summarized in Table VII. The OBr^- reactions are faster than the OCl^- reactions by a factor of more than 2.3×10^4 for I^- and by a factor of 4.4×10^3 for SO_3^{2-}. We propose that these enhanced rates are associated with the greater ease of Br^+-transfer compared to Cl^+-transfer reactions. In other words, nucleophilic attack at bromine with expansion of its valence-shell electrons is more favorable than the corresponding attack at chlorine. The reactivity of HOBr is much greater than that of OBr^- (by a factor of 7.4×10^3 for I^- and a factor of 50 for SO_3^{2-}). The HOBr reactions with I^- and with SO_3^{2-} are so favorable that the rate constants reach the diffusion limit. The high reactivity of HOBr is again associated with the greater ease of Br^+ transfer to the nucleophiles (I^- or SO_3^{2-}) accompanied by the rapid loss of OH^-. The indicator experiments provide evidence for the formation and decay of $BrSO_3^-$.

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Registry No. OBr^-, 14380-62-2; I^-, 20461-54-5; SO_3^{2-}, 14265-45-3; HOBr, 13517-11-8; $BrSO_3^-$, 44047-97-4.

Contribution from the Departments of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.,
and University Center at Binghamton, State University of New York, P.O. Box 6000, Binghamton, New York 13902-6000

Time-Resolved Infrared Spectrum of the MLCT Excited State of $W(CO)_5(4\text{-CNpyr})$ (4-CNpyr = 4-Cyanopyridine): Photophysics and Photochemistry

Paul Glyn,[†] Frank P. A. Johnson,[†] Michael W. George,[†] Alistair J. Lees,[‡] and James J. Turner[*,†]

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Fast time-resolved infrared spectroscopy is employed to probe the lower metal to 4-CNpyr charge-transfer (MLCT) excited state of $W(CO)_5(4\text{-CNpyr})$ (4-CNpyr = 4-cyanopyridine). On visible irradiation, the CO stretching vibrations shift to higher frequency, confirming that in this excited state the metal center is oxidized. The excited state decays back to the ground state and, via the LF excited state, decomposes to $W(CO)_5$ and 4-CNpyr. The rate constants for these processes are equal (ca. 4×10^6 s^{-1}), suggesting that there is a rapid equilibrium between the MLCT and LF states.

Introduction

The photochemistry of $(CO)_5ML$ species has been extensively investigated.[1-4] Low-temperature studies[1] showed that if L is an electron-withdrawing group then the MLCT state is lower than the LF excited states. Lees and Adamson[5] were the first to observe room-temperature emission from such systems. From very detailed studies[6-8] of the photochemistry and photophysics of $(CO)_5WL$, the following conclusions may be drawn in the case of L = 4-CNpyr.

(i) Irrespective of irradiation wavelength, multiple emission occurs from two ^{3}MLCT states,[9] separated by 990 cm^{-1}, in rapid thermal equilibrium with each other. In methylcyclohexane at 296 K, the emissions are centered at 545 and 613 nm and the lifetime is 0.292×10^{-6} s—see Figure 1.

(ii) Immediately following the laser flash, an absorption band with a maximum at ca. 400 nm was observed;[6] this was assigned to the excited state. The decay of this band followed a single exponential with a rate equal to the rate of decay of the emission.

(iii) Substitution photochemistry proceeds from a ^{3}LF state[9] that is some 2600 cm^{-1} above the lower ^{3}MLCT state, and is in steady-state thermal equilibrium with the emitting CT states; the first step involves ejection of 4-CNpyr.

The value of probing excited states of organometallics with resonance Raman spectroscopy[10-12] has already been demonstrated. We recently obtained the IR spectrum of the emitting excited state of $ClRe(CO)_3(4,4'\text{-bpy})_2$ and confirmed from the shift in $\nu(CO)$ frequencies that there is charge transfer from metal to the bpy ligand.[13] For $ClRe(CO)_3(4,4'\text{-bpy})_2$, the quantum yield for photodissociation is nearly zero. In this paper, we describe an investigation of $(CO)_5W(4\text{-CNpyr})$ and report the $\nu(CO)$ IR spectra of the photochemically active ^{3}MLCT excited state, its decay back to the ground state, *and* the dissociation via the excited ^{3}LF state to $W(CO)_5$ and 4-CNpyr.

Table I. Frequencies (cm^{-1}) and Assignment, Based on C_{4v} Symmetry, in the $\nu(CO)$ Region of Species Involved in Photochemistry of $W(CO)_5(4\text{-CNpyr})$ in Methylcyclohexane

	a_1	e	a_1
$W(CO)_5(4\text{-CNpyr})^a$	2072.5	1936.4	1929.5 (sh)
$[W(CO)_5(4\text{-CNpyr})]^*$	b	2000	1966
$W(CO)_5\cdots$solvent	b	1954	c
$W(CO)_6$	1984 (t_{1u})		

[a] FTIR spectrum. [b] Outside CO laser range. [c] Obscured by parent band.

Experimental Section

Materials. $W(CO)_5(4\text{-CNpyr})$ was prepared photochemically via $W(CO)_5(THF)$ (THF = tetrahydrofuran) following a published procedure[7] and purified by column chromatography on alumina. The 4-CNpyr ligand (Aldrich, 98%), methylcyclohexane (MCH, Aldrich, anhydrous

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[†] University of Nottingham.

[‡] State University of New York.

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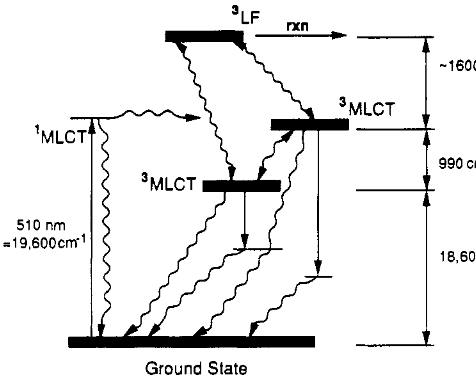

Figure 1. Schematic representation (not to scale) of the electronic energy levels of W(CO)$_5$(4-CNpyr) based on refs 6 and 7.

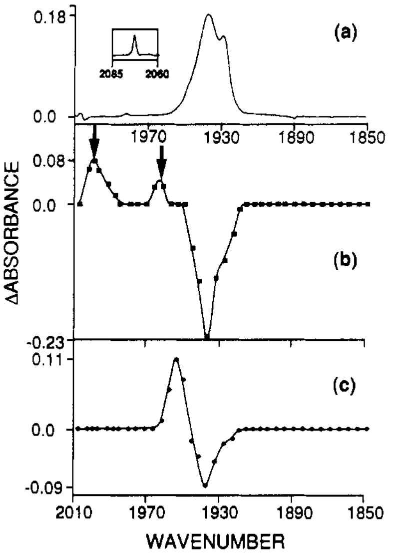

Figure 2. (a) FTIR spectrum of W(CO)$_5$(4-CNpyr) in methylcyclohexane (ca. 4 × 10^{-5} M; path length 4 mm), with the inset showing the high-wavenumber band. TRIR spectra at (b) 150 ns and (c) 5 μs, after the dye laser flash (510 nm, 10 ns) of solutions of W(CO)$_5$(4-CNpyr) in methyl cyclohexane (ca. 4 × 10^{-5} M; path length 5 mm). In these TRIR experiments, the solution contained excess ligand, 4-CNpyr; this is to suppress as much as possible the formation of dimer via reaction of W(CO)$_5$ with parent.

99+%), argon, and carbon monoxide (BOC research grade) were used without further purification. All solutions for the TRIR experiments were pump degassed and then overpressured to 2 atm with the desired gas (Ar or CO).

Spectroscopic Measurements. Standard infrared spectra were obtained in MCH with a Nicolet 730 FTIR instrument using 2-cm^{-1} resolution. The time-resolved IR apparatus[14] uses a dye laser (Oxford Instruments EDL 1, with output from coumarin dye at 510 nm) pumped by a pulsed UV excimer laser (Lumonics HyperEX 440, XeCl, 308 nm) as the photolysis source. The output energy of the dye laser is approximately 10 mJ/pulse of which approximately half is concentrated in a spot about 1 mm in diameter. 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 dye, are almost collinear and impinge on the same area of the solution cell. As used in these experiments, the rise time was ca. 1–2 μs with a photoconductive 77 K HgCdTe detector (Infrared Associates HCT-100) and ca. 100 ns with a photovoltaic 77 K HgCdTe detector (Laser Monitoring Systems S-0025). IR spectra are built up "point-by-point" by repeating the UV flash photolysis with the IR laser tuned to a different wavenumber for each UV shot. It is important to note that such spectra are *difference spectra*, comparing the intensity of bands before and after the flash. Thus species formed by the flash have *positive* absorptions (i.e. plotted upward in our spectra) while those destroyed by the flash (i.e. those of the ground state) appear as *negative* absorptions. All rate constants are accurate to ±10%.

Table II. Rate Constants (±10%) and Lifetimes (μs) in Brackets for Reactions Involved in the Photochemistry of W(CO)$_5$(4-CNpyr) at 298 K

	under Ar	under Ar/4-CNpyr (1.3 × 10^{-3} M)	under CO (2.4 × 10^{-2} M)
k_1,[a] 10^{-6} s^{-1}	3.8 [0.26]	4.1 [0.25]	3.6 [0.28]
k_2,[b] 10^{-6} s^{-1}	4.0 [0.25]	5.0 [0.20]	4.2 [0.24]
decay of [W(CO)$_5$(4-CNpyr)]*, 10^{-6} s^{-1}	4.0[c] [0.25]	4.1 [0.24]	3.9 [0.26]
k_3,[d] 10^{-6} M^{-1} s^{-1}		4.6	
k_4,[e] 10^{-6} M^{-1} s^{-1}			0.32

[a] From regeneration of the ground state. [b] From generation of W(CO)$_5$. [c] Under O$_2$ this rate increases to ca. 25 × 10^6 s^{-1}, and returns to ca. 5 × 10^6 s^{-1} on further degassing. [d] From loss of W(CO)$_5$, k_{obs} = 6 × 10^4 s^{-1}. [e] From loss of W(CO)$_5$ and growth of W(CO)$_6$, k_{obs} = 8.2 × 10^3 and 7.6 × 10^3 s^{-1}, respectively.

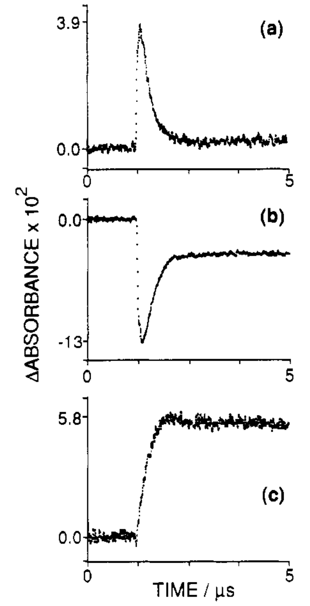

Figure 3. Traces recorded over the first 5 μs following the laser flash of W(CO)$_5$(4-CNpyr) in methylcyclohexane under Ar: (a) decay of short lived transient at 1997 cm^{-1}; (b) parent regeneration at 1937.5 cm^{-1}; (c) grow-in of species W(CO)$_5$··solvent at 1954 cm^{-1}.

Results

Figure 2 shows IR spectra at two different times after pulsed laser photolysis (510 nm; 10 ns; ca. 10 mJ) of (CO)$_5$W(4-CNpyr) in methylcyclohexane. Table I gives IR spectral details. Bearing in mind that the apparatus monitors *changes* in intensity, one can draw certain conclusions.

(i) Shortly after the flash, the major parent IR band has decreased in intensity and two new IR bands marked with arrows in Figure 2b have appeared at ca. 1966 and 2000 cm^{-1}. The average loss of parent over several experiments was 80%, for each flash.

(ii) After 5 μs, these two bands have disappeared and, at 1954 cm^{-1}, a new band has appeared that is readily assigned to W(CO)$_5$··solvent;[15] meanwhile, the parent band has recovered to approximately half of its original intensity.

After 500 μs (not shown), the 1954-cm^{-1} band has gone and the parent band has almost recovered its original intensity.

The rates of these changes at individual frequencies are shown in Figures 3 and 4; rate constants are given in Table II. Again some conclusions can immediately be drawn.

(i) The rate of decay of the two new bands equals both the initial recovery rate of the parent and the rate of formation of the 1954

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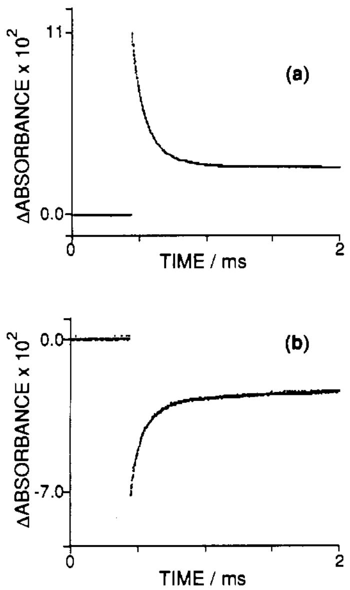

Figure 4. Traces in Figure 3 (curves c and b) recorded over a longer time scale: (a) decay of $W(CO)_5$ at 1954 cm^{-1} (does not return to the baseline because of absorption due to dimer); (b) parent regeneration at 1937.5 cm^{-1} (does not return to the baseline because of dimer formation).

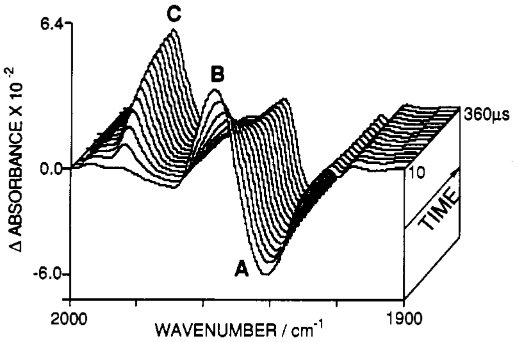

Figure 5. Series of TRIR spectra taken at 25-μs intervals following flash photolysis of $W(CO)_5(4\text{-}CNpyr)$ in methylcyclohexane (ca. 4×10^{-5} M; path length 5 mm). under 2 atm pressure of CO: A = $W(CO)_5(4\text{-}CNpyr)$; B = $W(CO)_5$⋯solvent; C = $W(CO)_6$.

cm^{-1} band ($W(CO)_5$⋯solvent). The lifetimes are close to the values observed for the emission lifetime of the excited state in methyl cyclohexane ($\tau = 0.292$ μs[7]) and the decay of the absorption band at 400 nm ($\tau \approx 0.34$ μs[6]).

(ii) The rate of loss of the 1954-cm^{-1} band ($W(CO)_5$⋯solvent) is equal to the later, slower rate of recovery of the parent. (Note that the recovery of parent is incomplete; this point is discussed below.)

Confirmation that the 1954-cm^{-1} band is indeed due to ($W(CO)_5$⋯solvent) comes from experiments with excess CO, see Figure 5 and Table II. Figure 5 shows clearly that the parent band does not recover its original intensity and that ($W(CO)_5$⋅⋅solvent) (1954 cm^{-1}) decays at the same rate as $W(CO)_6$ (1984 cm^{-1}) grows in.

Discussion

It is highly probable that a photoactive excited state is responsible for the two IR bands at 1966 and 2000 cm^{-1}; the most obvious assignment is that they are the a_1 and e modes of the effectively square-pyramidal $W(CO)_5$ group (the high frequency a_1 will be weak and is in any case outside the range of the CO laser). Thus there is a shift of the $\nu(CO)$ bands to higher frequency from the ground state of about 37 and 64 cm^{-1} for the a_1 and e modes, respectively. As we[13] and others[11] have demonstrated, this implies that there is electron transfer from the metal center and hence that the spectrum is that of a MLCT state. It should also be noted that we expect the molar intensity of the $\nu(CO)$ bands to decrease as the metal center becomes oxidized; this is observed.

If two MLCT states in equilibrium at room temperature are separated by 990 cm^{-1}, their approximate concentration ratio is 1 to 120. Thus the contribution of the upper MLCT state to the IR spectrum is negligible. Similarly the ^3LF state makes a negligible contribution to the IR spectrum. On the basis of the simple Cotton–Kraihanzel analysis,[16] the force constants for ground and excited states can be approximated:

	ground state	excited state[a]		
		a	b	c
$k^{ax}(CO)$, N m^{-1}	1524	1572	1574	1577
$k^{eq}(CO)$, N m^{-1}	1581	1666	1672	1677

[a] Here, a, b, and c assume that the high-frequency band is 2100, 2110, and 2120 cm^{-1}, respectively.

Thus $k^{ax}(CO)$ and $k^{eq}(CO)$ increase by some 50 and 80 N m^{-1} respectively. Similar conclusions follow from simple application of Timney's ligand effect constants.[17] The usual d orbital assignment for $W(CO)_5L$ species is $b_2^2(d_{xy})e^4(d_{xz}, d_{yz})a_1^0(d_{z^2})b_1^0(d_{x^2-y^2})$. Promotion of an electron from e into a π^* orbital on the 4-CNpyr would be expected, on the usual π back-bonding arguments, to increase $k^{ax}(CO)$ more than $k^{eq}(CO)$. That the reverse occurs *suggests* that in the lowest MLCT state the d-orbital ordering is $e^4b_2^1a_1^0b_1^0$, i.e., a $^3B_2$ state. However these suggestions assume the retention of pseudo-C_{4v} symmetry in the MLCT excited state; this may not be the case,[4,18] and work on a variety of systems is in progress to investigate possible distortions.

From Figure 1 we can conclude that the equality of the three initial rate constants (see Table II) implies that the photoactive LF state must also be in rapid equilibrium with the two equilibrating CT states,[19,20] since the laser frequency (510 nm = 19 608 cm^{-1}) is too low to excite the LF state directly (see Appendix for an explanation of this point). This agrees with previous observations.[8]

It is very revealing that during the lifetime of the pulse (10 ns) most of the ground state $W(CO)_5(4\text{-}CNpyr)$ is converted to the lowest ^3MLCT state, and that approximately half of the molecules in this excited state decay back to the ground state and the other half photoejects 4-CNpyr. The photosubstitution quantum yields at room temperature for

$$W(CO)_5(4\text{-}CNpyr) + L \rightarrow W(CO)_5L + 4\text{-}CNpyr$$

are 0.02 (L = 1-pentene; solvent = isooctane; irradiation at 514 nm)[1] and 0.021 (L = EtOH; solvent = methylcyclohexane; irradiation at 520 nm).[6] This means that, under continuous photolysis, the probability of prompt return to the ground state, presumably via internal conversion from ^1MLCT, must be nearly unity and that during the lifetime of the pulse there must be many absorptions and decays to populate the lowest ^3MLCT state. (See Appendix for justification of this conclusion.)

As mentioned above there is incomplete recovery of parent. We believe that this may be due to the formation of a dimer as suggested by Lees and Adamson[5] to explain some of their results. This could be the product of the reaction between $(CO)_5W$⋯solvent and $(CO)_5W(4\text{-}CNpyr)$, i.e., $(CO)_5W(NC_5H_4CN)W(CO)_5$. In this compound, one W atom is coordinated to the nitrogen in the pyridine ring and the other W atom is coordinated to the nitrogen in the CN group. This is a reasonable interpretation for two reasons: first, Wang and Lees[21] have shown that 4-CNpyr can coordinate to $(CO)_5W$ via either of the two nitrogen atoms; second,

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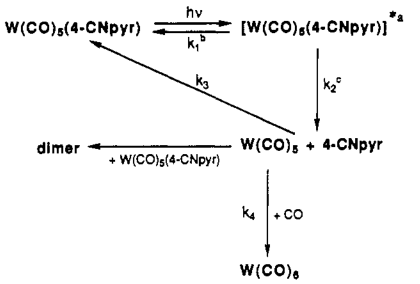
Scheme I



[a] $[\mathrm{W(CO)_5(4\text{-}CNpyr)}]^*$ represents the three equilibrating excited states. [b] k_1 represents all routes back to the ground state except the initial very fast prompt process. [c] k_2 represents dissociation from the ^{3}LF state.

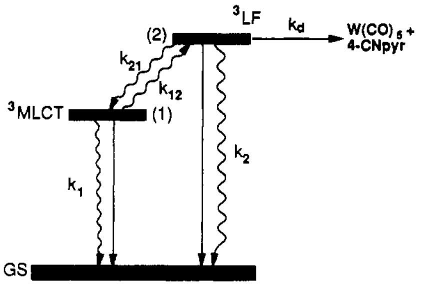


Figure 6. Schematic representation of part of the photosystem for $\mathrm{W(CO)_5(4\text{-}CNpyr)}$, ignoring the higher energy ^{3}MLCT state. k_1 and k_2 represent the sum of the radiative and nonradiative rate constants for decay of levels 1 and 2; k_d is the rate constant for decomposition to $\mathrm{W(CO)_5}$ and 4-CNpyr, assumed to occur only from the ligand field state.

stable phosphine analogues are known,[22] e.g. $\mathrm{(CO)_4(Bu_3P)W(NC_5H_4CN)W(PBu_3)(CO)_4}$. The overall photochemisty can be summarized as shown in Scheme I. Thus this work demonstrates again that IR spectroscopy of excited states can provide subtle information about the details of the excited states in photochemical reactions and of the photochemical processes themselves. We aim to exploit this in a wide variety of chemical systems.

Acknowledgment. The Nottingham authors thank the Science and Engineering Research Council, the Paul Instrument Fund of the Royal Society, and the EEC Science Programme (SCIENCE Contract ST 007); A.J.L. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society and the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (Grant DE-FG02-89E1214039). We are grateful to Professor M. Poliakoff and Drs. M. A. Healy, P. M. Hodges, and J. A. Timney for helpful discussions and Mr. J. G. Gamble, Mr. D. R. Dye, and Mr. J. M. Whalley for technical support. We also thank a reviewer for comments that have led us to clarify some points in the paper.

Appendix

The photosystem can be simplified and represented schematically in Figure 6. The upper ^{3}MLCT state is left out of the figure since it merely complicates the equations and does not affect the basic argument.

Following pulse excitation, some 80% of the $\mathrm{W(CO)_5(4\text{-}CNpyr)}$ is converted to level 1; this is in rapid equilibrium with level 2. Since the separation of these two levels is about 2500 cm^{-1}, the equilibrium constant ($K = [2]/[1] = k_{12}/k_{21}$) at room temperature is approximately 6×10^{-6}. Assuming that k_{12} and k_{21} are larger than other rate constants, then, with standard methods,[20] the time dependence of the concentrations of $\mathrm{W(CO)_5}$, ground state (GS), and level 1 are given by

$$[\mathrm{W(CO)_5}]_t = \frac{(k_d k_{12})[1]_0}{\lambda(k_{12} + k_{21})}(1 - e^{-\lambda t})$$

$$[\mathrm{GS}]_t = \frac{(k_1 k_{21} + k_2 k_{12})[1]_0}{\lambda(k_{12} + k_{21})}(1 - e^{-\lambda t}) + [\mathrm{GS}]_0$$

$$[1]_t = \frac{k_{21}[1]_0}{\lambda(k_{12} + k_{21})}(e^{-\lambda t})$$

where $[1]_0$ = the concentration of $\mathrm{W(CO)_5(4\text{-}CNpyr)}$ in level 1 immediately after the flash, $[\mathrm{GS}]_0$ = the concentration of ground state remaining immediately after the flash, and

$$\lambda = \frac{k_1 k_{12} + (k_2 + k_d)k_{21}}{k_{12} + k_{21}}$$

Thus the concentrations of the three IR-detectable components change exponentially with the same rate constant λ.

At the end of the fast stage of the photochemistry ($t = f$)

$$[\mathrm{W(CO)_5}]_f = \frac{(k_d k_{12})[1]_0}{\lambda(k_{12} + k_{21})}$$

$$[\mathrm{GS}]_f = \frac{(k_1 k_{21} + k_2 k_{12})[1]_0}{\lambda(k_{12} + k_{21})} + [\mathrm{GS}]_0$$

Since level 1 decays approximately 50/50 to $\mathrm{W(CO)_5}$ and GS

$$[\mathrm{W(CO)_5}]_t \approx [\mathrm{GS}]_t - [\mathrm{GS}]_0$$

i.e. $k_d k_{12} \approx k_1 k_{21} + k_2 k_{12}$. Furthermore, since $k_{21} \gg k_{12}$

$$k_d k_{12} \approx k_1 k_{21}$$

or

$$k_d \approx k_1/K$$

From femtosecond studies on metal carbonyls,[23] we can assume k_d is very large, so the equation is reasonable. However, the quantum yield at 510 nm under continuous irradiation is 0.02. To reconcile this with the pulsed observations, we compare the number of photons absorbed with the number of molecules in solution.

With an exctinction coefficient of $\mathrm{W(CO)_5(4\text{-}CNpyr)}$ at 510 nm of ca. 2000 M^{-1} cm^{-1}, a concentration of 5×10^{-5} M, and a path length of 0.5 cm and assuming 5 mJ are incident on a cylinder of 1 mm diameter and 0.5 cm length, the number of photons absorbed (p) is given by

$$\begin{aligned} p &= 0.005(1 - 10^{-0.05})/h\nu \\ &= 1.4 \times 10^{15} \end{aligned}$$

The number of molecules (n) in this cylinder of solution is

$$n = 1.2 \times 10^{14}$$

Thus, provided the decay of the singlet MLCT state is very fast compared with 10 ns, there is enough energy for ca. 12 excitations. A single pulse converts 80% of the ground state to the ^{3}MLCT state, from which half dissociates to $\mathrm{W(CO)_5}$. For a (continuous) quantum yield of 0.02, approximately 20 excitations and decays to and from the excited singlet state are required. These numbers are in reasonable agreement given the approximate nature of many of the measurements. In previous experiments[6] with higher energy density, there was no evidence for two-photon processes.

The experiment is thus interpreted on the basis of a cylinder of excited states in the solution. It is worth adding the comment that diffusion out of this cylinder of solution will be very slow compared with the time scales of the observations.[24]

Registry No. 4-CNpyr, 100-48-1; $\mathrm{W(CO)_5(4\text{-}CNpyr)}$, 60166-32-7; $\mathrm{W(CO)_5}$, 30395-19-8; $\mathrm{W(CO)_6}$, 14040-11-0.

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