Contribution from the Department of Chemistry and Canadian Centre for Picosecond Spectroscopy,
Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, Quebec, Canada H3G 1M8

Wavelength-Dependent Photochemical Ligand Substitution in $W(CO)_5L$ (L = Pyridine, Piperidine)

Carol Moralejo,[†] Cooper H. Langford,[*,†] and D. K. Sharma[‡]

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$W(CO)_5L$ (L = pyridine, piperidine) undergoes photochemical replacement of L by solvent (S). If the solvent is a poor ligand, $W(CO)_5S$ can be rapidly converted to an alkene complex to render the primary product observable. Across the region of LF singlet absorption, quantum yields increase with decreasing excitation energy, but quantum yields in the triplet region are smaller. The solvo intermediate $W(CO)_5S$ is formed from $W(CO)_5L$ in less than 10 ps under 355-nm irradiation. This contrasts with the result of irradiation for $W(CO)_6$. Transient absorption spectroscopy of $W(CO)_6$ in neat 1-hexene reveals the growth of a $W(CO)_5$(alkyl) intermediate identical with that observed for this complex in cyclohexane. Between 50 ps and 10 ns, rearrangement to form the stable $W(CO)_5$(1-hexene) product is observed. The triplet reactivity can be understood from spectroscopic results on the structure of the vibrationally equilibrated triplet. Singlet reactivity is interpretable by using Hollebone's octapole rule.

Introduction

The photochemistry of the group VIB metal hexacarbonyls, $M(CO)_6$ (M = Cr, Mo, W), has been studied extensively during the past 2 decades.[1] The primary event upon irradiation of these complexes in low-temperature matrices,[2-5] solution,[6-9] and in the gas phase[10-12] is efficient loss of CO to give $M(CO)_5$. Transient absorption spectroscopy of these complexes in alkane solvents has provided evidence that formation of a solvated intermediate, $M(CO)_5S$, where S is a solvent molecule, occurs within picoseconds.[13,14] For $Cr(CO)_6$ in cyclohexane, the formation of $Cr(CO)_5$(cyclohexane) has been found to occur with a time constant of ~0.8 ps[13] while the formation of $W(CO)_5$(perfluoromethylcyclohexane) from $W(CO)_6$ in perfluoromethylcyclohexane occurs with a time constant of ~20 ps.[14] Quantum yields for the photosubstitution of CO by a suitable ligand in these complexes are high (>0.65),[6,7] and in the case of $W(CO)_6$, the quantum yield is independent of the wavelength of irradiation.[7] The behavior of $W(CO)_6$ appears to present a classical photochemical case that involves rapid internal conversion and efficient prompt intersystem crossing to the triplet with all substitutional reactivity originating in the LF triplet.

Steady-state photolysis of monosubstituted $W(CO)_5L$ complexes, where L is a nitrogen donor or an alkene, has revealed that both loss of L and loss of CO occur depending on the wavelength of irradiation.[15-18] Loss of L remains the predominant reaction. For $W(CO)_5L$ (L = pyridine, *trans*-2- and *trans*-4-styrylpyridine,[15] piperidine[16], Wrighton et al. have reported an increase in substitution quantum yields with decrease of excitation energy in the LF singlet region from 31 950 cm^{-1} (313 nm) to 22 950 cm^{-1} (436 nm). This behavior contrasts with the substitution reactivity initiated by excitation of ligand field singlets of another group of d^6 complexes, the Co(III) complexes. In these compounds, photosubstitution quantum yields decrease with decreasing energy across the LF singlet region.[19]

The evidence of wavelength dependence for the substituted $W(CO)_5L$ complexes[15,16] indicates that the story for $W(CO)_5L$ must be more complicated than that reported for $W(CO)_6$.[7] This has prompted us to reexamine the wavelength dependence for the LF singlet irradiation of $W(CO)_5L$ (L = pyridine, piperidine), and using laser sources that permit accurate quantum yield determination of weakly absorbing samples,[20] we have also extended studies of $W(CO)_5L$ to direct irradiation into the triplet region. Since $W(CO)_5py$ (py = pyridine) has a MLCT state[21] that lies at higher energy than the first LF singlet state, we have also investigated the reactivity as a function of the separation of LF and CT bands induced by solvent polarity change. Finally, we have examined the formation of $W(CO)_5S$ from $W(CO)_5L$ (L = CO, pyridine, piperidine) in both alkane and alkene solvents using picosecond spectroscopy.

Experimental Section

Materials. $W(CO)_6$ (99%), isooctane (spectroscopic grade), pyridine (reagent grade), piperidine (reagent grade), 1-hexene (99%+), and tetrahydrofuran (reagent grade) were purchased from Aldrich. Benzene (distilled in glass) and dichloromethane (spectroscopic grade) were purchased from Caledon. Cyclohexane (spectroscopic grade) was purchased from Anachemia. THF was distilled over potassium metal before use. All other reagents were used without further purification.

$W(CO)_5py$ and $W(CO)_5pip$ (pip = piperidine) were prepared by the following method. Approximately 0.65 g of $W(CO)_6$ was dissolved in 30 mL of THF in a 100-mL Pyrex flask. 5 mL of pyridine or piperidine was added. Prepurified N_2 was passed through a THF bubbler before being passed over the solution to sweep out displaced CO. The solution was exposed to cool-white fluorescent lab lights, which emit light of wavelengths ≥350 nm, with continuous stirring, for 72 h. The reaction was monitored for remaining $W(CO)_6$ by TLC on alumina plates using isooctane as the eluting solvent. An unidentified white amorphous solid precipitated from solution in both cases. For $W(CO)_5py$, no $W(CO)_6$ remained after 72 h. For $W(CO)_5pip$, no further decrease in $W(CO)_6$ occurred after 72 h. The yellow solution was filtered to remove the white precipitate, and the THF was removed by rotary evaporation. The products were purified by chromatography on neutral activated alumina (pH 6.5–7.5). Isooctane was used first to elute any unreacted $W(CO)_6$, and benzene was used to elute the product. The excess ligand was eluted with ethanol (99%). Both products, bright yellow crystals, were recrystallized from benzene/isooctane (1:1). Purity of the compounds was established by comparison with published UV–vis spectra.[21] The yield of product in both cases was at least 70%.

Irradiation Procedures. Samples were irradiated in a cylindrical fused-quartz cell (Hellma, 1 cm path length, 19 mm diameter, volume 2.8 mL). Photolysis and analysis were carried out by using the same cell. All steady-state reactions were monitored by UV–visible absorption

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[†] Department of Chemistry.

[‡] Canadian Centre for Picosecond Spectroscopy.

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Table I. Photosubstitution Quantum Yields for $W(CO)_5L \rightarrow W(CO)_5$(1-hexene) in Isooctane/1-Hexene (2:1)[a]

L		quantum yields				
		313 nm[b]	365 nm	436 nm	457.9 nm	488.0 nm
pyridine	N_2	0.48 (0.02)^{3}	0.54 (0.02)^{13}	0.63 (0.04)^{10}	0.42 (0.04)^{13}	0.23 (0.02)^{14}
	O_2	0.52 (0.03)^{4}	0.55 (0.03)^{12}	0.64 (0.06)^{5}	0.44 (0.03)^{7}	0.22 (0.01)^{4}
piperidine	N_2		0.48 (0.03)^{11}	0.53 (0.02)^{6}	0.42 (0.02)^{4}	0.38 (0.02)^{4}
	O_2		0.47 (0.02)^{3}	0.51 (0.02)^{5}	0.44 (0.01)^{6}	0.38 (0.02)^{5}

[a] Concentrations of reactants are between 1.5×10^{-4} and 6.5×10^{-4} M. Light intensities are between 3×10^{-10} and 2×10^{-6} einstein/s. Numbers in parentheses represent standard deviations. Superscripts represent the numbers of trials. [b] Wavelengths are ±2 nm.

spectroscopy using a microprocessor-controlled Hewlett-Packard Model No. 8452A diode array spectrophotometer. A PRA Model No. 3402 xenon medium-pressure arc lamp (150 W), coupled with the appropriate interference filters, was used for photolysis at 313, 365, and 436 nm. An argon ion laser (Spectra-Physics, 4 W) was used for photolysis at 457.9 and 488.0 nm. The beam was expanded to the diameter of the photolysis cell by passing it through a plano-convex lens. Samples were degassed by passing solvent-saturated prepurified N_2 through the sample for 5–30 min. Each sample was irradiated for successive time intervals, and a full spectrum was taken after each irradiation. The solutions were hand mixed at intervals during each irradiation and prior to analysis. Solution concentrations ranged from 1.5×10^{-4} to 1×10^{-3} M. Thermal reactions for both complexes were either nonexistent or very slow compared to photochemical reactions, and quantum yields needed no corrections for thermal products.

Light Intensity Measurements. The light intensity entering the photolysis cell through the 313- and 365-nm filters (±10 nm) was determined by using the well-known potassium ferrioxalate actinometer.[22] Solutions of $W(CO)_5py$ for irradiations at these wavelengths were sufficiently concentrated so that the absorptivity over the bandwidth of the filters was >98%. The average absorptivity of $W(CO)_5pip$ over the bandwidth of the filters was >75%. Attempts at increasing the absorptivity to 100% resulted in problems with precipitation of product. The average absorptivity was used to calculate the number of photons absorbed by $W(CO)_5pip$. The quantum yields reported for 436-, 457.9-, and 488.0-nm irradiation were determined based on matching absorbances for reactant and actinometer. Since the absorption spectra of both reactant and actinometer were similar in this region, the absorbances of both were matched as closely as possible by using optically dilute solutions. For irradiations at 457.9 and 488.0 nm, the absorbances of reactant and actinometer were matched to within 1%. Quantum yields for photosubstitution at these wavelengths were then determined by parallel irradiations of reactant and actinometer. Since the number of molecules of substitution product and Fe^{2+} could be determined experimentally and the quantum yield for formation of Fe^{2+}, at these wavelengths, has been documented,[22,23] the quantum yield for product formation could be determined.

The same photolysis cell was used for irradiation of the reactant and actinometer. The actinometer was mixed in the same manner as the reactant. Several actinometer measurements were taken during the day, and the average value was obtained. The standard deviation for the actinometer measurements was usually less than 5%.

Analysis of Data. For solutions of $W(CO)_5L$ (L = pyridine, piperidine) in S/1-hexene (2:1) (S = isooctane, benzene, dichloromethane) the decrease of the absorbance of the reactant was monitored as a function of time of irradiation. The wavelength of analysis depended on the initial concentration of the reactant and was most often 412 nm, since the concentrations of the reactants increased the absorbances of the peaks at 382 nm (for pyridine) and 404 nm (for piperidine) to values greater than 2. Irradiations of both compounds at wavelengths ≥436 nm produced no loss of isosbestic points in their absorption spectra up to 100% conversion. The molar extinction coefficients of reactant and product, in alkane solvents, were determined by converting the reactant to 100% product using irradiation wavelengths ≥436. The molar extinction coefficents of reactant and product, determined in this manner, were used to correct for reactant or product absorption. Data from less than 10% conversion were used for calculation of quantum yields.

Picosecond Spectra. Picosecond flash photolysis was conducted with a 2.5-mJ, 355-nm, 20-ps pulse and monitored with a 425–675-nm probe pulse. The system is a mode-locked Nd/YAG laser system with an OMA for data collection. Operation is as in ref 14. Among convenient solvents, only saturated hydrocarbons produce an intermediate, $W(CO)_5S$, with a LF band at sufficiently long wavelength[5] to allow monitoring with the available probe pulse. Spectra are the average of 7–10 recordings.

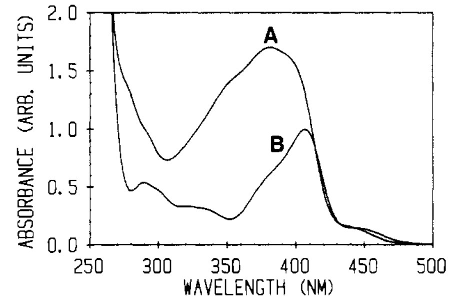

Figure 1. Absorption spectra for $W(CO)_5py$ (A) and $W(CO)_5pip$ (B) in isooctane at 25 °C. The concentration for both compounds is 2.5×10^{-4} M.

Results

Electronic Spectra. The electronic spectra of $W(CO)_5py$ and $W(CO)_5pip$ exhibit similar features in alkane solvents. In isooctane, each compound exhibits a low-energy band, near 442 nm (~600 L mol^{-1} cm^{-1}), which has been previously assigned as a LF $^1A_1 \rightarrow {}^3E$[24] transition and which appears as a shoulder on the more intense LF $^1A \rightarrow {}^1E$[16] transition centered near 382 nm for pyridine (~7000 L mol^{-1} cm^{-1}) and 404 nm for piperidine (~3900 L mol^{-1} cm^{-1}) (Figure 1). In both compounds, there is a very intense absorption band at approximately 270 nm, which, by analogy to the MLCT assignment for $W(CO)_6$,[25] is probably the W → CO charge-transfer transition. In $W(CO)_5py$, near 350 nm, there appears to be a hidden absorption band that blue shifts and is resolved from the LF singlet–singlet band in more polar media. This band, which is not present in the piperidine complex, has been tentatively assigned as a W → pyridine CT transition.[21]

Quantum Yields. Photolysis of $W(CO)_5py$, from 313 to 488.0 nm, and $W(CO)_5pip$, from 365 to 488.0 nm, in isooctane/1-hexene (2:1), leads to substitution of pyridine or piperidine by 1-hexene. Quantum yields are listed in Table I. Spectroscopic analysis indicates that 313-nm irradiation of the piperidine complex may lead to a disubstituted product at low conversion. For 100% conversions, there is no loss of isosbestic points in the electronic spectra of either compound, for irradiations at wavelengths ≥436 nm, but the loss of the isosbestic points, precipitation, and significant changes in the electronic spectra suggest that secondary photolysis is occurring as the reaction proceeds past 50% conversion under 313- and 365-nm irradiation.

In agreement with Wrighton et al.,[15,16] photolysis in the wavelength region of the LF singlet band (365–436 nm) produces substitution quantum yields that are measurably wavelength dependent for both compounds, although the yield for the pyridine complex is higher than the yield for the piperidine complex. Photolysis into the lower energy band, designated as the LF triplet, results in lower substitution quantum yields than those found in the LF singlet region. The yields are nearly identical for both compounds under 457.9-nm irradiation, and the yield at 488.0 nm, in the piperidine complex, is slightly lower than that reported for 457.9-nm irradiation. At 488.0 nm, experimental uncertainty of absorbance matching of reactant and actinometer solutions that

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Table II. Photosubstitution Quantum Yields for $W(CO)_5L \rightarrow W(CO)_5$(1-hexene) in Benzene/1-Hexene (2:1)[a]

		quantum yields			
L		313 nm[b]	365 nm	436 nm	457.9 nm
pyridine	N_2	$0.47\ (0.04)^4$	$0.52\ (0.02)^4$	$0.57\ (0.03)^2$	$0.40\ (0.04)^5$
	O_2		$0.53\ (0.02)^4$	$0.54\ (0.02)^4$	$0.41\ (0.05)^3$
piperidine	N_2		$0.42\ (0.02)^4$	$0.45\ (0.03)^8$	$0.38\ (0.01)^4$

[a] Concentrations of reactant are between 2.4×10^{-10} and 7×10^{-10} M. Light intensities are between 3×10^{-10} and 3×10^{-6} einstein/s. Numbers in parenthesis represent the standard deviation. Superscripts represent the number of trials. [b] Wavelengths are ±2 nm.

Table III. Photosubstitution Quantum Yields for $W(CO)_L \rightarrow W(CO)_5$(1-hexene) in Dichloromethane/1-Hexene (2:1)[a]

		quantum yields			
L		313 nm[b]	365 nm	436 nm	457.5 nm
pyridine	N_2	$0.36\ (0.01)^2$	$0.47\ (0.04)^2$	$0.51\ (0.02)^2$	$0.39\ (0.01)^3$
	O_2	$0.40\ (0.05)^5$	$0.47\ (0.05)^{10}$	$0.52\ (0.03)^9$	
piperidine	N_2		$0.37\ (0.04)^8$	$0.40\ (0.01)^3$	$0.34\ (0.03)^4$
	O_2		$0.41\ (0.02)^4$	$0.43\ (0.05)^6$	$0.32\ (0.03)^2$

[a] Concentrations of the reactants are between 3×10^{-4} and 7×10^{-4} M. Light intensities are between 3.5×10^{-10} and 9×10^{-7} einstein/s. Numbers in parentheses represent the standard deviations. Superscripts represent the number of trials. [b] Wavelengths are ±2 nm.

Table IV. Molar Extinction Coefficients (L^{-1} mol cm^{-1}) for $W(CO)_5py$[a]

		molar extinction coeff			
L	solvent	344 nm[b]	382 nm	412 nm[c]	442 nm
pyridine	isooctane	5150	7000		660
	isooctane/1-hexene (2:1)	5250	6630	3575	580
	benzene/1-hexene (2:1)	6010	5490	2825	605
	dichloromethane/1-hexene (2:1)	5650	4740	2360	565

		molar extinction coeff		
L	solvent	404 nm[b]	412 nm[c]	442 nm
piperidine	isooctane	3900		560
	isooctane/1-hexene (2:1)	3630	3180	550
	benzene/1-hexene (2:1)	3510	2950	570
	dichloromethane/1-hexene	3300	2670	580

[a] Extinction coefficients are ±10%. [b] Wavelengths are ±2 nm. [c] These extinction coefficients represent wavelengths of analysis rather than absorption peaks.

transmit >95% increases uncertainty. Photolysis at 313 nm produces a substitution quantum yield for $W(CO)_5py$ which is similar to that obtained at 365 nm whereas, as previously mentioned, 313-nm irradiation of $W(CO)_5pip$ may lead to a disubstituted product at low conversion. Except for the quantum yield at 313 nm, the present results confirm by an independent method those reported by Wrighton et al.[15,16] for the photosubstitution of $W(CO)_5L$ (L = pyridine, piperidine) by 1-pentene under 365- and 436-nm excitation. It is interesting to note that the presence of oxygen does not affect the results. This is explained by picosecond flash photolysis studies, which reveal that the formation of the solvo complex $W(CO)_5S$ occurs within 10 ps. If this is the rate-determining step, then events occur too quickly for the diffusion of O_2 to interfere with the reaction.

A major difference between the electronic spectra is the presence of the W → pyridine CT band in the pyridine complex. No corresponding CT transition exists in the piperidine complex. Studies of $W(CO)_5L$ complexes where the MLCT state is the lowest energy state have revealed that the MLCT state is essentially unreactive.[21] An investigation into the possible contribution of the MLCT state to the quantum yields when it lies higher in energy than the first LF singlet state was undertaken. The two solvents, benzene and dichloromethane, were chosen because polarity differences are sufficient to change resolution of the CT and LF bands but neither formed stable products that would interfere with rapid coordination of the 1-hexene ligand. The results are reported in Tables II and III. Irradiation at 313 nm for $W(CO)_5py$ results in efficient photosubstitution, and the quantum yields, within experimental error, are comparable to those observed upon irradiation at 365 nm.

As can be seen from the absorption spectra, the W → pyridine CT band is blue shifted and separated from the LF singlet band when $W(CO)_5py$ is dissolved in either benzene/1-hexene or dichloromethane/1-hexene (2:1) compared to isooctane/1-hexene (Figure 2). The molar extinction coefficient of the CT transition increases while that of the LF singlet correspondingly decreases in the polar solvents. A slight decrease in the extinction coefficient of the LF singlet transition is observed for $W(CO)_5pip$ in these more polar solvents. Values are reported in Table IV. There is a slight decrease in the substitution quantum yields for both compounds when irradiated at 365 and 436 nm, in benzene/1-hexene, and a further decrease in the quantum yields for both compounds when they are irradiated in dichloromethane/1-hexene. This decrease is also observed for the quantum yields at 313 nm, which suggests that a general solvent effect is responsible rather than CT state participation. It is likely, given the nonreactivity of the MLCT state when lowest in energy, that the reactivity of the higher energy MLCT is due to efficient internal conversion to the lower singlet LF state from which substitution occurs.

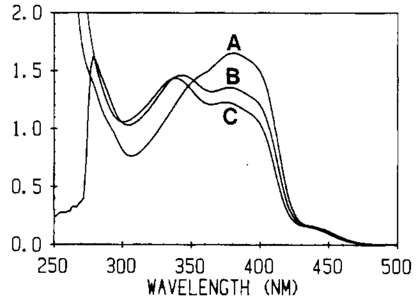

Figure 2. Absorption spectra for $W(CO)_5py$ in (A) isooctane, (B) benzene, and (C) dichloromethane at 25 °C. The concentration for the complex in all three solvents is 2.8×10^{-4} M.

The decrease in the quantum yields observed upon irradiation in benzene and dichloromethane/1-hexene, as compared to isooctane, may have some relationship to the dielectric constant of the solvent. The dielectric constant of isooctane (1.94) is slightly

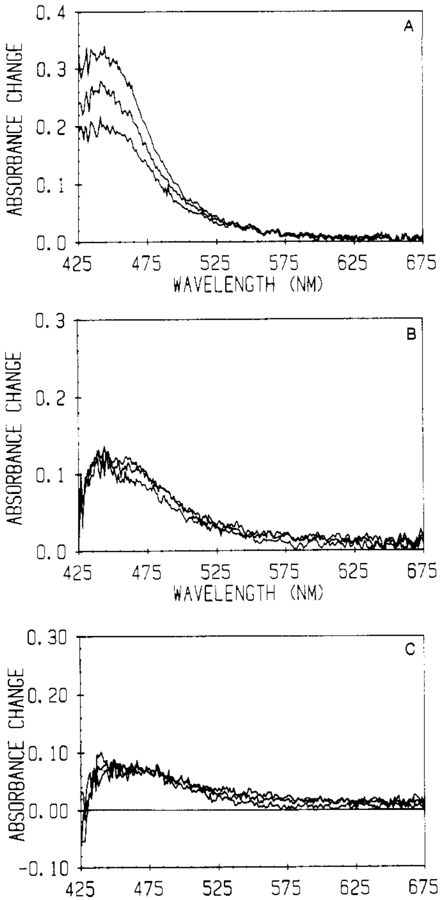

Figure 3. Picosecond flash photolysis of (A) $W(CO)_6$, (B) $W(CO)_5py$, and (C) $W(CO)_5pip$ in cyclohexane at 25 °C. Irradiation wavelength is 355 nm. Typical laser intensity is 2.5 mJ. For $W(CO)_6$, the transient absorptions are at 0, 20, and 50 ps in order of increasing absorbance change. For $W(CO)_5py$ and $W(CO)_5pip$, the transient absorptions are at 0, 20, and 50 ps with little observable difference among the spectra. The initial concentration is 4.7×10^{-3} M for $W(CO)_6$, 6×10^{-4} M for $W(CO)_5py$, and 3.3×10^{-3} M for $W(CO)_5pip$. The ground-state absorbance at 355 nm for each complex, in a 2 mm cell, is approximately 0.70.

lower than that of benzene (2.27) and significantly lower than that of dichloromethane (9.08). The inverse relationship between the photosubstitution quantum yields and the dielectric constant is consistent for both compounds, and although this observation is interesting, there is no clear basis for a claim that this solvent parameter is controlling these photochemical mechanisms.

Figures 3 and 4 show the results of picosecond experiments on $W(CO)_6$, $W(CO)_5py$, and $W(CO)_5pip$ in cyclohexane and $W(CO)_6$ and $W(CO)_5py$ in 1-hexene, respectively. Qualitative examination of the spectra indicates a common $W(CO)_5S$ from every $W(CO)_6$, $W(CO)_5py$, and $W(CO)_5pip$ experiment. In cyclohexane, after formation of the intermediate, no further change in the spectra is observed within the instrument time limit of 10 ns. A more quantitative examination indicates the intensity of the fully developed $W(CO)_5S$ band is proportional to 355-nm absorption and the quantum yield for formation of the $W(CO)_5$–1-hexene complex observed in steady-state irradiation experiments in isooctane by using 365-nm light. In other words, all 355-nm-initiated reactions share an initial dissociative step.

The picosecond spectra of $W(CO)_6$ in 1-hexene indicate growth of the signal for $W(CO)_5S$, where S is the alkyl portion of 1-hexene chain, from 0 to 50 ps, as is seen for this complex in cyclohexane. Between 50 ps and 10 ns, the $W(CO)_5$(alkyl) transient decays to form the final $W(CO)_5$(1-hexene) product where W is bonded to the alkene donor of 1-hexene. The time constants for formation of $W(CO)_5$(alkyl) from $W(CO)_6$ in both cyclohexane and 1-hexene are ~25 ps. Steady-state photolysis of these compounds in 1-hexene solvents shows that the product $W(CO)_5$(1-hexene)

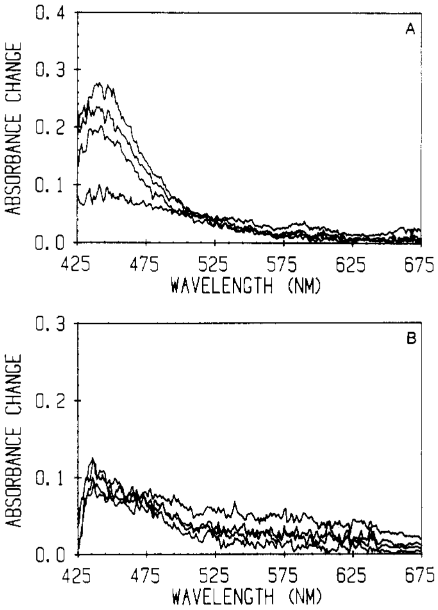

Figure 4. Picosecond flash photolysis of (A) $W(CO)_6$, and (B) $W(CO)_5py$ in 1-hexene at 25 °C. Irradiation wavelength is 355 nm, and the typical laser intensity is 2.5 mJ for $W(CO)_6$ and 1.5 mJ for $W(CO)_5py$. For $W(CO)_6$, the transient absorptions are 10 ns and 0, 20, and 50 ps in order of increasing absorbance change. For $W(CO)_5py$, the transient absorptions are 0, 20, and 50 ps with little observable difference among spectra. Concentrations are 4.4×10^{-3} M for $W(CO)_6$ and 8.8×10^{-4} M for $W(CO)_5py$.

does not absorb past 400 nm. The spectra of $W(CO)_5py$ in 1-hexene also indicate that the initial transient is $W(CO)_5$(alkyl), which is fully developed within 20 ps. This behavior is similar to that observed for this complex in cyclohexane. The issue of the kinetics of rearrangement raises an interesting question about the tungsten–alkane interaction and will be discussed elsewhere.

The 2.5-mJ pulse is sufficient to approach excitation saturation in the 2-mm sample cell when concentrations of between 6×10^{-4} and 4.5×10^{-3} M are used. Thus, the effective pulse width is narrower than 20 ps. This allows the resolution of the 17-ps grow-in of $W(CO)_5S$ from $W(CO)_6$ and allows the conclusion that the prompt appearance of $W(CO)_5S$ from $W(CO)_5L$ indicates a grow-in time of less than 10 and probably less than 5 ps. (The effective pulse width is near 5 ps when saturation is taken into account.)

Five important points emerge from these results.

First, the observation by Wrighton et al.[15,16] that there is a wavelength dependence across the LF singlet region is confirmed by independent experimental methods but it is small.

Second, there is no evidence for a reaction that occurs directly from the CT state. Internal conversion to the LF state is probably efficient.

Third, there is clear evidence for direct reaction from the LF singlet. Direct irradiation of the LF triplet produces smaller yields.

Fourth, there is some evidence that the solvent effects play a role in the substitution process that is not large.

Fifth, the common $W(CO)_5S$ intermediate is formed faster from $W(CO)_5L$ (L = pip or py) than from $W(CO)_6$. Wavelength dependence is associated with this faster substitution.

Discussion

Tutt and Zink[26] have analyzed the excited-state distortions in the vibrationally equilibrated LF triplets of $W(CO)_5py$ and $W(CO)_5pip$ using comparisons of emission and preresonance Raman spectra in the framework of time-dependent theory.[27] For $W(CO)_5py$ the most elongated bond in the excited state is the W—N bond, which is extended by 18 pm. The trans M—C bond is extended 12 pm. The bond length changes for $W(CO)_5pip$ are

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(26) Tutt, L.; Zink, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 5830.
(27) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 368.

larger. The W—N bond is extended by at least 30 pm (a limit in the analysis), and the trans W—C bond is extended 25 pm. These results were shown to conform to ligand field predictions in which the ^3E state ($d_{z^2} \leftarrow d_{xz}, d_{yz}$ in first order) has larger d_{z^2} character than $d_{x^2-y^2}$ character to the extent that the unique ligand differs from CO in ligand field strength. Tutt and Zink pointed out that triplet photoreactivity is correctly predicted on the assumption that increased distortion in the vibrationally equilibrated excited state correlates with a smaller barrier to substitutional relaxation. This approach provides a good account of our data at 488.0 nm.

Heller's theory is inherently dynamic, but the use of luminescence data in Tutt and Zink's analysis limited their results to the vibrationally equilibrated triplet. Hollebone, Langford, and Serpone[28] have pointed out two photochemical limits. In one limit vibrational equilibration allows search for decay paths over all nuclear coordinates. The excited-state reaction is the analogue of the ground-state reaction. The excited state is an "electronic isomer". In the other limit, rapid reaction requires decay along selected nuclear coordinates.

Hollenbone et al.[28] have developed vectorial selection rules for identification of such coordinates based on the treatment of vibrational coordinates by subduction from the group describing fluctuations of a spherical mass distribution. This provides vibrational quantum numbers entirely analogous to electronic quantum numbers for subduction analysis of angular momentum selection rules. Since $W(CO)_5L$ systems produce a fully equilibrated $W(CO)_5S$ spectrum in a few picoseconds, they are obvious candidates for analysis in the fast limit. This is especially true since the singlet pathway clearly differs from the well-documented Tutt and Zink predictions for the reactivity of the vibrationally equilibrated excited states, ^1E and ^3E, both of which have the same orbital configurations.

The simplest of Hollebone's selection rules is the octapole rule for angular momentum changes in a transition. The objective of the octapole rule is to identify the vibrational mode of the excited state. The rule states that

$$\Delta V = 3 - (\Delta L + \Delta S)$$

where ΔL is the change of electronic angular momentum quantum number, ΔS is the change of the spin quantum number, and ΔV is the vibrational angular momentum quantum number. The observed ΔV can be converted to V_{EX} by assuming that $V_{GR} = 0$ in

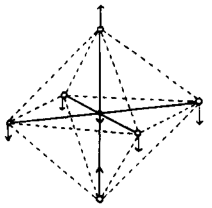
$$\Delta V = (V_{EX} - V_{GR}) = V_{EX}$$

This is applicable at room temperature for vibrations higher than 400 cm^{-1}.

In a d^6 octahedral system, the first two excited states are $^1T(D)$ and $^3T(P)$. If the primary product is, like the intermediate $W(CO)_5S$, which is formed in less than a few picoseconds a $^1A(D)$ state, then the reaction process is $^1T \rightarrow {}^1A$ and requires $\Delta V = 3$. $^3T \rightarrow {}^1A$ requires $\Delta V = 1$ as described as follows:

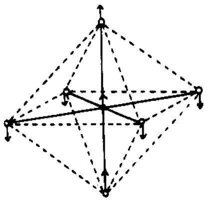
transition	ΔL	ΔS	ΔV	(O_h)
$^1T_1(D) \leftarrow {}^1A_1(D)$	0	0	3	t_{1u} buckle
$^3T_1(P) \leftarrow {}^1A_1(D)$	1	1	1	t_{1u} stretch

In octahedral symmetry, the requirements of the point group imply a t_{1u} vibration of which there are two types. The vibration corresponding to $\Delta V = 1$ is the asymmetric stretch t_{1u} shown in Figure 5a. In this mode, there is substantial extension along one axis and the ligand on that axis should be susceptible to substitution. On descent in symmetry to C_{4v}, the Hollebone prompt reaction model gives the same prediction as the thermally equilibrated excited-state model for reactivity from the triplet.



ASYMMETRIC

(A)



BUCKLE

(B)

Figure 5. Simplified diagrams representing (A) an asymmetric t_{1u} vibration and (B) a buckle t_{1u} vibration.

From the singlet, $\Delta V = 3$. The t_{1u} vibration is called a "buckle"[28] and is shown in Figure 5b. This mode, which is also responsible according to the Hollebone model for the efficient photosubstitution reactions from ^4T Cr(III) d^3 species,[29] is expected to be very reactive toward substitutions via a nonselective path because the metal is highly exposed to second sphere (solvating) molecules on four octahedral faces above the x,y plane in Figure 5b.

What remains is to account for the wavelength dependence. This requires consideration of the C_{4v} components. Octahedral ^1T correlates with ^1E and ^1A in C_{4v}, and ^1E is the lower electronic state. ^1A is the upper state. The wavelength dependence suggests more efficient substitution on irradiations of ^1E than ^1A. Hollebone and Stillman[30] have shown that vibronic coupling is a vector product that must conserve overall degeneracy. The splitting of the octahedral t_{1u} vibration into e_u and a_u requires the combination of the E electronic state with the a_u vibration and the A electronic state with the e_u vibration. Thus, excitation of the lower electronic state leads to selection of a relaxation pathway buckling to release the L ligand of $W(CO)_5L$. In contrast, excitation of the higher ^1A electronic state leads to selection of a relaxation pathway where the more exposed ligand is a CO not an L.

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