adatoms. We have thus refrained from comparing this bond energy to those of complexes. Note, however, that the weak bond energy for C_2H_4 on Fe(100)–H does not reflect the possible enhancement of metal–adsorbate π interactions for a surface relative to a single metal atom. That ethylene readily decomposes on clean Fe(100)[22-24] but not on Fe(100)–H[1] at least reflects the altered reactivity for the H-presaturated surface, if not the interaction strength.

5. Summary and Conclusions

Previously we have reported the reaction pathways and kinetics for ethylene on H-presaturated Fe(100). The formation of ethyl groups and their decomposition to regenerate ethylene was demonstrated using H–D exchange reactions and kinetic isotope effects. A thermochemical cycle has been constructed for these reactions and has been used to accurately determine Fe–C_2H_5 and Fe–H bond energies on this surface of 38 ± 4 and 59.5 ± 2 kcal/mol, respectively. It is the first instance we know of where a metal–alkyl bond strength has been determined for a transition metal surface.

Comparison of our Fe–C_2H_5 and Fe–H bond energies to those of mononuclear transition metal complexes shows that the values on the Fe surface are precisely in the range expected for a sterically unhindered complex containing a first or second row transition metal. That both bond energies should follow the same trend with degree of metal nucleation is reasonable since they are both of σ character. Our results suggest that the extended surface does not lead to a bond strength appreciably greater than expected in mononuclear complexes.

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Rare Gas–Metal Carbonyl Complexes: Bonding of Rare Gas Atoms to the Group VI Pentacarbonyls

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Abstract: Transient infrared spectroscopy has been used to study reactions of M(CO)$_5$ generated by 355-nm photolysis of M(CO)$_6$ where M = Cr, Mo, and W. At 298 K, M(CO)$_5$ reacts with CO with bimolecular rate constants of $(1.4 \pm 0.2) \times 10^{-10}$, $(1.5 \pm 0.1) \times 10^{-10}$, and $(1.4 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for Cr, Mo, and W, respectively. M(CO)$_5$ also reacts with Xe with bimolecular rate constants of $(0.9 \pm 0.4) \times 10^{-10}$, $(0.9 \pm 0.4) \times 10^{-10}$, and $(2.6 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for Cr, Mo, and W, respectively. Infrared absorptions attributed to M(CO)$_5$Xe and W(CO)$_5$Kr were observed. The rate of dissociative loss of the Xe atom from the M(CO)$_5$Xe complexes was determined by the observation of the rate of regeneration of M(CO)$_6$ in a reaction mixture consisting of M(CO)$_5$, CO, and Xe. The bond dissociation energy for the loss of the Xe atom from M(CO)$_5$Xe for all three metals is the same within experimental error and has an average value of 8.5 kcal/mol. A bond dissociation energy was estimated for the loss of Kr from W(CO)$_5$Kr, and an upper limit can be estimated for the bond dissociation energy for loss of Ar from W(CO)$_5$Ar.

I. Introduction

Time resolved infrared spectroscopy (TRIR) has been employed to observe coordinatively unsaturated organometallic species in real time, monitor their kinetic behavior, and generate infrared spectra of these short lived species.[1] One conclusion of this body of work is that coordinatively unsaturated organometallic species can be extraordinarily reactive, with rate constants often approaching the gas kinetic limit. It has recently been shown that these species can even bind "poor" ligands such as N_2O and CF_2Cl_2.[2] Reports also exist of coordination of coordinatively unsaturated organometallics with normally inert solvents on a picosecond time scale.[3]

The rate constants for and energetics of solvation of coordinatively unsaturated species have potential ramifications for a host of organometallic systems.[4] If the rate constant for solvent coordination by the coordinatively unsaturated species is comparable to the rate constant for reaction of the other ligand(s) present in the system and the bond energy of the coordinated solvent molecule is comparable to the bond energy of the other ligands present, then the solvent molecule is in effect competing with the other potential ligands for the open site(s) on the coordinatively unsaturated organometallic species. Since the solvent is typically present in far greater concentration than added ligands, the kinetics of competitive binding can be biased toward the solvent. Thus the solvent could affect the measured rate constant or potentially even the pathway of a solution-phase chemical reaction.

The gas phase is the phase of choice for studying ligand interactions (including potential reactions with solvent molecules) via TRIR because the interaction between potential ligands and isolated nonsolvated coordinatively unsaturated species can be studied in detail in real time using the technique employed in ref 2. It has been shown that the bond energy between a weakly bound ligand (solvent molecule) and the coordinatively unsaturated organometallic can be determined by monitoring the rate of dissociative loss of the ligand (solvent) from the M(CO)$_x$S species as a function of temperature. Additionally, the infrared spectrum of the complex formed from the coordinatively unsaturated organometallic complexed with a solvent molecule can give clues to the nature of the solvent bond by monitoring the carbonyl

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Table I[a]

M	k_{Xe}	k_{CO}	$M(CO)_6$ absorption (cm^{-1})	$M(CO)_5Xe$ absorption (cm^{-1})	shift[b] (cm^{-1})	bond dissociation energy (kcal/mol)	activation parameter energy (kcal)	activation parameter ln (preexp)
Cr	0.9 ± 0.4	14.0 ± 2.0	2000	1979	21	9.0 ± 0.9	8.4 ± 0.9	29.5 ± 1.4
Mo	0.9 ± 0.4	15.0 ± 1.0	2004	1982	22	8.0 ± 1.0	7.4 ± 1.0	27.3 ± 1.8
W	2.6 ± 0.2	14.0 ± 1.0	2000	1975	25	8.2 ± 1.0	7.6 ± 1.0	26.2 ± 1.6

[a] Rate constants have units of 10^{-11} cm^3/(molecule·s) and were measured at 298 K. Errors bars are 2σ. [b] Difference between $M(CO)_6$ and $M(CO)_5Xe$ absorptions.

stretches of the complexed organometallic species relative to the "unsolvated" or "naked" species.

We report the infrared spectrum and the bond energy for binding of Xe to the group VI pentacarbonyls. A spectrum of a $W(CO)_5Kr$ complex has also been obtained, and an estimate can be made for the $W(CO)_5$ (rare gas) bond energies in this complex. On the basis of the lack of a distinct $W(CO)_5$–Ar spectrum and the lack of Ar inhibition of the reaction of $W(CO)_5$ with CO, an upper limit for the $W(CO)_5$–Ar bond can be estimated. The group VI metals were chosen because their photochemistry is simple and well understood.[5] We view rare gases as the simplest solvent molecules and as a starting point for the investigations of solvent interactions with coordinatively unsaturated organometallic species.

II. Experimental Section

The apparatus used in this study has been described previously in detail.[2] However, a brief description will be provided here for convenience. Measurements were performed using a 16-cm Pyrex cell terminated by CaF_2 windows. The hexacarbonyl compound under study was introduced directly into the IR cell as a solid or by equilibration of the cell volume with the contents of a tube containing the solid hexacarbonyl.

The output of a frequency tripled Nd:YAG laser (355 nm), used to photolyze $M(CO)_6$, delivered 7–10 mJ/cm^2 at the cell window. This photolysis flux photolyzes at most 5% of the total parent ($M(CO)_6$) concentration in the 100 photolysis pulses that are typically used between cell fills. Formation of the metal carbonyl products was detected by the attenuation of infrared radiation from a home-built, liquid nitrogen-cooled, line-tunable CO laser. Infrared beam intensity was monitored by a fast ($\tau_{1/2} \sim 60$ ns) InSb detector. The detector output (transient waveform) was amplified (Perry ×100), digitized, signal averaged (Lecroy 9400), and sent to a computer for storage and manipulation. Time resolved infrared spectra were constructed from waveforms acquired at probe frequencies within the carbonyl stretch region by joining together the amplitude of various waveforms at common delay times. Data used to construct the spectra of the $M(CO)_5L$ species were obtained using static cell fills of 5–20 mTorr of $M(CO)_6$ and 80–500 Torr of rare gas. Static cell fills of 5–20 mTorr of $M(CO)_6$, 0.1–100 Torr of L (CO and Xe), and 80 Torr of helium were used for the determination of rate constants for the reaction of $M(CO)_5$ + L. Static cell fills of 5–20 mTorr of $M(CO)_6$, 0.2–2 Torr of CO, 2–70 Torr of Xe, and He up to 80-Torr total pressure were used to obtain k_{obs} and k_d (see eqs 5 and 6). Experiments were performed to verify that k_{obs} and k_d obtained under these conditions were not dependent on pressures of added He (i.e., they were in the high pressure limit). Kinetic information was obtained by probing the relevant regions of the time resolved spectrum while varying the concentration of added reactant. Resulting waveforms were analyzed as multiple exponentials by a Provencher routine.[7] The relatively high pressures used for these measurements assures that the bulk temperature rise due to the energy released on photolysis and/or bond formation is negligible (less than 1 K) and that relaxation of the internal degrees of freedom of the reactants and products is fast on the time scale of the current experiments.

$Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were obtained from Strem Chemicals, Alpha Products, and Aldrich Chemicals, respectively, and were sublimed in situ. The gases used in the experiments were used as supplied without further purification. The gases had the following stated purity and vendor: for CO, 99.9%, Matheson; for He, 99.999%, Matheson, and for Xe, 99.999%, Cryogenic Rare Gas. The temperature range of the experiments was 298–340 K with an uncertainty of ±2 K.

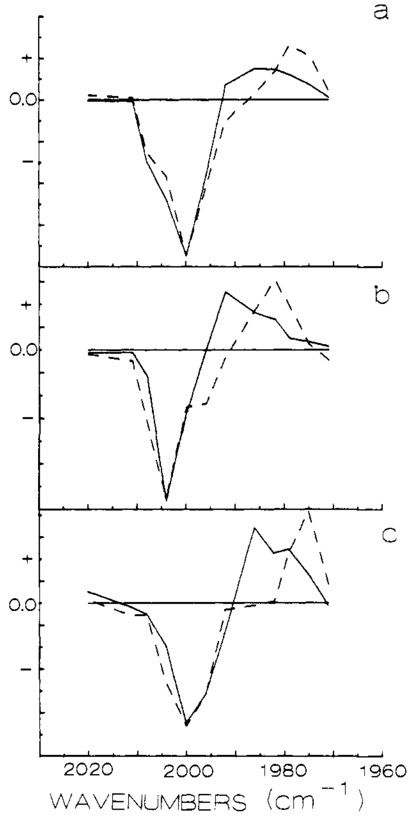

Figure 1. Transient time resolved infrared spectra generated upon 355-nm photolysis of $M(CO)_6$ where M = Cr, Mo, W. (a) The solid line spectrum (—) is the one obtained at 1 μs after ~10 mTorr of $Cr(CO)_6$ and 80 Torr of He are photolyzed with 355-nm radiation. The dotted line spectrum (--) is the same as above but 80 Torr of Xe replaces He. (b) Same description as above but M = Mo. (c) Same description as above but M = W.

III. Results

A. Spectra. It has previously been shown that absorption of a 355-nm photon by $Cr(CO)_6$ and $W(CO)_6$ produces almost exclusively the respective $M(CO)_5$ species.[2,6] The current study has demonstrated that this is also true for $Mo(CO)_6$. The time resolved spectra for the $M(CO)_5$ species (M = Cr, Mo, and W) in the presence of He and Xe are shown in Figure 1 (1 μs after photolysis). These spectra are in essence "snapshots" of the infrared absorbances at this time. The solid line spectrum was obtained by photolyzing the hexacarbonyl in the presence of 80 Torr of He, while the dotted line spectrum was obtained when 80 Torr of Xe was present in the cell along with $M(CO)_6$. Note that the spectum changes substantially when He is replaced by Xe. As will be discussed in more detail in the following section, this change is due to formation of a $M(CO)_5Xe$ complex. This assignment is consistent with prior spectroscopic evidence for the formation of $Cr(CO)_5Xe$ following photolysis of $Cr(CO)_6$ in liquid Xe or in Xe doped liquid Kr and evidence that group VI pentacarbonyls interact with inert gases as light as neon.[8,9] The

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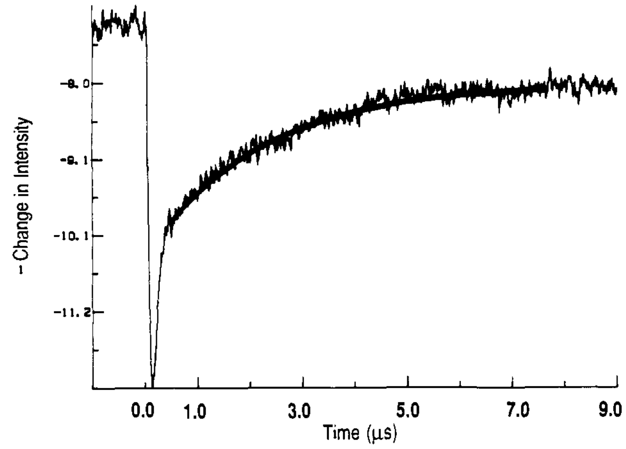

Figure 2. Transient signal obtained at 2000 cm^{-1} when 5–10 mTorr of $W(CO)_6$, 5.2 Torr of Xe, 80 Torr of He, and 1.2 Torr of CO are photolyzed with 355-nm radiation. Decrease is due to loss of $W(CO)_6$ while increase in signal is return of $W(CO)_6$. Line drawn through slow part of $W(CO)_6$ regeneration is the computed fit, k_{obs}.

observed absorption (Figure 1) is not due to polynuclear $M_2(CO)_{11}$ because the parent concentration is kept sufficiently low so as to inhibit polynuclear formation. Since there is no evidence for coordination of He to coordinatively unsaturated metal carbonyls at room temperature, the spectrum of $M(CO)_5$ in He is taken to be that of naked coordinatively unsaturated $M(CO)_5$. As such, Table I lists the absorptions of $M(CO)_5$ and $M(CO)_5Xe$ in the carbonyl stretch region of the infrared covered in this study.

B. Kinetics. 1. Kinetic Scheme. A complete description of the kinetic scheme used to determine bond dissociation energies from measurements of the rate of regeneration of $M(CO)_6$ has been previously described in detail.[2] A brief description will be provided here for convenience.

The unimolecular rate for the dissociative loss of a weakly bound ligand can be extracted from the following kinetic scheme, where Xe is specifically indicated as such a ligand.

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO \tag{1}$$

$$M(CO)_5 + Xe \xrightarrow{k_{Xe}} M(CO)_5Xe \tag{2}$$

$$M(CO)_5Xe \xrightarrow{k_d} M(CO)_5 + Xe \tag{3}$$

$$M(CO)_5 + CO \xrightarrow{k_{CO}} M(CO)_6 \tag{4}$$

Reaction 4 in this scheme is not reversible on the relevant experimental time scale since the first bond dissociation energies of the group VI hexacarbonyls are on the order of 40 kcal/mol.[10] It is desirable that, under experimental conditions, the bimolecular rate for reactions 2 and 4 are both much larger than the unimolecular dissociation rate for $M(CO)_5Xe$. Therefore, assuming dissociative loss of Xe, as has typically been observed for weakly bound ligands,[2] regeneration of $M(CO)_6$ is rate limited by the loss of the weakly bound Xe atom. The unimolecular dissociation rate constant k_d can then be determined by monitoring the rate of recovery of $M(CO)_6$ in the presence of various pressures of CO and Xe.

Solving eqs 2–4 using the steady-state approximation for $[M(CO)_5]$ yields

$$k_{obs} = \frac{k_d k_{CO}[CO]}{k_{CO}[CO] + k_{Xe}[Xe]} \tag{5}$$

where k_{obs} is now the rate of recovery of $M(CO)_6$, which under the experimental conditions typically takes place on the time scale of 10–50 µs. Figure 2 is an example of the type of signal observed for the regeneration of parent ($M(CO)_6$) when a mixture of 5.2 Torr of Xe, 1.2 Torr of CO, 80 Torr of He, and 5–10 mTorr of $W(CO)_6$ is photolyzed with 355-nm radiation. $M(CO)_6$ is regenerated from the reaction $M(CO)_5 + CO$. When Xe is present in the cell mixture, the return of parent occurs on two distinct time scales. The fast (early) part of the $M(CO)_6$ regeneration signal is due to the reaction of some of the $M(CO)_5$ that is generated by the photolysis pulse with CO. The slower part of the $M(CO)_6$ regeneration signal results from the reaction of $M(CO)_5 + CO$ when the latter species is produced by dissociative loss of the Xe atom from the $M(CO)_5Xe$ complex: this part of the regeneration signal has a rate given by k_{obs} (see eq 5). Equation 5 can be rearranged to give

$$k_d = k_{obs}\left(1 + \frac{k_{Xe}[Xe]}{k_{CO}[CO]}\right) \tag{6}$$

Thus, to obtain k_d from k_{obs} it is necessary to measure k_{CO}, and k_{Xe}. A measurement of the temperature dpendence of k_d allows for a determination of the bond enthalpy for the relevant complex. The k_d value at each temperature is an average calculated from the measured k_{obs} values for different cell conditions at each temperature. k_{CO} and k_{Xe} were separately established at each temperature from the appropriate pressure dependencies of the rates of reactions for processes 1 and 2, respectively (see sections 2 and 3 below). These measurements will now be discussed.

2. Measurement of k_{CO}. Absorption of a 355-nm photon by group VI hexacarbonyls produces a $M(CO)_5$ species that is vibrationally excited, which can be relaxed by added He buffer gas.[1,11] Helium also serves to collisionally stabilize the reaction product(s) (in this case, $M(CO)_6$ and $M(CO)_5Xe$) and to act as a thermal buffer, and thus it inhibits formation of acoustic waves that could be generated by inhomogeneous absorption of photolytic radiation.[1]

The rate constant for reaction of $M(CO)_5 + CO \rightarrow M(CO)_6$ was determined from the slope of the line obtained by plotting the rate of regeneration of $M(CO)_6$ vs CO pressure (probed at 2000, 2004, and 2000 cm^{-1} for Cr, Mo, and W, respectively). These reactions have a slight negative temperature dependence. The behavior for k_{CO} for $Cr(CO)_5 + CO$ is typical. It ranges from (1.4 ± 0.1) × 10^{-10} cm^3/(molecule·s) at 298 K to (1.0 ± 0.2) × 10^{-10} cm^3/(molecule·s) at 340 K. The origin of this temperature dependence has been discussed in ref 2. Care was taken to ensure that all experiments were performed in the high pressure limit. Under these conditions the measured rate of the addition reaction

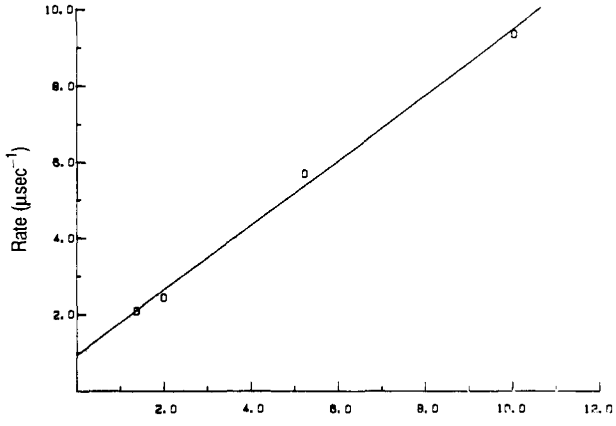

Figure 3. Plot of pseudo-first-order rate constant at 298 ± 2 K for the reaction of $W(CO)_5$ with Xe. The rate of disappearance of $W(CO)_5$ at 1986 cm^{-1} is plotted against the pressure of added Xe. The slope of the line gives a bimolecular rate constant of (2.6 ± 0.2) × 10^{-11} cm^3 molecule^{-1} s^{-1}.

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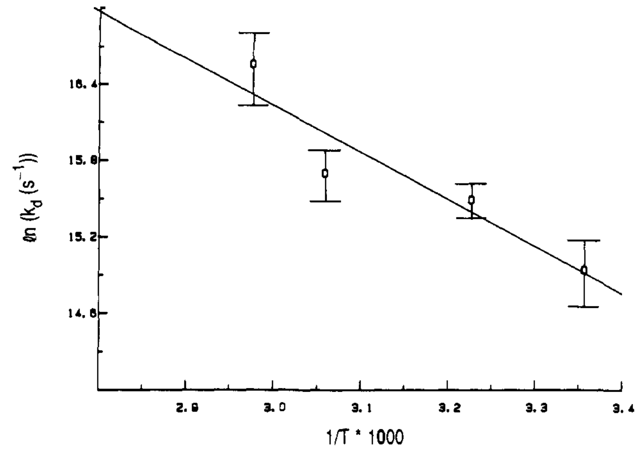

Figure 4. Plot of ln k_d versus $1/T$ for Mo(CO)$_5$Xe. The slope of the line is -3.7 ± 0.5 K^{-1}, which gives an activation energy of 7.4 ± 1.0 kcal mol^{-1} for the loss of Xe from Mo(CO)$_5$Xe.

is invariant to addition of further He buffer gas.

3. Measurement of k_{Xe}. Rate constants for the addition of Xe to M(CO)$_5$ (M = Cr, Mo, W) were determined in separate experiments (probed at 1986, 1992, and 1986 cm^{-1}, respectively) from the slope of the line obtained by plotting the decay rate of the M(CO)$_5$ transient signal versus the pressure of Xe (Figure 3). These rate constants were virtually temperature independent. The rate constant for W(CO)$_5$ + Xe, for example, ranges from $(2.6 \pm 0.2) \times 10^{-11}$ cm^3/(molecule·s) at 298 K to $(2.7 \pm 0.2) \times 10^{-11}$ cm^3/(molecule·s) at 340 K; the rate constant k_{Xe} for reaction of Xe with the other two metal centers (Cr, Mo), although somewhat smaller, shows the same temperature independent behavior. The bimolecular rate constants for the reaction of group VI pentacarbonyls with CO and Xe are listed in Table I.

4. Determination of Bond Energies. The dependence of k_d on temperature can be used to calculate the activation energy, E_a, and the preexponential factor for reaction 3 from an Arrhenius expression. A plot of ln k_d versus $1/T$ for Mo(CO)$_5$Xe is shown in Figure 4. The slope of the line for this plot gives an activation energy of 7.4 ± 1.0 kcal/mol.

The bond dissociation energy is related to the activation energy by

$$\Delta H = E_a + \Delta(PV)$$

Under constant volume conditions and ideal gas behavior, $\Delta(PV)$ reduces to ΔnRT. Thus the bond dissociation energies are as follows:

$$\mathrm{Cr(CO)_5Xe} \rightarrow \mathrm{Cr(CO)_5} + \mathrm{Xe} \quad 9.0 \pm 0.9 \text{ kcal/mol}$$

$$\mathrm{Mo(CO)_5Xe} \rightarrow \mathrm{Mo(CO)_5} + \mathrm{Xe} \quad 8.0 \pm 1.0 \text{ kcal/mol}$$

$$\mathrm{W(CO)_5Xe} \rightarrow \mathrm{W(CO)_5} + \mathrm{Xe} \quad 8.2 \pm 1.0 \text{ kcal/mol}$$

The above procedure is equivalent to obtaining ΔH from a plot of the logarithm of the equilibrium constant versus $1/T$ because the reverse reaction (reaction 2) is unactivated. Since the latter procedure requires the quotient of two experimentally determined rate constants, it can introduce more error into the determination of ΔH than the procedure actually employed.

The activation energies, preexponentials and bond enthalpies for the M(CO)$_5$Xe complexes are listed in Table I.

5. Other Rare Gases. The bonding of Ar and Kr to the W(CO)$_5$ species was also investigated. Evidence of an interaction with Kr was observed spectroscopically. On photolysis of 5–10 mTorr of W(CO)$_6$ in approximately 500 Torr of Kr, an infrared absorption centered at ~1983 cm^{-1} was obtained that is attributed to the W(CO)$_5$Kr product (Figure 5). Consistent with the formation of a W(CO)$_5$Kr complex, the rate of regeneration of W(CO)$_6$ decreased on addition of Kr. However, from the behavior of the experimental signals as a function of added CO and Kr, it was apparent that dissociative loss of Kr is not the rate limiting step in regeneration of W(CO)$_6$ as two distinctly different time regimes (Figure 2) for the regeneration of W(CO)$_6$ (as observed with Xe) could not be observed when a mixture of 5–10 mTorr of W(CO)$_6$, 500 Torr of Kr, and 1 Torr of CO was photolyzed with 355-nm radiation. However, it is possible to estimate an upper limit for the W(CO)$_5$Kr bond energy as 6 kcal/mol, assuming a similar rate constant for addition of Kr to W(CO)$_5$ as measured for Xe addition to W(CO)$_5$. It was necessary to assume a value for k_{Kr} because experimental difficulties made the measurement of k_{Kr} elusive. The rate constant for addition of Kr to W(CO)$_5$ in principle could be determined by monitoring either the rate of loss of the W(CO)$_5$ absorption or the rate of appearance of the W(CO)$_5$Kr absorption as a function of Kr pressure. However, as seen in Figure 5, the absorption of the W(CO)$_5$Kr complex significantly overlaps the W(CO)$_5$ absorption, making it difficult to accurately determine k_{Kr} by either method.

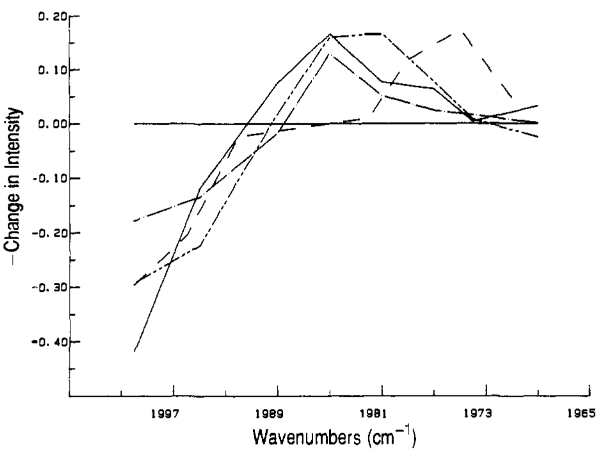

Figure 5. Transient time resolved spectra of W(CO)$_5$(RG) at 8.0 μs after photolysis. Each spectrum was collected from a cell that contained 5–10 mTorr of W(CO)$_6$ and the following gas pressures: (—) 500 Torr of He, (-·-) 500 Torr of Ar, (---) 500 Torr of Kr, (--) 80 Torr of Xe.

Since the rate of loss of Kr from W(CO)$_5$Kr may not be truly rate limiting, this called into question the use of the steady-state approximation for W(CO)$_5$. To resolve this question, the rate expressions for the kinetic scheme (eqs 1–4) were solved exactly.[13] The exact solution predicted a rising signal with an amplitude dominated by a single exponential with a rate that yielded a k_d very similar to that which resulted from the steady-state treatment.

The interaction of W(CO)$_5$ with Ar is even weaker than that with Kr. Spectra of W(CO)$_5$ obtained in the presence of 500 Torr of Ar were essentially identical to spectra obtained with 80 Torr of He (Figure 5). The interaction of Ar with W(CO)$_5$ is sufficiently weak and the complex has a sufficiently short half-life that photolysis of a mixture of 5–10 mTorr of W(CO)$_6$, 500 Torr of Ar, and 1 Torr of CO yielded, within experimental error, the same rate for regeneration of parent as photolysis of a mixture of 5–10 mTorr of W(CO)$_6$, 80 Torr of He, and 1 Torr of CO. This leads to the conclusion that loss of the Ar atom is certainly not the rate limiting step in the kinetic scheme comprised by eqs 1–4. Under these conditions, the steady-state treatment leading to eq 5 is no longer valid, and the exact solution of eqs 1–4 was used to obtain an estimate for the W(CO)$_5$ Ar bond dissociation energy. For $k_{CO} = 4.4$ μs^{-1} Torr^{-1}, $k_{Ar} = 0.9$ μs^{-1} Torr^{-1} (assuming the same rate constant for Ar addition to W(CO)$_5$ as measured for Xe addition to W(CO)$_5$), with [CO] = 1 Torr and [Ar] = 500 Torr, $k_d \gtrsim 5000$ μs^{-1}. Assuming the same preexponential as obtained for k_d for the W(CO)$_5$Xe system, a value of ~3 kcal/mol can be estimated as an *upper limit* for the bond dissociation energy for Ar binding to W(CO)$_5$.

IV. Discussion

A. Xe Bond. The infrared spectra of the gas-phase M(CO)$_5$ species are consistent with C_{4v} symmetry assigned on the basis of matrix isolation data.[12] Thus there is a large open site for ligand

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[13] Pearson, R. G.; Moore, J. W. *Kinetics and Mechanism*; John Wiley & Sons: New York, 1981.

attack. The metal centers of these coordinatively unsaturated organometallics are formally Lewis bases and strong electrophiles.[4] The Xe atom is polarizable[14] and may be able to donate electron density to the metal center. From Table I it can be seen that, within experimental error, the bond energy between Xe and $M(CO)_5$ is the same for all of the group VI metal centers. This leads to the conclusion that all three metal centers interact with the Xe atom in a similar fashion. Another feature of the interaction with Xe is the observed shift to lower frequencies in the infrared spectrum of the $M(CO)_5Xe$ carbonyl stretches relative to "naked" $M(CO)_5$. This can be seen in Figure 1. Table I lists the magnitude of this shift for the peak of the group VI pentacarbonyl absorptions.

The shifts to lower energy suggest that the Xe interaction involves some electron donation from the Xe atom to the metal center. The metal center in turn delocalizes this increased electron density into the π antibonding orbitals of the CO ligands via back-bonding. This causes a decrease in the CO infrared stretching frequency. Because of its fully occupied orbitals, Xe is probably unable to significantly back-bond with the metal center. The small (~21-cm^{-1}) shift of the CO stretching frequencies of $M(CO)_6$ compared to $M(CO)_5Xe$ makes it apparent that the metal does not change oxidation state, implying that the Xe–$M(CO)_5$ bond is of a covalent nature. The fact that Xe binds once again demonstrates the extreme reactivity of these coordinatively unsaturated organometallics.

Since Xe reacts with $M(CO)_5$ at a near gas kinetic rate and binds with a modest energy, it is clear that a kinetic barrier does not prevent formation of a stable (long lived) complex but rather it is the bond enthalpy that limits the stability of these complexes. The half-life ($\tau_{1/2}$) for the $M(CO)_5Xe$ species is on the order of 1.0 μs at 298 K.

B. Other Rare Gases. Evidence of an interaction between Kr and $W(CO)_5$ was obtained from both spectroscopic and kinetic data. The interaction is weak enough so that two distinct time regimes (Figure 2) for the regeneration of $W(CO)_6$, as observed for Xe, N_2O, and CF_2Cl_2, were not observed with added Kr.[2] The addition of Kr resulted in a slightly slower rate of regeneration of parent allowing for an estimate of ~17 ns for a half-life for the $W(CO)_5Kr$ species at 298 K. The *lack* of any change in the rate of regeneration of $W(CO)_6$ in the presence of 500 Torr of Ar allowed for an estimate of an upper limit for ΔH for $W(CO)_5Ar$. Assuming the same preexponential for k_d for $W(CO)_5Ar$ as determined for $W(CO)_5Kr$, an upper limit for $\tau_{1/2}$ for $W(CO)_5Ar$ is ~0.2 ns at 298 K. The binding energy for the rare gases to group VI pentacarbonyls is quantitatively and qualitatively consistent with the trend in the polarizability of the rare gas atoms: Xe > Kr > Ar.[14] This implies that the lighter rare gases provide less electron density on the metal center to delocalize. If all of the metal centers had the same ability to delocalize electron density, this would imply a smaller shift in the CO frequency as the mass of the rare gas in a $W(CO)_5$–rare gas complex decreased. One concludes that the polarizability of the rare gas atom does play a part in the bonding of rare gases to $W(CO)_5$. However, the *detailed description* of the bonding of the rare gas atom to the $M(CO)_5$ species is likely to be more complex.

V. Conclusions

A competitive kinetic scheme has been employed to determine bond energies for the binding of rare gas atoms to coordinatively unsaturated organometallic compounds. Bond dissociation energies of 9.0 ± 0.9, 8.0 ± 1.0, and 8.2 ± 1.0 kcal/mol were measured for the dissociation of Xe from $Cr(CO)_5$, $Mo(CO)_5$, and $W(CO)_5$, respectively. These numbers are all within experimental error of one another and give an average bond energy of 8.5 kcal/mol for Xe binding to these $M(CO)_5$ species.

A $W(CO)_5Kr$ complex was also observed spectroscopically (Figure 5). However due to overlap of the $W(CO)_5$ and $W(CO)_5Kr$ absorptions (see preceding discussion), a direct measurement of the bond energy of this complex was precluded. A bond dissociation energy of ~6 kcal/mol was estimated as an upper limit for loss of Kr from $W(CO)_5Kr$. The lack of either spectroscopic or kinetic evidence for a $W(CO)_5Ar$ complex allows for an estimate of an upper limit for the bond dissociation energy of a $W(CO)_5Ar$ complex as 3 kcal/mol. These bond energies follow the same trend as the polarizabilities of the rare gas ligands.

These studies demonstrate the usefulness of time resolved infrared spectroscopy in measuring bond energies of weakly bound ligands to coordinatively unsaturated organometallic compounds. Continuation of these studies hold promise of providing further insights into the nature of solvent interactions with coordinatively unsaturated organometallics.

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