further destabilization of the N-protonated forms and associated k_2 transition states. At the same time, those factors that inhibit N protonation will also acidify the remaining OH group of T_0^- and facilitate departure of the N either in an anionic form that may be H bonded to solvent or with general-acid catalysis, but requiring no prior complete protonation.[23] In this case, the hydrolysis kinetics will exhibit second-order terms: ^{18}O exchange and substantial reversal of T_0^- will be observed at low [OH$^-$], with diminishing amounts occurring as the [OH$^-$] is raised. In the limit at high [OH$^-$], each time T_0^- is formed it is immediately converted to VII and reversal is eliminated.

For *p*-nitroacetanilide, exactly the above situation is observed[1e] where k_{ex}/k_{hyd} varies from 1.6 to 0.17 as [OH$^-$] changes from 0.02 to 0.24 M. Similarly, it is reported that *N*-benzoyl- and *N*-toluoylpyrrole[19b] exhibit hydrolysis kinetics with a second-order dependence on [OH$^-$], merging into a first-order dependence with increasing [OH$^-$], consistent with the above mechanism: ^{18}O-exchange studies were not reported,[19] but the mechanism demands that these must follow the expected pattern.

The change in mechanism between III and *N*-benzoyl- or *N*-toluoylpyrrole results from the low basicity of the latter amine (pK_a(conjugate acid) = −3.80[24]). Thus, within the tertiary toluamide or benzamide series the point of transition between the first- and second-order hydrolysis mechanism occurs when the departing amine has a basicity intermediate between those of pyrrole and *N*-ethyl-*N*-(trifluoroethyl)amine.

Conclusions

1. Tertiary toluamide III exhibits substantial ^{18}O exchange accompanying hydrolysis in base at 100 °C. Exchange and hydrolysis are both first-order in [OH$^-$]; $k_{ex}/k_{hyd} = 33.4 \pm 1.6$. Amide III is at least as, or more, sterically demanding than *N*,*N*-dimethyltoluamide (I) or *N*-toluoylpyrrolidine (II) but exhibits 2300–3500-fold more exchange than the latter two amides. Thus, in contrast to analyses based upon the stereoelectronic theory preferred by Deslongchamps,[4] conformational mobility of the anionic tetrahedral intermediate (T_0^-) is not the dominant factor in determining whether a tertiary amide will or will not exhibit ^{18}O exchange accompanying hydrolysis. Rather, amine leaving ability is the crucial factor, and this depends on basicity, with the least basic amine having the poorest leaving ability.

2. The solvent kinetic isotope effects on the exchange and hydrolysis processes for III are $(k_{ex})_{H/D} = 0.90 \pm 0.05$ and $(k_{hyd})_{H/D} = 1.05 \pm 0.04$. The predominantly rate-limiting step for exchange is k_1, the attack of OH$^-$, while the rate-limiting step for hydrolysis is k_2, the breakdown of the anionic tetrahedral intermediate(s) to product. Analysis of the SKIE in terms of isotopic fractionation factors indicates that the small observed isotope effect on k_{hyd} is most consistent with breakdown via one or both of two anionic but N-protonated forms, an anionic zwitterion (T_{ZW}^-) or a zwitterionic OH$^-$ H-bonded encounter complex.

3. The observed SKIE on k_{ex} indicates the following: (a) the ^{16}O and ^{18}O atoms in T_0^- are in protonic equilibrium and (b) the intermediate that leads to exchange is on the hydrolytic pathway (i.e., T_0^-). If either of these circumstances were not true, then there would be substantially less ^{18}O exchange in D_2O.

4. Base hydrolysis of tertiary amides can exhibit first- or second-order terms in [OH$^-$], and whether ^{18}O exchange is observed depends upon the relative barrier heights for the transition states leading away from T_0^- to starting materials or products. Amides containing amines with low basicity are more prone to ^{18}O exchange than those containing amines with high basicity since breakdown to product proceeds via an anionic intermediate with a protonated N. When the amine basicity is intermediate between that of pyrrole or *N*-ethyl-*N*-(trifluoroethyl)amine, the hydrolytic mechanism will exhibit second-order terms in [OH$^-$] and there will be observed ^{18}O exchange that decreases with increasing [OH$^-$].

Acknowledgment. We gratefully acknowledge the financial assistance of the University of Alberta and Natural Sciences and Engineering Research Council of Canada. We are also indebted to Professor R. E. D. McClung (Department of Chemistry, University of Alberta) for the line-shape analysis used in determining the barriers to rotation of III.

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Bond Dissociation Energies and Kinetics for the Reaction of $W(CO)_5$ with the Unlikely Ligands N_2O and CF_2Cl_2

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Abstract: Transient infrared spectroscopy has been used to study reactions of $W(CO)_5$, the coordinatively unsaturated tungsten carbonyl generated by 351- or 355-nm photolysis of $W(CO)_6$. $W(CO)_5$ is highly reactive toward CO, CF_2Cl_2, and N_2O with bimolecular rate constants of 1.4 ± 0.1, 1.2 ± 0.2, and $0.5 \pm 0.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively, at 298 K. Infrared absorptions for the transiently stable $W(CO)_5(CF_2Cl_2)$ and $W(CO)_5(N_2O)$ complexes were observed. The rate of dissociative loss of the CF_2Cl_2 and N_2O ligands from these complexes can be determined by observation of the rate of regeneration of $W(CO)_6$ in a reaction mixture consisting of $W(CO)_5L$, CO, and L, where L is either CF_2Cl_2 or N_2O. The bond dissociation energy for the loss of the chlorofluorocarbon ligand from $W(CO)_5(CF_2Cl_2)$ is 19.6 ± 0.6 kcal/mol. A bond dissociation energy was estimated for the loss of the N_2O ligand from $W(CO)_5(N_2O)$.

I. Introduction

Knowledge of gas-phase transition-metal carbonyl chemistry has been expanded by the use of transient infrared spectroscopy. Information about the structures and reactivities of short-lived, unsaturated metal carbonyl species is now directly available from this technique.[1,2] Up to this point transient infrared studies of gas-phase metal carbonyl photofragments have largely centered

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on their reactions with CO and with the parent metal complex. Other ligands such as H_2 and olefins have also shown considerable reactivity toward unsaturated $M(CO)_x$ fragments.[3] Some of these studies have resulted in the characterization of new, unstable intermediates as precursors to the known stable complexes formed by the addition of incoming ligands.

A potential advantage of gas-phase versus solution-phase studies is that in the gas phase the reactions of an unsaturated complex can be studied without complications from solvent effects. In solution, solvation of these reactive species occurs on a picosecond time scale.[4] Under these circumstances, reactions that are simple associative addition reactions in the gas phase may be rate limited by loss of solvent molecules from the coordination sphere of the coordinatively unsaturated species under study. Further, the magnitude of the bond enthalpy of solvation can determine the incoming ligands L that will form a stable complex, $M(CO)_xL$, in solvent S; if L is less strongly bonded than S, the reaction of L with the $M(CO)_x$ complex in solution can be inhibited. Therefore, in the gas phase, it may be possible to observe and synthesize new $M(CO)_xL$ complexes with ligands that are weakly interacting relative to common solvents used in organometallic synthesis. By monitoring the temperature dependence of the rate of disssociative loss of such ligands it may be possible to directly determine the bond enthalpy for these species bonded to coordinatively unsaturated organometallics.

We report a transient infrared spectroscopy study of the interaction of two such "unlikely ligands", nitrous oxide and dichlorodifluoromethane, with $W(CO)_5$. These ligands were chosen because they are normally very inert and thus their reactions with a coordinatively unsaturated metal carbonyl would further demonstrate the high reactivity of unsaturated metal carbonyl complexes. $W(CO)_5$ was chosen because it has been suggested, on the basis of MO calculations, that third-row transition-metal complexes of N_2O would show the highest stability.[5] In addition, though gas-phase photolysis of $M(CO)_n$ species often results in a mixture of singly and multiply unsaturated species, $W(CO)_5$ has been reported to be virtually the only product generated by photolysis of $W(CO)_6$ at 351 nm, making it a particularly simple system for study.[6]

II. Experimental Section

The apparatus used in this study has been described previously in detail.[7] However, a brief description will be provided here for convenience. Measurements were performed in a 16-cm Pyrex cell terminated by CaF_2 windows. Tungsten hexacarbonyl was introduced directly into the IR cell as a solid, or by equilibration of the cell with the contents of a tube containing solid $W(CO)_6$.

The output of an excimer laser operating at 351 nm (XeF) or a tripled Nd:YAG laser (355 nm) was used to photolyze $W(CO)_6$. No significant wavelength-dependent differences were observed with these two photolysis sources which in each case delivered 7–10 mJ/cm^2 at the cell window. Formation of tungsten carbonyl products was detected by their attenuation of infrared radiation from a home-built liquid-nitrogen-cooled CO laser. Infrared beam intensity was monitored with a fast ($\tau_{1/2} \cong 60$ ns) InSb detector. The detector output (transient waveform) was amplified (Perry X100), digitized, signal averaged (Lecroy 9400), and sent to a computer for storage and manipulation. Time-resolved infrared spectra of the transients 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. Static cell fills of 6–10 mTorr of $W(CO)_6$, 0.1–2.5 Torr of L (CO, CF_2Cl_2, or N_2O), and 80 Torr of argon were used for the determination of rate constants for the reaction of $W(CO)_5$ + L. Static cell fills of 6–10 mTorr of $W(CO)_6$, 2–77 Torr of CO, and 2–67 Torr of L were used to obtain k_{obs} and k_d (see eqs 4 and 5). Experiments were performed to verify that k_{obs} and k_d obtained under these conditions were not dependent on pressures of added Ar. 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.[8] The relatively high pressures used for these measurements assure that the bulk temperature rise due to the energy released on photolysis and/or bond formation is negligible (less than 1 K) and that internal relaxation of the reactants and reaction products is fast on the time scale of the current experiments.

A Mattson FTIR was used in an attempt to obtain a spectrum of $W(CO)_5(N_2O)$. The photolysis cell was mounted in the optical cavity of the FTIR. Photolysis took place while a spectrum was being acquired. A spectrum of a cell (15 cm, terminated by CaF_2 windows) filled with 10 mTorr of $W(CO)_6$ and 10 Torr of N_2O was taken and subtracted from a spectrum of the same cell fill collected within 1 s of a photolysis pulse (351-nm output of a Questek excimer laser operating at 1 Hz). Loss of $W(CO)_6$ due to photolysis was observed, but no $W(CO)_5(N_2O)$ species was observed.

Solid $W(CO)_6$ was obtained from Alfa Products. The gases used in the experiments were obtained from Matheson and used without further purification. The gases had the following stated purities: CF_2Cl_2 (99.0%), N_2O (99.0%), Ar (99.999%), CO (99.9%). The temperature range of the experiments was 298–339 K with an uncertainty of 2 K.

III. Results

A. Spectra. The time-resolved infrared spectrum resulting from 351-nm photolysis of $W(CO)_6$ has been published by Ishikawa et al.[6] Photolysis of $W(CO)_6$ with 351- or 355-nm radiation produces $W(CO)_5$, an unsaturated species characterized by gas-phase infrared absorptions at 1985 and 1942 wavenumbers.[6] In the absence of added ligand, the absorptions of $W(CO)_5$ decay rapidly due to its reaction with parent $W(CO)_6$ with a rate constant close to gas kinetic.[6] For convenience and comparison purposes, a portion of the spectrum generated following 351-nm photolysis of $W(CO)_5$ in Ar is shown in Figure 1a. Reaction of $W(CO)_5$ with parent leads to the product band centered at ~2020 cm^{-1} due to formation of polynuclear tungsten carbonyl species. In the presence of added ligands L, the absorption bands of $W(CO)_5$ show a pressure-dependent decay with new bands growing in that are shifted from the $W(CO)_5$ absorptions and supression of the polynuclear product band at 2020 cm^{-1}. This behavior indicates the formation of a new species $W(CO)_5L$. Spectra b and c in Figure 1 show time-resolved spectra obtained after 351-nm photolysis of $W(CO)_6$ in the presence of N_2O and CF_2Cl_2. The peaks due to $W(CO)_5$ are indicated with downward arrows, as this species reacts with 0.7 Torr of ligand to produce $W(CO)_5L$ complexes on a time scale of a few microseconds. The $W(CO)_5(CF_2Cl_2)$ in Figure 1b has absorption bands at 1976 and 1958 cm^{-1} while the $W(CO)_5(N_2O)$ complex in Figure 1c has bands at 1980 and 1968 cm^{-1}. Additional evidence supporting these assignments will be presented in the Discussion Section. In the absence of other reactive ligands, the absorptions for these complexes grow to a maximum and then do not change intensity on a time scale of 500 μs. However, neither the N_2O nor CF_2Cl_2 complex is stable on the time scale of seconds as determined by attempts at FTIR detection of these species. Studies on other systems that yield stable products of photogenerated coordinatively unsaturated metal carbonyls demonstrate that if formed, such species can usually be detected via FTIR under experimental conditions comparable to those employed in this study.[9]

Also shown in Figure 1 (panel d) is a portion of the transient IR spectrum of the product of reaction of $W(CO)_5$ with N_2. The region shown allows for a comparison of the positions of the $W(CO)_5N_2$ bands with the corresponding absorption of $W(CO)_5(N_2O)$.

B. Kinetics. 1. The Kinetic Scheme. Since FTIR measurements made after photolysis of $W(CO)_6$ in excess L (N_2O and CF_2Cl_2) and CO showed neither the $W(CO)_5L$ product nor appreciable loss of $W(CO)_6$, it is likely that the addition reaction of ligand with $W(CO)_5$ is reversible. Dissociative loss of weakly bound ligands is expected, especially for systems in which the ligand hapticity does not change or where there is no change in the electron donating character of the ligand.[10] A dissociative

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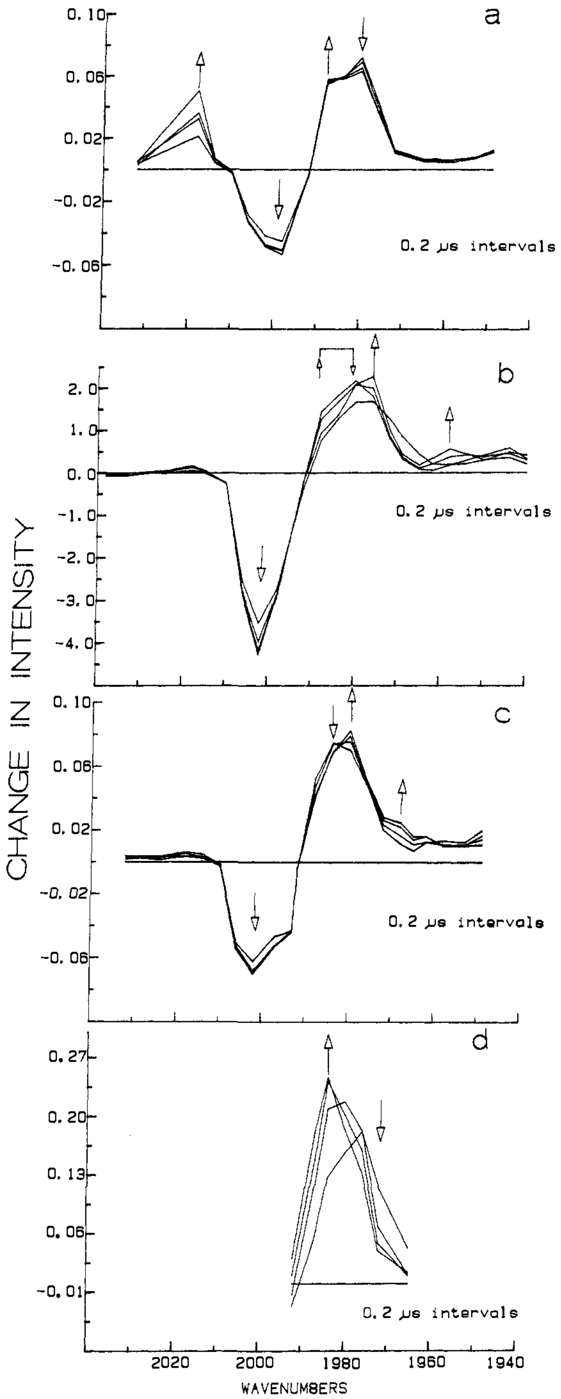

Figure 1. (a) Transient time-resolved infrared spectrum generated upon 351-nm photolysis of $W(CO)_6$. The IR band at 2014 cm^{-1} is due to $W_2(CO)_{11}$ that is produced by reaction of $W(CO)_5$ with $W(CO)_6$. Each trace is separated from the next trace by 0.2 μs. The direction of the change in absorbance at selected wavelengths is indicated by the appropriate arrows. (b) Transient time-resolved infrared spectrum generated upon 351-nm photolysis of $W(CO)_6$ in the presence of ~0.7 Torr of CF_2Cl_2. Absorptions due to the product $W(CO)_5(CF_2Cl_2)$ are indicated by upward arrows. (c) Transient time-resolved infrared spectrum generated upon 351-nm photolysis of $W(CO)_6$ in the presence of ~0.7 Torr of N_2O. Absorptions due to the product $W(CO)_5(N_2O)$ are indicated by upward arrows. (d) Partial transient time-resolved infrared spectrum generated upon 351-nm photolysis of $W(CO)_6$ in the presence of ~0.7 Torr for N_2. Absorptions due to the product $W(CO)_5(N_2)$ are indicated by upward arrows.

loss mechanism is also consistent with the observed dependence of the rate of regeneration of $W(CO)_6$ in a mixture of $W(CO)_5$,

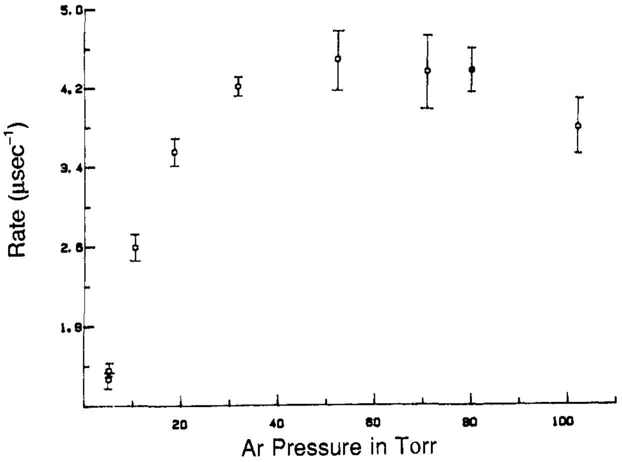

Figure 2. Plot of the rate of the reaction $W(CO)_5 + CO \rightarrow W(CO)_6$ as a function of Ar pressure. The CO pressure was 1.0 Torr. Error brackets are 2σ. The filled data point is the rate derived from a rate constant determination at the indicated Ar pressure.

L, and CO on the pressures of *both* CO and L. In the presence of both CO and L the pertinent kinetics can be written as

$$W(CO)_5L \xrightarrow{k_d} W(CO)_5 + L \tag{1}$$

$$W(CO)_5 + L \xrightarrow{k_f} W(CO)_5L \tag{2}$$

$$W(CO)_5 + CO \xrightarrow{k_{CO}} W(CO)_6 \tag{3}$$

Reaction 3 is not reversible on the relevant time scale because the first bond dissociation energy of $W(CO)_6$ is approximately 46 kcal/mol.[11]

If the rate for the bimolecular reaction of $W(CO)_5$ with both CO and L (N_2O and CF_2Cl_2) is much faster than the unimolecular dissociation of $W(CO)_5L$, then the rate-limiting step leading to regeneration of $W(CO)_6$ is the loss of the weakly bound ligand L. Experiments to measure the rate of loss of L were done in a large excess of CO to promote formation of the stable compound $W(CO)_6$ and to prevent the formation of polynuclear tungsten complexes by reaction of $W(CO)_5$ with $W(CO)_6$.[6] This allows us to neglect the reaction of $W(CO)_5$ with $W(CO)_6$ in the kinetic scheme for this system. The unimolecular dissociation constant k_d can then be determined by measuring the rate of recovery of $W(CO)_6$ (at 2002 cm^{-1}) with various mixtures of CO and L.

Solving eqs 1–3 with use of the steady state approximation for $[W(CO)_5]$ yields

$$k_{obs} = \frac{k_d k_{CO}[CO]}{k_{CO}[CO] + k_f[L]} \tag{4}$$

where k_{obs} is now the rate of recovery rate of $W(CO)_6$, which under the experimental conditions takes place on the time scale of 10–500 μs. We can also write

$$k_d = k_{obs}\left(1 + \frac{k_f[L]}{k_{CO}[CO]}\right) \tag{5}$$

Thus, to obtain k_d from k_{obs} it is necessary to measure k_{CO}, k_L, and their temperature dependence. These measurements will now be discussed.

2. Measurement of k_{CO}. The rate constant for $W(CO)_5 + CO \rightarrow W(CO)_6$ had been previously reported in ref 6. Experiments were performed to remeasure this rate constant with our apparatus. Virtually identical results to those reported in ref 6 were obtained under similar experimental conditions, 10 Torr of Ar and 0–2 Torr of CO at 298 K. However, it was observed that the rate of reaction 3 depended on the total gas pressure in the reaction cell, as would be expected for an addition reaction that is not in the "high-

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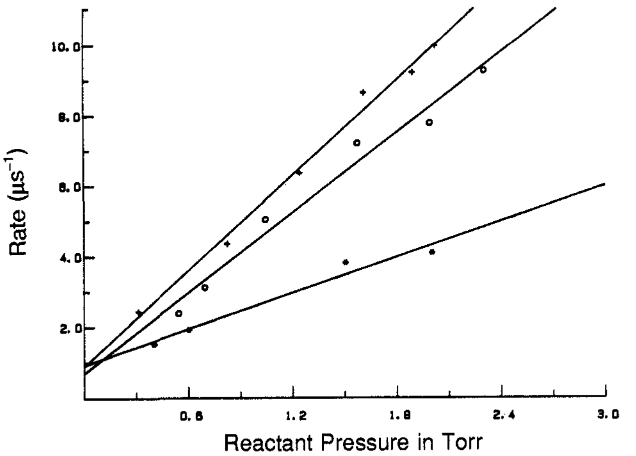

Figure 3. Plot of the pseudo-first-order rate constants at 298 ± 2 K for the reaction of $W(CO)_5$, N_2O (*), CF_2Cl_2 (O), and CO (+) [shifted up by 1.0 rate unit for clarity]. The rate of disappearance of $W(CO)_5$ at 1985 cm^{-1} is plotted against the pressure of added ligand. Data were taken in the high-pressure limit for these reactions. The slopes of these lines give the bimolecular rate constants of 1.4 ± 0.1, 0.5 ± 0.1, 1.2 ± 0.2 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} for the $W(CO)_5$ + CO, N_2O, and CF_2Cl_2 ligands, respectively.

Table I

$$W(CO)_5 + L \xrightarrow{k} W(CO)_5\text{-}L$$

L	$10^{10}k$, $cm^3/(molecule{\cdot}s)^a$
CO	1.4 ± 0.1
N_2O	0.5 ± 0.1
CF_2Cl_2	1.2 ± 0.2

[a] Error limits are 2σ. Reported values are at 298 K.

pressure" limit. Additional inert gas was necessary to achieve pressures for which the addition of further inert gas did not affect the rate of reaction 3. A plot of the Ar pressure dependence of the rate is shown in Figure 2. In the "high-pressure" regime, the rate constant is 1.4 ± 0.1 × 10^{-10} $cm^3/(molecule{\cdot}s)$. This value should then be considered as the high-pressure limit for the rate constant for this reaction. Care was taken to ensure that all further measurements were conducted in a pressure regime where reaction 3 was in the high-pressure limit. Experiments were performed to verify that reaction 3 was still in the high-pressure limit at the elevated temperatures used in this study. The rate constant k_{CO} has a mild negative temperature dependence ranging from 1.4 ± 0.1 × 10^{-10} $cm^3/(molecule{\cdot}s)$ at 298 K to 1.0 ± 0.2 $cm^3/(molecule{\cdot}s)$ at 340 K. This dependence is consistent with temperature-dependent changes in the volume of phase space available to reactants and products in this bimolecular association reaction.

3. Measurement of $k_{CF_2Cl_2}$ and k_{N_2O}. Reaction rates of the addition of N_2O and CF_2Cl_2 with $W(CO)_5$ were determined from the slope of the line obtained from plotting the decay rate of the $W(CO)_5$ transient signal versus the pressure of L (Figure 3). Similar procedures to those described above were employed to verify that the rates measured for these reactions were in the high-pressure limit.

The reaction of CF_2Cl_2 with $W(CO)_5$ appears virtually temperature independent. Values for the rate constant at 298 and 325 K were 1.2 ± 0.1 and 1.1 ± 10^{-10} $cm^3/(molecule{\cdot}s)$, respectively. The bimolecular rate constants for $W(CO)_5$ reaction with CO, N_2O, and CF_2Cl_2 at 298 K are listed in Table I.

4. Determination of k_d. For a given ligand, a determination of k_d as a function of temperature can be used to calculate the activation energy, E_a, and the pre-exponential factor from an Arrhenius expression for the rate constant. The value of k_d obtained from eq 4 for CF_2Cl_2 at room temperature (298 K) is (1.1 ± 0.2) × 10^4 s^{-1}. As expected from eqs 4 and 5, as CO pressure was increased at a constant CF_2Cl_2 pressure, k_{obs} approached k_d. Experiments involving variation of the presence of added inert gas verified that k_d was measured in the high-pressure limit. A plot of ln (k_d) versus $1/T$ is shown in Figure 4. The slope of this line gives an activation energy, (E_a), of 19.0 ± 0.6 kcal/mol. The intercept, ln (k_d), yields a value of 8 × 10^{17} for the pre-exponential. The bond dissociation energy for $W(CO)_5$–(CF_2Cl_2) can be determined from E_a by

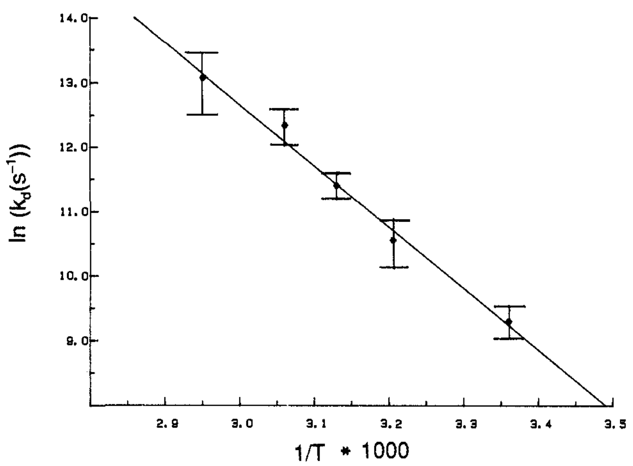

Figure 4. Plot of ln (k_d) versus $1/T$ for $W(CO)_5{\cdot}(CF_2Cl_2)$. The slope of the line is −9.5 ± 0.3, which gives an activation energy of 19.0 ± 0.6 kcal mol^{-1} for the loss of CF_2Cl_2 from the aforementioned complex.

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

Under constant volume conditions and assuming ideal gas behavior, the $\Delta(PV)$ term reduces to ΔnRT. This yields a value for the bond dissociation energy of 19.6 ± 0.6 kcal/mol.

For a reaction that has an unactivated reverse reaction, the above procedure is equivalent to obtaining ΔH from a plot of the log of the equilibrium constant vs. $1/T$. Since this latter procedure requires the quotient of two experimentally determined rate constants, it potentially introduces more error into the determination of ΔH than the procedure actually employed.

The bond dissociation energy of $W(CO)_5$–(N_2O) could not be directly determined by the above method because the $W(CO)_5$–N_2O complex did not dissociate appreciably on the time scale of approximately 500 μs over which the CO laser was sufficiently stable for accurate kinetic measurements. However, an approximate upper limit for the bond dissociation energy can be calculated. Clearly, the lifetime of the molecule is between the time scales for observation using the CO laser (no perceptible dissociation on 500 μs) and the FTIR (~1 s). That lifetime implies a k_d for the N_2O ligand between approximately 1 and 500 s^{-1}. If the pre-exponential for N_2O loss is the same as that for CF_2Cl_2 loss, this gives a bond dissociation energy of 22 ± 2 kcal/mol. Due to the assumption regarding the preexponential and the inability to directly measure the temperature dependence, this should be considered an approximate value.

IV. Discussion

A. Assignment of Products. 1. $W(CO)_5(N_2O)$. The known reaction chemistry of N_2O as a ligand for transition metals has been limited. In most cases, reactions of N_2O with metal complexes lead to its activation by rupture of the N–O bond.[12] One stable complex of N_2O has been spectroscopically characterized, the $[Ru(NH_3)_5(N_2O)]^{2+}$ cation.[13] Its structure is unknown, and the bonding of the N_2O in the complex (whether M–N–N–O or M–O–N–N) has been the subject of some debate.[14] The bromide salt has IR absorptions at 2236 (w), v_3 and 1175 (vs) ν_1 cm^{-1} that are shifted from the corresponding gas-phase N_2O absorptions at 2224 and 1286 cm^{-1}. A $W(CO)_5{\cdot}N_2O$ complex has been

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identified in a matrix isolation experiment, but explicit conclusions regarding bonding were not drawn in that study.[15] MO calculations suggest that the M–N–N–O configuration is the more stable bonding mode, that the primary bonding interaction is a nitrogen to metal center σ interaction, and that unlike CO there is very little π back-donation from the metal into the orbitals of the N_2O ligand.[5]

The absorption bands of metal-bonded N_2O are out of the range of the CO laser IR probe source. However, the positions of the M–CO stretches are a good probe of the electronic environment at the metal center. Addition of electron density, to a metal center, causes CO stretches to show a shift to lower wavenumbers, because of increased metal to ligand back-donation. Decrease in electron density at the metal center will cause CO ligand absorptions to appear at higher wavenumbers.[10] If $W(CO)_5$ activates N_2O to form $W(CO)_5O$, one would expect a large change in the positions of the $W(CO)_5$ bands to higher frequencies. This is not observed.

If the N_2O ligand is activated by $W(CO)_5$, one would expect a bimolecular rate constant for the addition of N_2O to $W(CO)_5$ that is much smaller than gas kinetic due to the activation energy that would result from bond breaking. In contrast to this expectation, a near gas kinetic rate constant is found for the addition of N_2O to $W(CO)_5$. Additionally, activation of N_2O would lead to the formation of "$W(CO)_5(O)$" or $W(CO)_5(N_2)$. The formation of $W(CO)_5O$ is unlikely in light of the above discussion. $M(CO)_5(N_2)$ compounds of chromium, molybdenum, and tungsten have been generated in matrices.[16] Since the reported absorptions for matrix-isolated $M(CO)_5(N_2)$ were similar to those observed in this study, a portion of the time-resolved gas-phase spectrum of $W(CO)_5(N_2)$ was generated by 351-nm photolysis of $W(CO)_6$ in the presence of N_2. This is shown in Figure 1d and agrees well with the recently reported spectrum for $W(CO)_5N_2$.[17] The major absorption feature for $W(CO)_5(N_2)$ is shifted to higher wavenumbers (~4 wavenumbers) than that observed for $W(CO)_5(N_2O)$. Thus $W(CO)_5N_2$ is *not* formed by reaction of $W(CO)_5$ with N_2O. Thus we conclude that N_2O binds to $W(CO)_5$ as an intact moiety.

2. $W(CO)_5(CF_2Cl_2)$. Chlorofluorocarbons in general are not known as good ligands for transition-metal compounds. Their reactivity increases with the number of carbon–chlorine bonds.[18] However, even very inert species such as dichlorodifluoromethane will react with metals such as zinc and cadmium.[19] The type of reaction observed is formally an oxidative addition, where the metal is inserted into the carbon–chlorine bond. Oxidative addition reactions have also been observed with chlorofluoroethanes and organorhodium complexes.[20] In the case of $W(CO)_5$ reacting with CF_2Cl_2, the oxidative addition of the carbon–chlorine bond to tungsten seems unlikely, since the CO stretches of the product are shifted in the opposite direction (relative to $W(CO)_5$) to what would be expected for metal center oxidation. Also, a bimolecular rate constant for a bond-breaking reaction would be expected to have an activation energy with a room temperature value significantly less than gas kinetic. The bimolecular rate constant for $W(CO)_5$ and CF_2Cl_2 is on the order of gas kinetic and does not have a significant temperature dependence. Therefore we also conclude that the CF_2Cl_2 molecule attaches to $W(CO)_5$ without bond scission. The reaction product is formulated as $W(CO)_5(CF_2Cl_2)$ and the interaction most likely involves electron donation to the tungsten center similar to the electron donation by the solvents present in liquid-phase reactions.

B. Stability of Complexes. The near gas kinetic rate constant for formation and the modest bond dissociation energies of the $W(CO)_5L$ complexes under study clearly indicate that these complexes are unstable on a long time scale not because of a kinetic barrier to their formation but simply because the ligands do not bind strongly to the $W(CO)_5$ metal centered complex. Nevertheless, for ligands that are generally considered to be "poor" or "unlikely" ligands, the bond dissociation energies are significant. For example, $W(CO)_5(CF_2Cl_2)$ should have a half-life in excess of 1 min at 200 K, while $W(CO)_5(N_2O)$ should be stable at this temperature for an even longer time period. Thus, it should be possible to obtain the conventional spectrum of each complex at low temperature with little difficulty, as has been done in liquid Xe for a number of other metastable species.[21]

The preexponential for the dissociation of $W(CO)_5(CF_2Cl_2)$ of 8×10^{17} s^{-1} is somewhat larger than preexponentials of approximately 10^{16} s^{-1} determined for the loss of CO from $Fe(CO)_5$, $Cr(CO)_5$, $Mo(CO)_6$, and $W(CO)_6$ determined with very low pressure pyrolysis methods.[11] However, the entropy change involved in the dissociation of a polyatomic molecule versus a diatomic would be expected to be larger and thus a larger preexponential might be anticipated. This is consistent with the reported preexponential of 10^{17} s^{-1} for loss of C_2H_4 from $Fe(CO)_3(C_2H_4)_2$.[22]

C. Rate Determination in the High-Pressure Limit. A meaningful measurement of the rate constant for a bimolecular association reaction requires that the system be in the high-pressure limit. In such an association reaction, the adduct is of necessity internally excited to at least the bond dissociation energy, which is released during bond formation. Energy associated with the thermal heat bath apportioned among the degrees of freedom of each of the reactants adds to the total energy of the adduct. In principle, unless the adduct is internally relaxed to below the dissociation energy for the weakest bond, the adduct will dissociate, reducing the apparent rate of the addition reaction. In the high-pressure limit, the rate of internal relaxation greatly exceeds the rate of the association reaction. Under these circumstances dissociation of the adduct is negligible and the measured association rate constant can be correlated with the rate constant for the elementary association reaction.[23]

Unlike the situation with a number of other metal carbonyl addition reactions, where the high-pressure limit was achieved by adding as little as 5 Torr of inert gas,[1] the reaction of $W(CO)_5$ with CO was found to require the addition of tens of Torr of inert gas to assure that it was in the high-pressure limit. The relative rates for dissociation and relaxation of a given adduct depend on the bond energy of the newly formed bond, the frequencies and the number of degrees of freedom of the complex, and the collisional efficiency of internal relaxation.[23] Another factor that may contribute to a higher pressure high-pressure limit in the $W(CO)_5$ + CO system is the fact that $W(CO)_5$ has been observed to be significantly vibrationally excited following 351-nm photolysis of $W(CO)_6$.[24] Unless relaxed prior to complexation, this vibrational energy would tend to increase the dissociation rate of the adduct. Additionally, it is possible that the potential energy surface for the addition reaction may be such that vibrational excitation of $W(CO)_5$ disfavors formation of the adduct. With the present experiments it is not possible to distinguish between these two effects.

V. Conclusions

A competitive kinetic scheme was used to obtain bond dissociation energies for ligands that are weakly bonded to coordinatively unsaturated organometallics. A bond dissociation energy of 19.6 ± 0.6 kcal/mol and a preexponential of 8×10^{17} was determined for loss of CF_2Cl_2 from $W(CO)_5$. The $W(CO)_5(N_2O)$ complex was stable on the time scale longer than was convenient

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for monitoring with the CO probe laser. Thus, its bond dissociation energy could not be directly determined. However, a bond dissociation energy could be estimated for this system based on the fact that though no dissociation was observed on a 500-μs time scale the compound was not stable for the few seconds necessary to obtain its FTIR spectrum. Assuming the same preexponential as measured for the $W(CO)_5(CF_2Cl_2)$ complex, $W(CO)_5(N_2O)$ has a bond dissociation energy of 22 ± 2 kcal/mol.

Clearly this study and others[25] demonstrate that the potential now exists to generate a wide variety of weakly bonded organometallic complexes using laser flash photolysis and to study them by time-resolved infrared spectroscopy. These studies hold promise of providing insights into the nature of solvent interactions with coordinatively unsaturated organometallics and quantitative information on the effects of solvation on the rates and pathways of condensed phase reactions of coordinatively unsaturated reaction centers.

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Asymmetric Aldol Reactions. A New Camphor-Derived Chiral Auxiliary Giving Highly Stereoselective Aldol Reactions of both Lithium and Titanium(IV) Enolates

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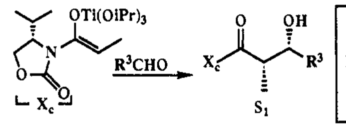
Abstract: A new, conformationally rigid camphor-derived *N*-propionyloxazolidinone effects asymmetric stereochemical control in syn-selective aldol condensations of the derived lithium and titanium(IV) enolates with a variety of aldehydes. Simple and diastereofacial selectivities of the reaction are high, and diastereomeric purities of the crude aldol adducts can be improved, usually by a single recrystallization, to levels of 98–99% in most cases. The observed facial selectivity is best explained by a transition structure in which intramolecular chelation between the oxazolidinone carbonyl oxygen and the metal induces an enolate π-facial differentiation; the major products observed are those expected from *chelation control*. Hydrolysis of the exocyclic carbonyl of the aldol adducts led to β-hydroxy-α-methylcarboxylic acids, with recovery of the chiral auxiliary. Consonant double-asymmetric induction with (*R*)-2-(benzyloxy)propanal gave the product expected from oxazolidinone chelation but nonchelation of the aldehyde benzyloxy group.

Stereoselective aldol reactions employing chiral boron enolates[1–5] and more recently chiral titanium(IV) enolates[6–11] have received significant synthetic and mechanistic attention. The discovery of the valine- and norephedrine-derived chiral *N*-propionyloxazolidinones[2] has led to their use in the synthesis of enantiomerically pure β-hydroxy-α-methylcarboxylic acids and related compounds[9,12] as well as α-amino acids.[13–16] Work in this laboratory has demonstrated that the triisopropoxytitanium enolate of the valine-derived *N*-propionyloxazolidinone (eq 1) reacts with benzaldehyde to give the product diastereomer predicted from chelation control (S_2) with a 92% level of selectivity.[6] This sense of diastereofacial selectivity is opposite to that observed for the corresponding di-*n*-butylboron enolates[2] and is consistent with the Lewis acidity of titanium(IV), which permits metal chelation to the oxazolidinone carbonyl.[17] It appears that chelation specifically orients the oxazolidinone ring in the transition structure. This capability is very promising for stereocontrol in synthetically useful reactions.



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To capitalize on the expected utility of this chemistry and to further explore the stereochemical control elements of the aldol

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