# Reaction of the Transient Species W(CO)₅(Cyclohexane) with Pyrrolidine and with Pyrrole

Alex Lugovskoy, A. Shagal, S. Lugovskoy, Ilan Huppert, and Richard H. Schultz*

*Department of Chemistry, Bar-Ilan University, 52900 Ramat-Gan, Israel*

*Received January 23, 2003*

Time-resolved infrared spectroscopy is used to examine the reactions of the transient intermediate $W(CO)_5(CyH)$ (CyH = cyclohexane), formed by photolysis of a cyclohexane solution of $W(CO)_6$, with L = pyrrole and pyrrolidine. Time- and temperature-dependent rate constants for the ligand substitution reaction to form $W(CO)_5(L)$ are determined. These reactions appear to go through an associative interchange mechanism. Eyring activation parameters for the ligand exchange are derived. For L = pyrrolidine, $\Delta H^{\ddagger} = 1.8 \pm 0.1$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -18.9 \pm 0.4$ eu; for L = pyrrole, $\Delta H^{\ddagger} = 5.1 \pm 0.2$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -11.6 \pm 1.2$ eu. Most unusually, the observed pseudo-first-order rate constant for reaction with pyrrole is not a linear function of pyrrole concentration. This deviation from simple first-order behavior is explained in terms of association of pyrrole in solution to form dimers and higher clusters that lower the ligand's effective concentration. The enthalpy of dimerization of pyrrole is estimated from the kinetic data to be approximately 4 kcal mol$^{-1}$. The results of reaction of $W(CO)_5(CyH)$ with pyrrole and pyrrolidine are discussed in terms of the behavior of this intermediate with other ligands.

## Introduction

The unstable coordinatively unsaturated pentacarbonyl species produced by photolysis of $W(CO)_6$ has been the subject of considerable research over the past two decades. Its behavior has been examined in the gas phase,[1] in low-temperature matrixes,[2] and in solution on time scales from ms/μs[3] to the sub-ps.[4] In solution, UV photolysis of $W(CO)_6$ leads to loss of a single carbonyl ligand, and solvation within tens of ps[4] to form $W(CO)_5(solv)$ (solv = a molecule of the solvent). In the presence of a Lewis base L, the intermediate reacts to form $W(CO)_5(L)$, reaction 1:

$$W(CO)_5(solv) + L \rightarrow W(CO)_5(L) \quad (1)$$
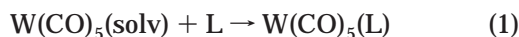
Second-order rate constants for reaction 1 are typically on the order of $10^6$–$10^7$ L mol$^{-1}$ s$^{-1}$. Considerable attention has been given to the mechanism of this reaction. When reaction 1 takes place in alkane solution, it appears to proceed via an associative pathway;[5,6] that is, L enters the coordination sphere before the solvent molecule has left.

We have recently performed in our laboratory a series of studies[5,6] in which we used time-resolved infrared spectroscopy (TRIR) to determine the activation parameters for reaction 1 for solv = cyclohexane (CyH) and L = a series of five-membered oxygen-containing heterocycles. Our goal was to understand how varying the properties of the incoming ligand changes the observed kinetics of the reaction. We found that for these ligands, $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ (300 K) for reaction 1 correlate with the *trans* C−O stretching force constant $(k_{CO}^{trans})$[7] in $W(CO)_5L$; that is, the better an electron donor L is, the lower the activation barrier to reaction 1. We also found a "compensation effect" in these reactions: as $\Delta H^{\ddagger}$ increases, so does $\Delta S^{\ddagger}$. Dobson and Zhang had previously noted a similar compensation effect in ligand substitution reactions of the $Cr(CO)_5(heptane)$ transient; no correlations with spectroscopic properties were reported in that study.[8] In addition, we observed that in reactions with 2-methyl- and 2,5-dimethyl-substituted THF and furan, steric interference can compete with the electronic effect, slowing the reaction.[9]

The present report discusses the results of an investigation of the reactivity of $W(CO)_5(CyH)$ with pyrrole (cyclo-$C_4H_4NH$) and pyrrolidine (cyclo-$C_4H_8NH$). In a

* To whom all correspondence should be addressed. E-mail: schultr@mail.biu.ac.il. Fax: (+972)-3-535-1250.

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**Table 1. C−O Stretch IR Absorptions and Force Constants for M(CO)$_5$L**

| | $v_{CO}$, cm$^{-1}$ | | | $k_{CO}$,[a] mdyn Å$^{-1}$ | | |
| L | $A_1(1)$ | $A_1(2)$ | $E$ | $k_{cis}$ | $k_{trans}$ | $k_i$ |
|---|---|---|---|---|---|---|
| CyH | 2087 | 1928 | 1954 | 16.075 | 15.233 | 0.326 |
| pyrrolidine | 2067 | 1910 | 1923 | 15.634 | 14.969 | 0.348 |
| pyrrole | 2074 | 1918 | 1939 | 15.844 | 15.079 | 0.328 |

[a] $k_{cis}$, C−O *cis* to L; $k_{trans}$, C−O *trans* to L; $k_i$, interaction force constant for mutually *cis* carbonyls. Force constants calculated using the Cotton−Kraihanzel method (ref 7).

preliminary communication,[10] we found that the room-temperature rate constant for reaction 1 correlates well with the average of the two strongest C−O stretches in W(CO)$_5$L. Here, we report the results of a more detailed study in which we determined the activation parameters for reaction 1 for pyrrolidine and pyrrole. The present study was undertaken primarily to test whether the correlation between the activation parameters and the electronic effects of the ligand previously observed is specific to O-containing ligands, or if ligands with a different heteroatom would follow the same trend.

## Experimental Section

These experiments were performed on the TRIR spectrometer in our laboratory, which has been described in detail elsewhere.[5] A CyH solution containing W(CO)$_6$ (~5 × 10$^{-4}$ mol L$^{-1}$) and an at least 10-fold excess of L is prepared. This solution is then photolyzed in an 0.5 mm path length CaF$_2$ cell, at a temperature held constant to ±1 °C, by the pulsed output of a 308 nm XeCl excimer laser (~20 ns, typically 60−100 mJ/pulse). A constant flow of solution is maintained so that each photolysis pulse irradiates a fresh sample. C−O stretching frequencies of the intermediate and product are determined by Step-Scan FTIR (S$^2$FTIR). Pseudo-first-order rate constants $k_{obs}$ are determined from the single-exponential time dependence of the change in absorption (Δ$A$) of the light emanating from a CW Pb-salt diode laser tuned to a frequency corresponding to a C−O stretch of W(CO)$_5$(CyH) or of W(CO)$_5$L.

HPLC-grade CyH was distilled from Na/benzophenone; the concentration of benzophenone in the distilled solvent was confirmed by UV−vis spectroscopy to be <10$^{-6}$ mol L$^{-1}$. Pyrrole and pyrrolidine were obtained from Aldrich in >97% purity (confirmed by NMR spectroscopy) and used as received except for distillation from an appropriate drying agent. W(CO)$_6$ (Strem, >98%) was used as received.

## Results and Discussion

**General Observations.** For reaction 1 with L = pyrrole or pyrrolidine, the absorbances corresponding to W(CO)$_5$(CyH) decay with a single-exponential time dependence to produce a single product (as shown by the S$^2$FTIR spectra) whose absorptions grow in at the same rate to within experimental error. We attribute these new absorptions, summarized in Table 1, to W(CO)$_5$L. Typical S$^2$FTIR spectra and transient absorptions measured using the laser IR source are shown in Figures 1 and 2. While some W(CO)$_5$L complexes formed from W(CO)$_5$(solv) in reaction 1 can undergo subsequent intramolecular reactions such as linkage isomerization or loss of a second CO ligand,[3b,11] both of the W(CO)$_5$L products observed in the present study are stable for at least several minutes following photolysis without



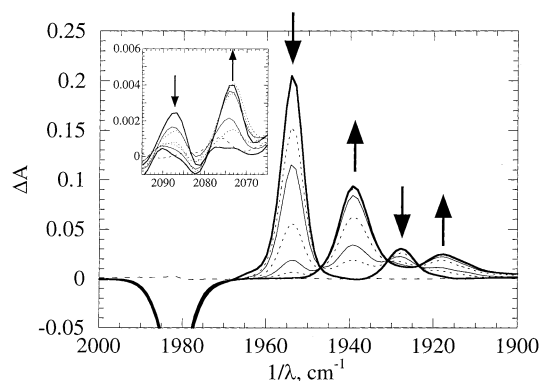**Figure 1.** Time-resolved S$^2$FTIR spectra (C−O stretching region) for the room-temperature reaction of W(CO)$_5$(CyH) with pyrrole. Shown are spectra obtained −1, 0, 1, 2, 5, 10, 15, and 25 μs after photolysis of a room-temperature CyH solution of 5 × 10$^{-4}$ mol L$^{-1}$ W(CO)$_6$ and 0.02 mol L$^{-1}$ pyrrole. The arrows show the direction of change in Δ$A$ with time.
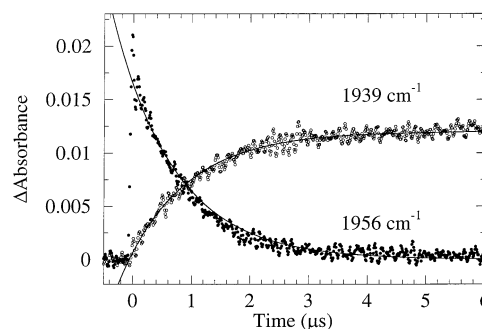


**Figure 2.** Time-dependent absorption changes at wavelengths corresponding to C−O stretching absorbances of W(CO)$_5$(CyH) (1956 cm$^{-1}$) and of W(CO)$_5$(pyrrole) (1939 cm$^{-1}$) following photolysis of a 50 °C CyH solution containing 5 × 10$^{-4}$ mol L$^{-1}$ W(CO)$_6$ and 0.1 mol L$^{-1}$ pyrrole. The solid lines are single-exponential fits to the data ($k_{obs}$ = 9.38 × 10$^5$ s$^{-1}$).

further reaction taking place. The results reported here thus all relate to the formation of the initial kinetic product of reaction 1 without consideration of any subsequent reactions that might be taking place on longer time scales.

**Pyrrolidine.** For L = pyrrolidine, reaction 1 was studied over the concentration range of [L] = 0.0054−0.143 mol L$^{-1}$. As shown in Figure 3, the pseudo-first-order rate constant, $k_{obs}$, is a linear function of [L] over this range. Second-order rate constants $k_a$ were determined as the slopes of a least-squares linear fit to $k_{obs}$; values of $k_a$ are given in Table 2. The linear fits to the data appear not to pass through the origin, having intercepts (that do not show any clear temperature dependence) of on the order of 10$^4$−10$^5$ s$^{-1}$. We believe that the most likely explanation for these nonzero intercepts is the finite lifetime of W(CO)$_5$(CyH) even at [L] = 0. Due to reactions with impurities such as residual H$_2$O[3a] or unphotolyzed W(CO)$_6$, even at [L] = 0 in "pure" CyH, W(CO)$_5$(CyH) is stable for <1 ms under typical "flash kinetics" conditions.[3a,12] Given that the intercepts of the

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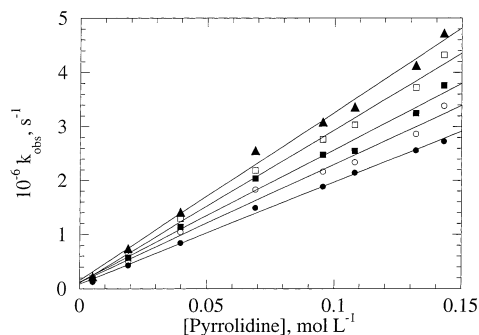(12) Paur-Afshari, R.; Schultz, R. H. Unpublished results.

**Figure 3.** Pseudo-first-order rate constants $k_{obs}$ ($10^6$ s$^{-1}$) as a function of [L] for reaction 1 with L = pyrrolidine. Shown are $k_{obs}$ at 20 °C (●), 30 °C (○), 40 °C (■), 50 °C (□), and 60 °C (▲) as a function of [L]. The solid lines are least-squares linear fits to the data.

**Table 2. Kinetic Parameters for Reaction 1**[a]

| | pyrrolidine | pyrrole | |
|---|---|---|---|
| $T$, °C | $k_a$, $10^6$ L mol$^{-1}$ s$^{-1}$ | $k_a$,[b] $10^6$ L mol$^{-1}$ s$^{-1}$ | $K_{eq}$,[c] mol$^{-1}$ |
| 20 | 20.0 (0.3) | 2.89 (0.07) | 0.42 (0.06) |
| 30 | 21.5 (0.5) | 4.24 (0.13) | 0.33 (0.05) |
| 40 | 24.3 (0.6) | 5.66 (0.28) | 0.26 (0.04) |
| 50 | 28.3 (0.4) | 7.34 (0.40) | 0.23 (0.08) |
| 60 | 31.4 (0.6) | 9.28 (0.34) | —[d] |

[a] 1σ uncertainties in parentheses. [b] Determined from measurements of $k_{obs}$ made with [pyrrole] < 0.5 mol L$^{-1}$; see text. [c] Equilibrium constant for pyrrole association, determined by fits to $k_{obs}$ using eq 2 and the values of $k_a$ given in this table. [d] Since the data for $k_{obs}$ do not show any significant curvature, it was not possible to obtain a reliable value of $K_{eq}$ by using eq 2.
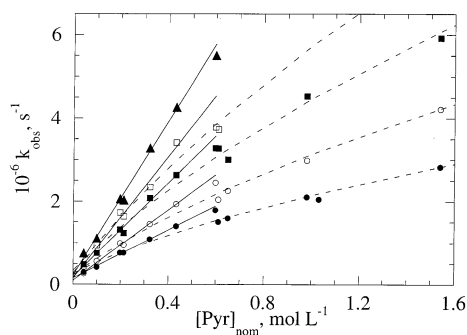


**Figure 4.** Pseudo-first-order rate constants $k_{obs}$ ($10^6$ s$^{-1}$) as a function of [L] for reaction 1 with L = pyrrole. Shown are $k_{obs}$ at 20 °C (●), 30 °C (○), 40 °C (■), 50 °C (□), and 60 °C (▲) as a function of [L]. The solid lines are least-squares linear fits to the data for [L] < 0.5 mol L$^{-1}$. The dashed lines represent fits to the entire data set that use eq 2.

linear fits to $k_{obs}$ are only ~1% of the slopes and that the rate constants for reaction with impurities or W(CO)₆ will be independent of [L] and thus not affect our determination of $k_{obs}$, this residual reactivity was not considered any further in our kinetic analyses. Furthermore, if our explanation is correct, "$k_{obs}$" at [L] = 0 will actually only be the *average* of [L]-independent rate constants that will vary depending on the concentrations of W(CO)₆ and impurities in a particular experiment.

**Pyrrole.** Results for pyrrole ($k_{obs}$ as a function of [L]) are shown in Figure 4. Two striking differences in the behavior of pyrrole from that of pyrrolidine are immediately apparent. First, for a given concentration and temperature, the reaction is slower for pyrrole than it

is for pyrrolidine. The mechanistic implications of this difference in behavior are discussed in detail below. More surprisingly, $k_{obs}$ is not a linear function of [pyrrole]. To our knowledge, this is the first observation of a nonlinear concentration dependence of $k_{obs}$ on [L] for *any* molecule L reacting with W(CO)₅(alkane);[13] even for 1-hexene, which reacts significantly more slowly with W(CO)₅(CyH) than pyrrole does, $k_{obs}$ remains a linear function of [L] to [1-hexene] = 5.5 mol L$^{-1}$.[14]

We believe that the most reasonable explanation for this unprecedented behavior is aggregation of pyrrole molecules. It has long been known[15] that in solution pyrrole associates to form hydrogen-bound dimers (and apparently higher clusters as well at sufficiently high concentration). The existence of these aggregates was deduced through measurements of the solution dipole moment of pyrrole[16] and through vibrational spectroscopy,[17] which revealed that while in neat pyrrole, the N−H stretch appears as a single broad band at about 3405 cm$^{-1}$, in dilute solution, it appears as a narrower band at higher frequency (3496 cm$^{-1}$ in CCl₄); in concentrated solutions, both peaks are observed. It is reasonable to assume that reaction 1 will form W(CO)₅(pyrrole) considerably more slowly from such clusters than it will from monomers, since the enthalpy necessary to dissociate a cluster will raise $\Delta H^{\ddagger}$ for reaction 1. While there has been some controversy in the literature about the exact structure of these pyrrole aggregates,[15,17] and various attempts to measure the monomer−dimer−cluster equilibria have failed to produce consistent values of the equilibrium constants,[15b,18] it is fairly clear that their enthalpy of association is on the order of several kcal mol$^{-1}$.[18,19] As the activation enthalpies for reaction 1 tend to be of the same order, there should be a significant enthalpic barrier to formation of W(CO)₅(pyrrole) from a pyrrole dimer relative to direct reaction of W(CO)₅(CyH) with a monomer. Furthermore, since a pyrrole dimer reacting with W(CO)₅(CyH) will not begin to dissociate until it is already interacting with the metal center, it is unlikely that the entropic contribution of the dissociation to $\Delta G^{\ddagger}$ will be sufficient to overcome the enthalpic barrier. Thus, pyrrole aggregates should be significantly less reactive than pyrrole monomers. If there is a significant amount of dimer present, then the concentration of reactive pyrrole monomers, [Pyr], will be lower than the nominal concentration of pyrrole added to the solution, [Pyr]$_{nom}$. Since the equilibrium constant for dimerization

(13) According to an early report (Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1981**, *20*, 4381), for the reaction W(CO)₅(methylcyclohexane) with 4-acetylpyridine, the dependence $k_{obs}$ on [L] is not linear. Dobson and Spradling[3b] were unable to reproduce the original result, however, and moreover showed that the UV−vis spectrum reported by Lees and Adamson was inconsistent with that of the product that appears on the μs time scale.

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is quadratic in [Pyr], a plot of $k_{obs}$ as a function of $[Pyr]_{nom}$ will show downward curvature at high values of $[Pyr]_{nom}$.

Unfortunately, the exact nature of the association equilibrium (or equilibria) remains unknown, so direct determination of [Pyr] is not possible in our experiment. We can, however, extract reasonable values of the second-order reaction rate constants by limiting the data fit to $[Pyr]_{nom} < 0.5$ mol $L^{-1}$. At these concentrations, $k_{obs}$ is linear in $[Pyr]_{nom}$, implying that pyrrole is present primarily as a monomer. This conclusion is consistent with the results of the most detailed study of the pyrrole association process to have appeared in the literature, a $^1$H NMR study by Ratajczak and Ladd,[20] who obtained the relaxation time $T_1$ for the pyrrole imido proton from a line-shape analysis of its $^1$H NMR signal. By measuring $T_1$ as a function of $[Pyr]_{nom}$ and of solvent viscosity in various solvents, they were able to determine under what conditions of $[Pyr]_{nom}$ and temperature there is a significant amount of pyrrole association. From their results, it is clear that at low values of $[Pyr]_{nom}$ and at the temperatures at which we made our measurements, pyrrole is present in CyH primarily as the free molecule, with little or no aggregation. Thus, we expect that values of $k_a$ determined from linear fits to $k_{obs}$ at $[Pyr]_{nom} < 0.5$ mol $L^{-1}$ should be reasonable approximations to the correct values of $k_a$; these values are given in Table 2.

We can also consider the kinetic results in terms of a model that explicitly takes pyrrole association into account. The simplest such model makes two basic assumptions: (a) in CyH solution, pyrrole exists in an equilibrium between monomers and dimers (equilibrium constant $K_{eq}$) with no higher clusters present; (b) the dimers are completely unreactive with $W(CO)_5(CyH)$ on the time scale of reaction 1. As shown above, these are not unreasonable approximations, at least for a semi-quantitative model. Under these two assumptions, the relationship between $k_{obs}$ and $k_a$ is given by eq 2:

$$k_{obs} = k_a \left[ \frac{(\sqrt{8K_{eq}[Pyr]_{nom} + 1}) - 1}{4K_{eq}} \right] \quad (2)$$

It is not possible from the observed dependence of $k_{obs}$ on $[Pyr]_{nom}$ to determine $k_a$ and $K_{eq}$ independently. Since [Pyr] is related to $[Pyr]_{nom}$ via $K_{eq}$, one can always compensate for an unrealistically high $K_{eq}$ by raising $k_a$ to an unrealistically high value that happens to reproduce $k_{obs}$. Indeed, attempts to fit the dependence of $k_{obs}$ on $[Pyr]_{nom}$ via eq 2 produce values of $k_a$ and $K_{eq}$ that do not show monotonic temperature dependences. If we assume, however, that $[Pyr] \approx [Pyr]_{nom}$ at low $[Pyr]_{nom}$, then the values of "$k_a$" determined at low $[Pyr]_{nom}$ should represent a reasonable approximation to the true values of $k_a$. We can then use these values of $k_a$ and eq 2 to find the value of $K_{eq}$ that provides the best fit to the $[Pyr]_{nom}$ dependence of $k_{obs}$. When this is done, we obtain the values of "$K_{eq}$" reported in Table 4. These values of $K_{eq}$ are (as expected from the way they were determined) consistent with our assumption that pyrrole is found primarily as a monomer at concentrations below 0.5 mol $L^{-1}$. More noteworthy is the analysis of the temperature

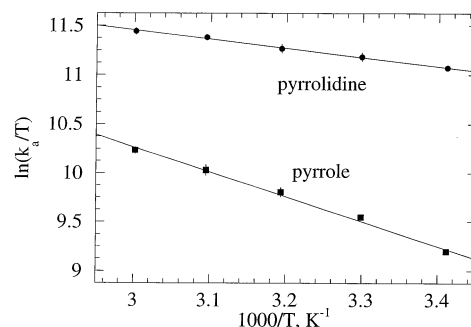(20) Ratajczak, H. M.; Ladd, J. A. *J. Mol. Liq.* **1984**, *29*, 97.



**Figure 5.** Eyring plot for reaction 1 for L = pyrrolidine (●) and for L = pyrrole (■). The straight lines represent linear fits to the data, weighted by the relative uncertainties.

dependence of $K_{eq}$, which yields $\Delta H° \approx -4$ kcal $mol^{-1}$ and $\Delta S° \approx -15$ eu for the association of pyrrole, consistent in general with values expected for association to form H-bound dimers and with previously measured values[18a] for the energetics of pyrrole–pyridine association. Obviously, our ability to produce reasonable results using this simple model is not a definitive proof of our explanation for the nonlinearity of the $[Pyr]_{nom}$ dependence of $k_{obs}$. The ability of the model to produce results that are self-consistent and consistent with independent determinations made by other methods does indicate, however, that aggregation of pyrrole is a reasonable explanation for the unusual kinetic results.[21]

**Mechanistic Considerations.** Eyring analyses of the temperature dependences of $k_a$ are presented in Figure 5. These analyses yield activation parameters for reaction 1 of $\Delta H^{\ddagger} = 1.8 \pm 0.1$ kcal $mol^{-1}$, $\Delta S^{\ddagger} = -18.9 \pm 0.4$ eu for L = pyrrolidine and $\Delta H^{\ddagger} = 5.1 \pm 0.2$ kcal $mol^{-1}$, $\Delta S^{\ddagger} = -11.6 \pm 1.2$ eu for L = pyrrole. The low values of $\Delta H^{\ddagger}$ relative to the $(CO)_5W-CyH$ bond dissociation energy, which has been estimated as $10-15$ kcal $mol^{-1}$,[22] and the negative values of $\Delta S^{\ddagger}$ imply that reaction 1 proceeds through an associative interchange ($\mathbf{I_a}$) mechanism where L enters the coordination sphere prior to dissociation of CyH. In the limit of a *dissociative* mechanism, in which dissociation of CyH is complete before L interacts with the metal center, the activation parameters we derive from $k_a$ would be equal to the sum of those for the two forward steps of the reaction (solvent dissociation and binding of L to "naked" $W(CO)_5$) minus those for solvent reassociation to $W(CO)_5$. Since solvation of $W(CO)_5$ is known to take place within ps of photolysis, and the unsolvated intermediate appears not to discriminate among binding sites in its intitial interaction with the solvent,[4] it seems unlikely that reaction of unsolvated $W(CO)_5$ to form $W(CO)_5L$ would be so much faster than solvation as to lower $\Delta H^{\ddagger}$ for

(21) It is unlikely that bleaching of pyrrole at high ligand concentrations can account for the kinetic behavior, since pyrrole does not have any appreciable UV absorbance at wavelengths longer than 250 nm. See: (a) Del Bene, J.; Jaffé, H. H. *J. Chem. Phys.* **1968**, *48*, 4050. (b) Mullen, P. A.; Orloff, M. K. *J. Chem. Phys.* **1969**, *51*, 2276. (c) Perkampus, H. H., Sandeman, I., Timmons, C. J., Eds. *UV Atlas of Organic Compounds*; Butterworth: London, 1971; Vol. V, spectrum G1/4. (d) Serrano-Andrés, L.; Merchán, M.; Nebot-Gil, I.; Roos, B. O.; Fülscher, M. *J. Am. Chem. Soc.* **1993**, *115*, 6184.

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reaction 1 by 5−10 kcal mol⁻¹ relative to the (CO)₅W− CyH bond dissociation enthalpy.

Another argument in favor of an associative mechanism is the strong dependence of $\Delta H^{\ddagger}$ on the electron-donating ability of L. Pyrrolidine is considerably more basic than pyrrole both as a free molecule[23] and as a ligand (Table 1), and the barrier for its reaction with W(CO)₅(CyH) is also considerably lower. This correlation implies that the ligand is involved in the rate-determining step of reaction 1 and is consistent with an associative mechanism in which a strongly electron-donating ligand can better stabilize an electron-poor transition state. In contrast, in CpMn(CO)₂(solv) systems (solv = THF or CyH), which appear to proceed via more dissociative mechanisms, $\Delta H^{\ddagger}$ for formation of CpMn(CO)₂L is nearly independent of the electron-donating ability of the incoming ligand.[24]

Above, we presented arguments that the nonlinear [L] dependence of $k_{obs}$ for L = pyrrole is a result of pyrrole association in solution. At this point, it is worthwhile to consider what is perhaps the most obvious alternative explanation, namely, that reaction 1 proceeds dissociatively and that we are observing kinetic saturation. We feel that this explanation is unlikely for several reasons. As mentioned above, even ligands such as 1-hexene that react more slowly with W(CO)₅(CyH) than pyrrole does fail to show any signs of saturation even at considerably higher ligand concentrations. In fact, we have shown elsewhere[25] that because [L] is not independent of [solv], even if reaction 1 proceeds dissociatively, we should not expect to see kinetic saturation in our experiment under any normal experimental conditions. In the present case, observation of kinetic saturation at [L] ≈ 1.5 mol L⁻¹ ([solv]/[L] ≈ 5) would imply that the rate constant for binding of pyrrole to "naked" W(CO)₅ is at least an order of magnitude greater than that for solvation. Solvation occurs with a rate constant of at least 10¹⁰ L mol⁻¹ s⁻¹, and it is difficult to believe that pyrrole would react an additional order of magnitude faster and yet be incapable of reacting associatively with W(CO)₅(CyH).

**Comparisons with Other Ligands.** In our prior studies of the reactivity of W(CO)₅(CyH) with furan, THF, and related compounds, we observed a correlation between $k_{CO}^{trans}$, the C−O stretching force constant for the carbonyl *trans* to L in the final product W(CO)₅L, and $\Delta H^{\ddagger}$.[6,9] We noted that this correlation implies a late transition state, further evidence for an associative mechanism for the reaction, and explained the relationship as being due to stronger [W]−L binding at the transition state for a more strongly electron-donating ligand. We have seen that this general trend continues to be observed in the relative behavior of pyrrolidine and pyrrole. Further insight into reaction 1 can be gained by a more detailed comparison of the present results to our previous observations for O-containing five-membered heterocycles.[5,6,9] Such a comparison of $\Delta H^{\ddagger}$ for reaction 1 as a function of $k_{CO}^{trans}$ is shown in
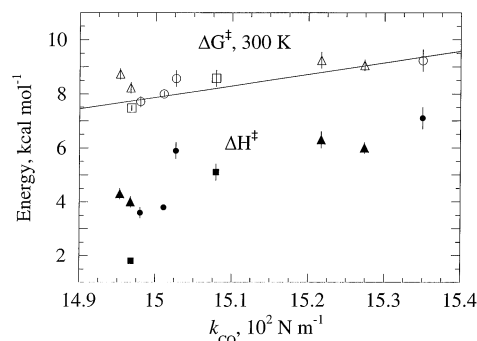


**Figure 6.** Activation enthalpies (solid symbols) and energies (open symbols) for reaction 1 as a function of the *trans* C−O stretching force constant[7] in W(CO)₅L for L = cyclo-C₄HₙO (●,○) (n = 4,6,8, refs 5 and 6), 2-methyl- and 2,5-dimethyl-substituted THF and furan (▲,△, ref 9), and cyclo-C₄HₙNH (■,□, this work). The solid line is a fit to $\Delta G^{\ddagger}$ for sterically unhindered ligands.[9] The error bars represent 1σ uncertainties.

Figure 6. One noteworthy observation is that $\Delta H^{\ddagger}$ for reaction with pyrrolidine is significantly lower than that for reaction with 2-methylTHF and 2,5-dimethylTHF, electron donors of approximately equal strength. This difference in $\Delta H^{\ddagger}$ is in keeping with our previous conclusion that steric interference caused by substitution near the heteroatom tends to raise $\Delta H^{\ddagger}$ above what would be expected due to purely electronic effects.[9,26] Although our previous results had implied a linear relationship between $\Delta H^{\ddagger}$ and $k_{CO}^{trans}$, inclusion of the results for pyrrolidine indicates that as $k_{CO}^{trans}$ rises, $\Delta H^{\ddagger}$ appears to approach an asymptotic limit for a very strongly electron-withdrawing ligand. This result is consistent with our conclusions about ligand electronic effects on $\Delta H^{\ddagger}$: if the incoming ligand is a sufficiently poor electron donor that it is unable to provide any significant amount of stabilization to the transition state, then a dissociative pathway will become energetically favorable. By this line of argument, $\Delta H^{\ddagger}$ should approach the (CO)₅W−CyH bond dissociation energy (BDE) as L becomes more and more electron withdrawing. From our results, it appears that the upper limit on $\Delta H^{\ddagger}$ is several kcal mol⁻¹ below the (CO)₅W−CyH BDE. Apparently, since reaction via a dissociative pathway will have a significantly positive $\Delta S^{\ddagger}$, entropic effects can cause dissociative reaction to become favored even when enthalpically, associative reaction might still be able to take place.

Figure 6 also shows $\Delta G^{\ddagger}$ as a function of $k_{CO}^{trans}$ for reaction 1. This figure shows that the qualitative relationship we found between the room-temperature rate constant and $\nu_{CO}$ is true quantitatively as well. Over the range of $k_{CO}^{trans}$ observed, $\Delta G^{\ddagger}$ rises linearly with $k_{CO}^{trans}$ (except for those cases in which steric factors intervene). We can draw two conclusions from this correlation. First, since the N-containing ligands lie on the same line as the O-containing ligands, we can

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(25) Schultz, R. H. *J. Phys. Chem. A*, submitted for publication.

(26) It might appear surprising at first glance that pyrrole is such a strong electron donor relative to furan. Unlike furan, however, pyrrole lacks a lone pair to donate to the metal atom. To bond to the metal center, the pyrrole N atom must rehybridize toward an sp³ geometry, losing aromaticity in the process. A DFT calculation of the structure of W(CO)₅(pyrrole) (Aped, P.; Schultz, R. H. Unpublished results) predicts that the pyrrole ligand is significantly distorted from planarity in the equilibrium geometry of the complex.
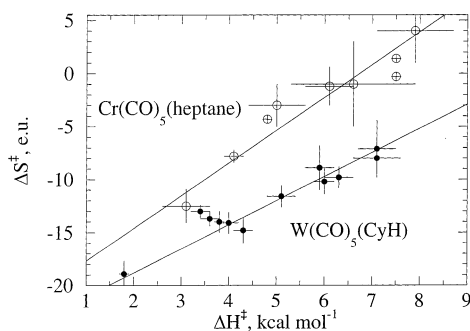
**Figure 7.** $\Delta S^{\ddagger}$ as a function $\Delta H^{\ddagger}$ for reaction 1. Shown are results for reactions of $W(CO)_5(CyH)$ (●) and for reactions of $Cr(CO)_5$(*n*-heptane) (○, ref 8). Error bars show $1\sigma$ uncertainties in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The solid lines are least-squares linear fits to the data.

see that the electronic factors that control the reactivity are an intrinsic property of the intermediate without regard to the exact nature of the incoming ligand. In addition, the linearity of the plot of $\Delta G^{\ddagger}$ in contrast to the nonlinearity of the plot of $\Delta H^{\ddagger}$ points to a "compensation effect"; that is, as $\Delta H^{\ddagger}$ increases, so does $\Delta S^{\ddagger}$, so that there is a linear *free-energy* relationship with $k_{CO}^{trans}$ in this system.

A more detailed look at this "compensation effect" is shown in Figure 7. This figure shows the relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ not only for the O- and N-heterocycles studied in our laboratory but also for L = 4-acetylpyridine[3b] and 1-hexene,[14] and as expected, the two parameters are well-correlated. Such a compensation effect has been attributed[8] to a gradual shift from more dissociative to more associative behavior as $\Delta H^{\ddagger}$ increases. Since $\Delta H^{\ddagger}$ also correlates with the electron-donating ability of the incoming ligand, we can also understand this compensation effect in terms of the transition state for the reaction.[6] When L is a strong electron donor (lower $\Delta H^{\ddagger}$), it can interact more effectively with the intermediate and lead to a tighter transition state with a lower $\Delta S^{\ddagger}$, while conversely, a poor electron donor (or strongly electron-withdrawing ligand) will not interact strongly with the electron-poor intermediate, leading to a looser, more "dissociative" transition state with a higher $\Delta S^{\ddagger}$.

Shown for comparison in Figure 7 are results obtained by Dobson and Zhang[8] for ligand substitution at Cr-$(CO)_5$(*n*-heptane), the only other alkane-bound transition metal intermediate for which the activation parameters of reaction 1 have been determined for a significant number of ligands. We can see that there is a similar compensation effect for that species as well, although the two data sets are not coincident.[27] For a

given value of $\Delta H^{\ddagger}$, the Cr system has a higher $\Delta S^{\ddagger}$. This result is in keeping with the observation that reactions of Cr-containing solvated intermediates tend to be more dissociative than those for the analogous species that contain W.[28] Moreover, these results once again confirm our observation that for $M(CO)_5$(solv) complexes, the *electronic* effects that determine the activation parameters are intrinsic to the intermediate and that given a particular intermediate, the expected values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for reaction 1 can be predicted from a knowledge of the spectroscopy of $M(CO)_5(L)$ without regard to the exact nature of L. Deviations from the predicted values must then be due to other factors such as steric interference with the ligand's ability to approach the intermediate sufficiently closely for effective interaction.

## Summary and Conclusions

We have used TRIR to observe ligand exchange by pyrrole and pyrrolidine at the $W(CO)_5$(cyclohexane) transient intermediate. In general, their reactivity is consistent with their relative electron-donating abilities as ligands in $W(CO)_5L$ and with the general trends we have observed for the reactivity of the intermediate. These results indicate that for a given ligand, unless steric factors intervene, the reaction rate can be predicted from a knowledge of the IR spectrum of $W(CO)_5L$. The correlation between the reaction rate constant and a property of the *product* implies that the reaction follows an associative pathway.

We also observe that for reaction with pyrrole, the pseudo-first-order reaction rate constant $k_{obs}$ is not a linear function of [L]. To our knowledge, this is the first time that a nonlinear dependence of $k_{obs}$ on [L] has been observed for any ligand interacting with any alkane-solvated group 6 $M(CO)_5$(solv) intermediate. We attribute this unusual kinetic behavior to association of pyrrole in solution. We have shown that it is possible to derive the true kinetic behavior of pyrrole with transition metal intermediates from careful observation of its behavior at low pyrrole concentions. In addition, to account for the kinetic behavior of pyrrole with $W(CO)_5(CyH)$ at *high* pyrrole concentrations, we estimate that $\Delta H^o$ for association of pyrrole in CyH solution to form aggregates is approximately 4 kcal mol$^{-1}$.

**Supporting Information Available:** Derivation of eq 2 and tables of pseudo-first-order reaction constants. This material is available free of charge via the Internet at http://pubs. acs.org.

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(27) The difference in the two data sets is unlikely to be due to some systematic difference in the methods by which the kinetic measurements were made or the activation parameters determined in different laboratories, since Dobson's measurements of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for reactions of $W(CO)_5(CyH)$ lie on the same line as ours.

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