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When the ligands go marching in: a step-scan Fourier transform infrared spectroscopic study of ligand attack at the transient species $W(CO)_5(CyH)$

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Received 2nd October 1998, Accepted 1st December 1998

Time-resolved step-scan Fourier transform infrared spectroscopy (S^2FTIR) is used to probe the reactions of the transient species $W(CO)_5(CyH)$, produced by photolysis of $W(CO)_6$ in cyclohexane solution, with a series of incoming ligands L. This study marks the first time that S^2FTIR has been used to obtain mechanistic information for an irreversible chemical process.

Although photolytic ligand substitution reactions of Group 6 carbonyls have long been of interest,[1] some of the most basic questions about these systems remain unresolved. One of these is the mechanism by which the transient intermediate "$M(CO)_5$(solv)" (solv = solvent molecule) reacts with an incoming ligand L to form the stable complex $M(CO)_5L$ [reaction (1)].

$$M(CO)_5(\text{solv}) + L \longrightarrow M(CO)_5L \qquad (1)$$

In alkane solution, reaction (1) appears to proceed through an associative or associative interchange (A or I_a) mechanism in which there is more bond forming than bond breaking in the transition state,[2–5] although in some cases the data are also consistent with a more dissociative mechanism.[1,2] Furthermore, because of the direct participation of the solvent in the reaction and the large rate constants typically encountered (*ca.* 10^6–10^7 M^{-1} s^{-1}), purely *kinetic* experiments (*i.e.*, experiments in which the only experimental parameter measured is the reaction rate) rarely lead to unambiguous mechanistic conclusions in these systems.

Differentiation among the various mechanistic possibilities must therefore be made by *chemical* studies that determine the relationship between the reaction kinetics and some other aspect of the the reaction system.[2b,2d,3–6] To this end, we have undertaken a time-resolved S^2FTIR spectroscopic study† of the reactions of the transient "$W(CO)_5(CyH)$" complex with a variety of incoming ligands in order to determine the relationship (if any) between the properties of the attacking ligand and the kinetics of reaction (1). We monitored the reaction of $W(CO)_5(CyH)$ with a series of ligands L of the form cyclo-C_4H_nE, where E = O (n = 4, 6, 8), NH (n = 4, 8), or CH_2 (n = 6),‡ as well as with L = 2-MeTHF and 2,5-Me_2THF. While S^2FTIR has been used extensively in investigation of *reversible* processes,[7,8] its use in *irreversible* processes has been limited to detection and identification of reaction intermediates.[9] This study marks the first use, to our knowledge, of S^2FTIR to obtain *mechanistic* information about a bimolecular chemical reaction, as well as the first *systematic* study of the influence of L on reaction (1) for any $M(CO)_5$(alkane) complex.

The experiments reported here were performed with a Bruker Equinox 55 S^2FTIR system. A continuously flowing solution of $W(CO)_6$ (5–6 × 10^{-4} mol L^{-1}) in CyH containing a large excess of L (for hex-1-ene and cyclopentene, [L] = 0.149 mol L^{-1}; for the other ligands, [L] = 0.015 ± 0.001 mol L^{-1}) was photolyzed in an 0.5 mm CaF_2 cell at room temperature (20 °C) by the pulsed output of an excimer laser (XeCl, 308 nm, 5–6 Hz). At each FTIR mirror position, the time-dependent IR signal was measured by a fast detector (<55 ns risetime), digitized, averaged over 8–15 photolysis shots, and converted to time-resolved interferograms and spectra. A detailed description of the instrument is given elsewhere.[3] HPLC grade cyclohexane (either freshly opened or stored over molecular sieves and used within 2 days) and other reagents were used without further purification; ligand purities of at least 97% were confirmed by NMR.

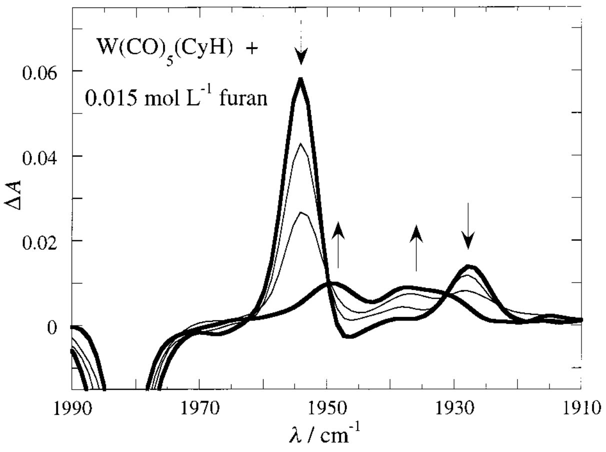

Fig. 1 Time-resolved S^2FTIR spectra (4 cm^{-1} resolution) showing changes in sample absorbance in the 1910–1990 cm^{-1} carbonyl stretching region following photolysis of $W(CO)_6$ in the presence of 0.015 mol L^{-1} furan. Shown are spectra for t = 0 and for t = 10 μs, 20 μs, and 45 μs after photolysis. The $W(CO)_6$ bleach appears as a negative peak (1981 cm^{-1}). Positive peaks that decrease in size with time (1954 cm^{-1} and 1928 cm^{-1}) are attributed to the $W(CO)_5(CyH)$ intermediate, and the peaks that increase in intensity with time (1949 cm^{-1} and 1936 cm^{-1}) to the $W(CO)_5$(furan) product.[11b]

Typical time-resolved S^2FTIR difference spectra are shown in Fig. 1. At the laser flash, a bleach, due to loss of $W(CO)_6$, appears at 1981 cm^{-1}. Simultaneously, positive absorbances appear at 1954 cm^{-1} and 1928 cm^{-1}, indicating formation of $W(CO)_5(CyH)$.[10] These peaks decrease in intensity with time while two new peaks, assigned to E and A_1 symmetry C–O stretches of $W(CO)_5L$,[11] grow in with the same time dependence. The IR peaks observed in this study for $W(CO)_5L$ (Table 1) are consistent with literature values for those complexes for which IR spectra have been reported.[11] No spectroscopic or kinetic evidence for significant amounts of side reaction [*e.g.*, reaction with trace amounts of H_2O[3,10b] or with unphotolyzed $W(CO)_6$] was seen. Sample kinetic traces (*i.e.* the time dependence of the absorption intensity) for the reaction of $W(CO)_5$-(CyH) with various ligands are shown in Fig. 2. Pseudo-first order reaction rates were determined from single-exponential fits to such kinetic traces and converted to second-order rate constants (Table 1).

The kinetic behavior of the ligands studied here falls into three categories: (a) for all L except for 2-MeTHF, 2,5-Me_2-THF, and the alkenes, there is an inverse correlation between

Table 1 Observed W(CO)$_5$L ν_{CO} frequencies for complexes W(CO)$_5$L and room-temperature second-order rate constants[a] (k_{obs}) for reaction (1) in cyclohexane solution

Ligand (L)	ν_{CO}[b]/cm^{-1}	10^{-6} k_{obs}/L mol^{-1} s^{-1}
Hex-1-ene	1963, 1948	0.68 ± 0.04[c]
Cyclopentene	1960, 1943	0.64 ± 0.03[c]
Furan	1949, 1936	2.58 ± 0.15[d]
Cyclohexane	1954, 1928	—
Pyrrole	1939, 1919	6.14 ± 0.18
2,3-DHF	1936, 1915	6.41 ± 0.40
2,5-DHF	1934, 1913	12.4 ± 0.7
THF	1933, 1911	13.4 ± 0.7[d]
Pyrrolidine	1926, 1917	20.9 ± 1.0
2-MeTHF	1933, 1910	6.59 ± 0.32
2,5-Me$_2$THF	1930, 1909	6.48 ± 0.18

[a] Second-order reaction rate constants (20 °C) calculated from observed pseudo-first order reaction rates measured at [L] = 0.015 ± 0.001 mol L^{-1} are given with 1 standard deviation relative uncertainties. [b] Peak positions for E and A$_1$ C–O stretches; 4 cm^{-1} resolution. [c] Reaction rates for these two ligands were measured at [L] = 0.149 mol L^{-1}. [d] Reported values for these two ligands include results from an IR laser flash kinetic study performed in our laboratory.[3]

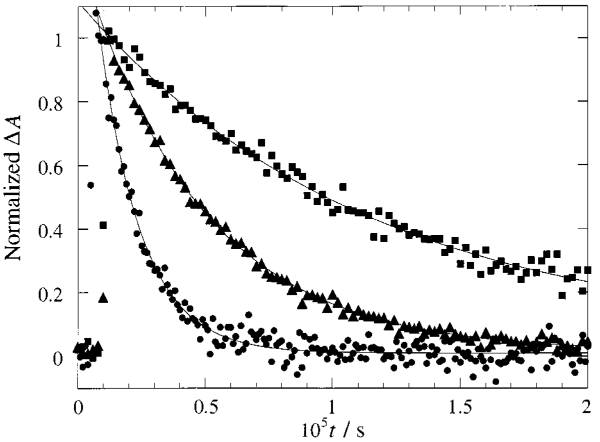

Fig. 2 Time dependence of the W(CO)$_5$(CyH) IR absorbance at 1954 cm^{-1} for three incoming ligands (reaction 1), normalized to the same ΔA at t = 0. Shown are results for reaction of W(CO)$_5$(CyH) with 0.15 mol L^{-1} cyclopentene (■), 0.015 mol L^{-1} THF (▲), and 0.015 mol L^{-1} pyrrolidine (●). The lines are single-exponential fits to the data (*cf.* Table 1).

the rate of reaction (1) and ν_{CO} of the product W(CO)$_5$L (Table 1);§ (b) 2-MeTHF and 2,5-Me$_2$THF react at about half the rate of THF despite having ν_{CO} similar to those of THF; (c) the alkenes react much more slowly than any of the other ligands. These results are easily rationalized in terms of the CDD "back-bonding" model of the metal–ligand interaction.[12] According to this model, the C–O stretching frequencies in any carbonyl complex will be inversely related to the electron density at the metal center. In the product W(CO)$_5$L complexes, the relative amount of electron density at the metal (and thus the values of ν_{CO}) should depend primarily on the relative electron donating ability of the ligand L. The data in Table 1, shown graphically in Fig. 3, reveal that for the C$_4$H$_n$E ligands from pyrrolidine to furan, the rate of reaction (1) correlates directly with the electron-donating ability of the ligand in the W(CO)$_5$L product. The correlation of the reaction rate with properties of the reaction *product* implies that for these ligands, the transition state for reaction (1) is nearer to the products than to the reactants; that is, the *spectroscopic* data for reaction (1) implies an *associative* (A or I$_a$) mechanism in which the transition state occurs while the solvent CyH molecule is still in the coordination sphere of the W atom. The more electron-donating the incoming ligand is, the better able it is to stabilize the transition state by continuing to maintain electron density at the metal center as the CyH molecule leaves. The trend in the rates of reaction (1) observed here is consistent with the relative values of $\Delta H^{\ddagger}$ for those cases in which it is known (L = THF, $\Delta H^{\ddagger}$ = 14 ± 3 kJ mol^{-1};[3] L = furan, $\Delta H^{\ddagger}$ = 23 ± 3 kJ mol^{-1};[3] L = hex-1-ene, $\Delta H^{\ddagger}$ = 30 ± 2 kJ mol^{-1}[13]) and with the negative values of $\Delta S^{\ddagger}$ observed for reaction (1) in these cases.

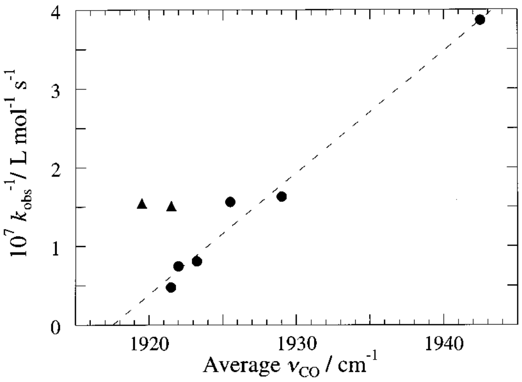

Fig. 3 Inverse dependence of the reaction rate constant on the CO stretching frequency. Shown is 10^7 k_{obs}^{-1} (Table 1) as a function of the average of ν_{CO}(A$_1$) and ν_{CO}(E) of W(CO)$_5$L. The circles represent results for (in order of increasing ν_{CO}) L = pyrrolidine; THF; 2,5-DHF; 2,3-DHF; pyrrole; furan. The dashed line is a linear fit through these data points. The triangles represent results for L = 2,5-Me$_2$THF and 2-MeTHF.

2-MeTHF, 2,5-Me$_2$THF, and the alkenes react more slowly than one would predict from their W(CO)$_5$L C–O stretching frequencies. In the cases of 2-MeTHF and 2,5-Me$_2$THF, the IR spectra of the product complexes show that these two ligands are strongly electron-donating. For these two ligands, steric hindrance appears to inhibit access of the incoming ligand to the associative, leading to slower reaction. Indeed, although the average ν_{CO} is lower for 2,5-Me$_2$THF than for MeTHF, it does not react any more quickly. This observation can be explained by the additional inductive effect of the second methyl group (shown by the lower values of ν_{CO}) being offset by its additional steric repulsion. On the other hand, for the strongly electron-*withdrawing* alkene ligands [which have higher values of ν_{CO} than the W(CO)$_5$(CyH) intermediate does], any transition-state stabilization due to electron donation will necessarily be much less significant, so according to the model developed here, the rate of reaction (1) should be much slower in these systems. Indeed, a *dissociative* (D or I$_d$) mechanism has been proposed for reaction (1) for L = hex-1-ene,[2c] and we observe here that reaction (1) proceeds at the same rate for hex-1-ene and cyclopentene despite the significant differences in ν_{CO} of the two product compounds.

Thus, for ligands of the type C$_4$H$_n$X (X = O or NH), the kinetics and spectroscopy observed here are entirely consistent with an *associative* (I$_a$) type of mechanism for ligand substitution at W(CO)$_5$(CyH). The reaction rate correlates to the electron-donating ability of the incoming ligand as measured by the C–O stretching frequencies of the *product* W(CO)$_5$L, implying a late transition state. This study marks the first time that such a correlation has been observed, as well as being the first time that S^{2}FTIR has been used to draw mechanistic conclusions about an irreversible chemical process. Additional studies are underway to further probe the steric and electronic influences on the reaction kinetics and mechanism and to determine the activation parameters of the reactions studied here.

Acknowledgements

This research was supported in part by the Israel Science Foundation, founded by the Israel Academy of Sciences and Humanities, and by funds provided by the Bar-Ilan University Research Authority. The authors would also like to thank Dr Heinz Frei (Lawrence Berkeley Laboratory) for helpful suggestions about the experimental setup.

Notes and references

† Abbreviations: S^{2}FTIR = Step-scan Fourier transform infrared; CyH = cyclohexane; CDD = Chatt–Dewar–Duncanson; THF = tetrahydrofuran; DHF = dihydrofuran; MeTHF = methyltetrahydrofuran; Me$_2$THF = dimethyltetrahydrofuran (mixture of *cis* and *trans*).

‡ Since these ligands have essentially the same geometry, but differing basicities, differences in reactivity among them will presumably be due primarily to electronic effects.

§ ΔA for the additional, very weak, A$_1$ symmetry C–O stretch for a W(CO)$_5$L species (usually found around 2075 cm^{-1}) was below the detectibility limit (*ca.* 0.002 absorbance units) of our instrument. The frequency of this peak tends to be less sensitive to changes in the ligand L in W(CO)$_5$L[10,11] than the other two IR-active C–O stretching frequencies, however. Furthermore, its value invariably correlates (at least qualitatively) with the average of the other two. Thus, the correlation shown in Fig. 3 is unlikely to be affected by including or not including the third peak in the calculation of the average ν_{CO}.

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13 Calculated from the rate data reported in the Supplementary Material to ref. 2(*c*). The authors of that study interpreted their results in terms of a *dissociative* mechanism and derived $\Delta H^\ddagger = 34 \pm 2$ kJ mol^{-1}, $\Delta S^\ddagger = -15 \pm 0.5$ kJ mol^{-1} K^{-1} for the W–CyH bond breaking step.

Communication 8/07672C