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A Kinetic Study of the Thermal Loss of Ethylene from $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$ in Supercritical Fluid Solvents

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Researchers have increasingly used supercritical fluids (SCF) as reaction media and reactants in organometallic reactions.[1] The many advantages of SCF over liquid solvents include higher mass transport rates and higher gas reactant (i.e., H_2, CO, ethylene, etc.) concentrations. In addition, a truly homogeneous SCF has all the reactants in one continuous phase without the usual gas/liquid interfaces which routinely limit reaction rates and complicate reaction kinetics in liquid systems. In this study we take advantage of this homogeneity to investigate rates of reactions involving small molecules (CO and ethylene) in the condensed SCF phase which are normally only obtainable in the gas phase. Here we present the first identification of group V, $CpM(CO)_3(\eta^2\text{-}C_2H_4)$ (M = Nb and Ta) (Cp is η^5-cyclopentadienyl) complexes and the kinetics of ethylene loss from $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$ in SCF solvents.

Photolysis of a $CpNb(CO)_4$ [2] solution in SCF ethylene at 30 °C[3] yields an IR spectrum consistent with a single ethylene-for-CO substitution at the niobium center.[4] The $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$ product has density-dependent IR bands at 1986, 1909, and 1882 cm^{-1} at 689 bar.[5] The proton NMR of this material anaerobically transferred from the IR cell into benzene-d_6 shows only the resonances expected for the proposed complex.[6] Similar complexes could also be identified upon irradiation of the tantalum analogue, and the known ethylene complexes of manganese ($CpMn(CO)_2(\eta^2\text{-}C_2H_4)$) and rhenium ($CpRe(CO)_2(\eta^2\text{-}C_2H_4)$) were produced from the respective tricarbonyls.[7]

The niobium−ethylene complex, $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$, formed in situ from the photolysis of $CpNb(CO)_4$ in SCF ethylene thermally decomposes to the tetracarbonyl starting material. Since this reaction is performed in a closed system and the observed kinetics are first order in $[CpNb(CO)_3(\eta^2\text{-}C_2H_4)]$ with no observed dependence upon $[CpNb(CO)_4]$, the source of the CO appears to be the free CO in the SCF solvent liberated from the photolysis of $CpNb(CO)_4$.[8] A reaction scheme for the disappearance of $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$, previously described for gas-phase decompositions of similar complexes, is shown in Scheme 1.[9]

Scheme 1

$$CpNb(CO)_3(\eta^2\text{-}C_2H_4) \underset{k_a}{\overset{k_d}{\rightleftharpoons}} CpNb(CO)_3 + C_2H_4 \qquad (1)$$

$$CpNb(CO)_3 + CO \xrightarrow{k_{CO}} CpNb(CO)_4 \qquad (2)$$

Applying the steady-state approximation to eqs 1 and 2 and assuming that $k_a \cong k_{CO}$, the rate expression reduces to (3) in which

$$k_d = k_{obs}([C_2H_4]/[CO]) \qquad (3)$$

k_d is directly dependent on k_{obs} and the concentrations of CO and ethylene.[10] The solvent concentration, $[C_2H_4]$, was essentially constant for any given temperature.[11] The [CO] is time dependent and equal to the difference between the initial $[CpNb(CO)_4]$ and the $[CpNb(CO)_4]$ at time *t* determined by IR. Plots of $\ln\{[CpNb(CO)_3(\eta^2\text{-}C_2H_4)]_t/[CpNb(CO)_3(\eta^2\text{-}C_2H_4)]_o\}\{[C_2H_4]/[CO]\}$ vs time show first-order kinetic behavior with the temperature-dependent rate constants shown in Table 1.[12]

An activation energy (E_a) of 23.7 ± 0.4 kcal/mol ($\Delta H^\ddagger = 23.2 \pm 0.4$ kcal/mol) for the ethylene loss from $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$ was determined from the Arrhenius plot of the kinetic data.[12] Assuming the loss of ethylene from $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$ is through a dissociative pathway, our activation barrier provides an experimental measure of the ethylene−niobium bond strength. The log *A* of 15.3 ± 0.3 ($\Delta S^\ddagger = 9.7 \pm 0.3$ eu) is consistent with a dissociative unimolecular scission and is lower than the log *A* values reported for unimolecular scissions occurring in the gas phase for the ethylene complexes of $Fe(CO)_3(\eta^2\text{-}C_2H_4)_2$ (log *A* = 17),[13] $Cr(CO)_5(\eta^2\text{-}C_2H_4)$ (log *A* = 16.7),[9] and $W(CO)_5(\eta^2\text{-}C_2H_2Cl_2)$ (log *A* = 17.9),[9] presumably resulting from the higher

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(1) See for example: Jessop, P. G.; Ikariya, T.; Noyori, R. *Science* **1995**, *269*, 1065. Jessop, P. G.; Ikariya, T.; Noyori, R. *Organometallics* **1995**, *14*, 1510. Banister, J. A.; Lee, P. D.; Poliakoff, M. *Organometallics* **1995**, *14*, 3876. Klinger, R. J.; Rathke, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 4772. Burk, M. J.; Feng, S.; Gross, M. F.; Tumas, W. *J. Am. Chem. Soc.* **1995**, *117*, 8277. Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344. Ji, Q.; Lloyd, C. R.; Eyring, E. M.; van Eldik, R. *J. Phys. Chem. A* **1997**, *101*, 243. Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207.

(2) $CpNb(CO)_4$, (*n*-butyl-Cp)$Nb(CO)_4$, and $CpTa(CO)_4$ used in this study were synthesized according to Bitterwolf, T. E.; Gallagher, S.; Rheingold, A. L.; Yap, G. P. A. *J. Organomet. Chem.* **1997**, *27*, 545−546, and Bitterwolf, T. E.; Gallagher, S.; Bays, J. T.; Scallorn, B.; Rheingold, A. L.; Guzei, I. A.; Liable-Sands, L.; Linehan, J. C., in press.

(3) Samples of $CpNb(CO)_4$ were dissolved in a minimum of pentane in a glovebox and syringed anaerobically into the SCF IR setup described in Fulton, J. L.; Pfund, D. M.; Ma, Y. *Rev. Sci. Instrum.* **1996**, *67*, 1. The cell was evacuated and back-filled with the solvent gas. The complete dissolution of the compound in the SCF was visibly observed. Photolysis was accomplished with an Oriel high-pressure Hg/Xe arc lamp. Time-dependent IR spectra were collected on a Nicolet 740 FT-IR spectrometer.

(4) George, M. W.; Haward, M. T.; Hamley, P. A.; Hughes, C.; Johnson, F. P. A.; Popov, V. K.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 2286. Freeman, J. W.; Bassolo, F. *Organometallics* **1991**, *10*, 256.

(5) The IR bands shift to higher frequency at lower pressure. The 1986 cm^{-1} band at 689 bar shifts to 1989 cm^{-1} at 172 bar.

(6) ^1H NMR spectra of $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$ in benzene-d_6: 4.603 ppm (Cp, 5 H), 2.331 ppm (C_2H_4, 4 H). ^{93}Nb NMR: −1929 ppm (br, 1800 Hz fwhh) relative to $CpNb(CO)_4$ at −2017 ppm (23 Hz fwhh) at 30 °C. The $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$ complex in benzene-d_6 thermally decomposes to an unidentified insoluble material.

(7) Angelici, R. J.; Loewen, W. *Inorg. Chem.* **1967**, *6*, 682. Hamley, P. A.; Kazarian, S. G.; Poliakoff, M. *Organometallics* **1994**, *13*, 1767.

(8) All kinetic data were based on the average peak areas from the 1986 and 1882 cm^{-1} bands for $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$ and the 1932 cm^{-1} band for $CpNb(CO)_4$. The extinction coefficient, 1166 M^{-1}, was determined for the 1932 cm^{-1} band of $CpNb(CO)_4$ in SCF ethylene over a range of pressures and temperatures and found to be independent of pressure, temperature, and density. The extinction coefficient for *n*-butyl-$CpNb(CO)_4$ was determined in petroleum ether and compared to ϵ of $CpNb(CO)_4$ in petroleum ether. The ratio of the extinction coefficients was used to determine the ϵ in SCF ethylene for *n*-butyl-$CpNb(CO)_4$.

(9) McNamara, B.; Becher, D. M.; Towns, M. H.; Grant, E. R. *J. Phys. Chem.* **1994**, *98*, 4622. Bogdan, P. L.; Wells, J. R.; Weitz, E. *J. Am. Chem. Soc.* **1991**, *113*, 1294.

(10) A detailed derivation is given in the Supporting Information. The rate constants k_a and k_{CO} represent processes which are close to diffusion controlled. Experimentally determined values of k_{CO} and k_a (for H_2) show that these rate constants are indeed nearly equal. George, M. W.; Haward, M. T.; Hamley, P. A.; Hughes, C.; Johnson, F. P. A.; Popov, V. K.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 2286.

(11) Angus, S.; Armstrong, B.; de Reuck, K. M. *International Thermodynamic Tables of the Fluid State Ethylene*, Butterworths: London, 1974.

(12) Kinetic plots, including the Arrhenius plot, and data are available in the Supporting Information.

(13) Miller, M. E.; Grant, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 7951.

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Table 1. Rate Constants, k_d, Measured for the Dissociation of Ethylene from $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$ in Supercritical Fluid Ethylene at 689 bar

temp (°C)	rate constant $(k_d)^a$ (s^{-1})	temp (°C)	rate constant $(k_d)^a$ (s^{-1})
30	0.0141 ± 0.0003	70	1.47 ± 0.04
40	0.0563 ± 0.0008	80	>2
40[b]	0.067 ± 0.005	55[c]	0.125 ± 0.005[c]
55	0.292 ± 0.005		

[a] All uncertainties are quoted as 2 standard deviations of a least-squares fit. [b] Reaction medium was 7% ethylene in CO_2. [c] For *n*-butyl-$CpNb(CO)_3(\eta^2\text{-}C_2H_4)$.

symmetry of the organometallic intermediates in the latter complexes when compared to the $CpNb(CO)_3$ fragment.

As expected, photolysis of $CpNb(CO)_4$ dissolved in a SCF solution composed of 17% mole fraction CO in ethylene showed no observable reaction even after 24 h of photolysis at 30 °C. The high CO concentration forces reaction 2 far to the right so that no ethylene addition is observed on the relatively long time scale (seconds to minutes) of these experiments.

The observed rate for ethylene loss from (*n*-butyl-Cp)$Nb(CO)_3(\eta^2\text{-}C_2H_4)$ was half the observed rate of ethylene loss from $CpNb(CO)_3(\eta^2\text{-}C_2H_4)$ at 55 °C, Table 1. The factor of 2 difference in the observed rates corresponds to a $\Delta\Delta H^\ddagger$ of less than 1 kcal/mol or a $\Delta\Delta S^\ddagger$ of less than 0.5 eu. We assume the electron-donating butyl group in (*n*-butyl-Cp)$Nb(CO)_3(\eta^2\text{-}C_2H_4)$ stabilizes the niobium−ethylene bond. However, more experiments over a greater temperature range are planned to test this hypothesis.

We have also briefly investigated the effect of solvent on these kinetics. The use of a 7% mole fraction mixture of ethylene in CO_2 as the SCF solvent yielded a much faster observed rate of ethylene loss, but when corrected for the ethylene and CO concentrations, the rate constant was comparable to the rate constant obtained in pure ethylene. The CO_2 acts as an inert diluent in this experiment, which is consistent with the niobium−ethylene bond being stronger than the niobium−CO_2 bond.

Comparison of the rate of ethylene loss from the niobium complex with other similar Cp−metal complexes shows the relative thermal stability in SCF ethylene to be $CpMn(CO)_2(\eta^2\text{-}C_2H_4) \gg CpRe(CO)_2(\eta^2\text{-}C_2H_4) > CpNb(CO)_3(\eta^2\text{-}C_2H_4) \gg CpTa(CO)_3(\eta^2\text{-}C_2H_4)$. The stability of the manganese complex is such that it showed no evidence of ethylene loss over a week at room temperature and no ethylene loss over 24 h at 100 °C.

There is no evidence of stable multiple ethylene substitutions for the manganese, niobium, or tantalum systems investigated. An IR band at 1962 cm^{-1} consistent with $CpRe(CO)(\eta^2\text{-}C_2H_4)_2$ was observed during prolonged photolysis of $CpRe(CO)_3$ in pure ethylene at 35 °C. The thermal decomposition kinetics of this diethylene-substituted complex have not been quantitatively measured but appear faster than ethylene loss from the mono-substituted complex $CpRe(CO)_2(\eta^2\text{-}C_2H_4)$. Proton NMR analysis of products of this photolysis yields an AA′BB′ second-order spectrum and supports the assignment of $CpRe(CO)(\eta^2\text{-}C_2H_4)_2$ with hindered rotation about each metal−ethylene bond.[14] This is in contrast to the monoethylene complex, which shows only a singlet for the rapidly rotating ethylene bound to the metal.

These experiments show the advantages that SCF can bring to the field of physical organometallic chemistry. Performing the reactions described here in SCF allowed the observation of what are typically gas-phase kinetics in a condensed phase. In a typical solvent system the CO solubility is minimal and the reaction rate would be dependent upon CO transfer from the gas phase to the solution phase. In addition the long kinetics in this paper allowed the use of low concentrations of CO, which eliminates potential phase separation problems which we have observed during photolysis of cymantrene in SCF due to the change in the ethylene:CO ratio.[15] We are continuing to investigate organometallic reactions with small molecules in supercritical fluids using both in situ IR and NMR spectroscopy.

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Supporting Information Available: Kinetic derivation, kinetic plots, IR spectra and data tables (10 pages, print/PDF). See any current masthead page for ordering and Internet access instructions. See any current masthead page for ordering information and Web access instructions.

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(14) ^1H (C_6D_6) NMR of $CpRe(CO)_2(\eta^2\text{-}C_2H_4)$: 5.169 ppm (Cp, 5H, s), 2.074 ppm (C_2H_4, 4H, s). ^1H (C_6D_6) NMR of $CpRe(CO)(\eta^2\text{-}C_2H_4)_2$: 4.953 ppm (Cp, 5H, s) 1.97 ppm (C_2H_4, 8H, m).

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